Supporting Information (SI)

$Ba_4(BS_3S)_2S_4$: A New Thioborate with Unprecedented [BS_3-S] and [S_4] Fundamental Building Blocks

Guangmao Li,[a#] Junjie Li,[a#] Kui Wu,[a] Zhihua Yang,[a] Shilie Pan[a*]

[†]*Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices; 40-1 South Beijing Road, Urumqi 830011, China*

#These authors contributed equally.

To whom correspondence should be addressed:

E-mail: slpan@ms.xjb.ac.cn (Shilie Pan).

Supporting Information

1. Synthesis of the $Ba_4(BS_3S)_2S_4$ Crystals

The crystals of $Ba_4(BS_3S)_2S_4$ for single crystal X-ray diffraction were obtained by spontaneous crystallization method. The reagents are barium sulfide (98%), amorphous boron powder (99.9%), sulfur powder (99.9%) and zinc powder (99.99%), purchased from Aladdin Bio-chemical Technology Co., Ltd. The synthesis process is as follows: (1) The reagents were preserved and weighted in an Ar-filled glove box in a molar ratio of 2.5 : 1 : 2.5 : 7.5 for BaS/Zn/B/S, and then loaded into a graphite crucible; (2) The crucible was covered with a tight crucible cap and then moved into a silica tube; (3) The crucible was sealed in a silicon tube by alkoxide flame under a vacuumed environment (10^{-4} Pa); (4) After that, the sealed tube was put into a temperature program-controlled furnace with the heating progress as follow:

30 ºC (25 ºC/h) →180 ºC (keep for 3 h) (25 ºC/h) →450 ºC (keep for 3 h) (20 ºC/h)→850 ºC (keep for 30 h) (3 ºC/h) →400 ºC (30 ºC/h) →30 ºC

The resultant samples were pale yellow. The powder samples of $Ba_4(BS_3S)_2S_4$ were synthesized through high-temperature solid state method. The reagents of BaS, B powder and S powder were weighted with a stoichiometric molar ratio of 2 : 1 : 6. The heating process was similar to that of synthesis of the crystals, except that the highest temperature is adjusted to 860 ºC. The powder XRD was performed and the pattern was compared with the theoretical one, which demonstrates the successful fabrication of $Ba_4(BS_3S)_2S_4$, as shown in Fig. S2. The synthesis of the $Ba_4(BS_3S)_2S_4$ phase was achieved with the byproducts of Ba_2SiS_4 and BaB_2S_4 (Fig. S2), which can be attributed to the B-Si exchange reaction ($2B_2S_3 + 3SiO_2 = 2B_2O_3 + 3SiS_2$) in the quartz container at the high temperature. In the future, we will try to develop special container for the synthesis of thioborates.

2. Structural Refinement and Crystal Data

A transparent single crystal of $Ba_4(BS_3S)_2S_4$ was selected firstly and fixed on the top of a glass fiber with epoxy and mounted on the machine for structure characterization by single crystal X-ray diffraction. The structure data were collected on a Bruker SMART APEX II 4K CCD diffractometer equipped with Mo Ka radiation (λ = 0.71073 Å) operating at 50 kV and 40 mA at room temperature. The data were refined through full-matrix least-squares on F^2 using SHELXTL program

package.[1] Structure determination was based on the direct method, and the face-indexed absorption correction was made with XPREP Program. The final structure was checked with PLATON[2] and no higher symmetries were found. Single crystal data and structure refinement parameters of $Ba_4(BS_3S)_2S_4$ are listed in Table S1. Bond length and angles, atomic coordinates and isotropic displacement parameters for $Ba_4(BS_3S)_2S_4$ are provided in Tables S2-S3.

3. Experimental and Computational Characterization

Powder X-ray Diffraction Measurement.

Powder X−ray diffraction (XRD) characterization was implemented on an automated Bruker D2 X-ray diffractometer from 10° to 50° (2θ) with a scan step width of 0.02° and a fixed counting time of 1 s/step.

Energy Dispersive X-ray Spectroscopy

Elemental analysis was carried on clean single crystal surfaces with the aid of a field emission scanning electron microscope (SEM, SUPRA 55VP) equipped with an energy dispersive X-ray spectroscope (EDX, BRUKER x-flash-sdd-5010). The results are shown in Fig. S1.

UV-VIS-NIR Diffuse Reflectance Spectroscopy.

Optical diffuse reflectance spectrum of $Ba_4(BS_3S)_2S_4$ was measured at 298 K on Shimadzu SolidSpec-3700DUV spectrophotometer with a wavelength range of 190–2600 nm, which can provide the visible or UV cut-off edge. The experimental band gap of $Ba_4(BS_3S)_2S_4$ can be estimated by converting the reflectance spectrum to absorbance using Kubelka-Munk function[3].

Infrared Spectrum.

The IR spectrum was recorded on a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer with a resolution of 2 cm^{-1}, covering the wavenumber range from 400 to 4000 cm^{-1}. The mixture of crystal samples and KBr in the molar ratio of about 1 : 100, was dried and ground into fine powder, and then pressed into a transparent sheet on the tablet machine. The sheet was loaded in the sample chamber and then the IR spectrum was measured.

Theoretical Calculations.

The first principle calculations for the experimental crystal structure were obtained based on *ab initio* calculations implemented in the CASTEP package through density functional theory (DFT).[4] The generalized gradient approximation (GGA) was

adopted and Perdew–Burke–Ernzerhof (PBE) functional was chosen to calculate the exchange-correlation potential, with an energy cutoff of 650.0 eV. The *k* integration over the Brillouinzone was performed by the tetrahedron method[5] using a Monkhorst−Pack grid of 4 × 3 × 2.

Anionic Group Calculation.

The Gaussian 09 package[6] was employed to explore the NLO-related effect of the thioborate group of [BS_3-S]. B3LYP (Becke, three parameter, Lee-Yang-Parr) exchange-correlation functional with the Lee-Yang-Parr correlation functional at the 6-31g basis set was performed to calculate the cluster.

4. Figures and Tables.

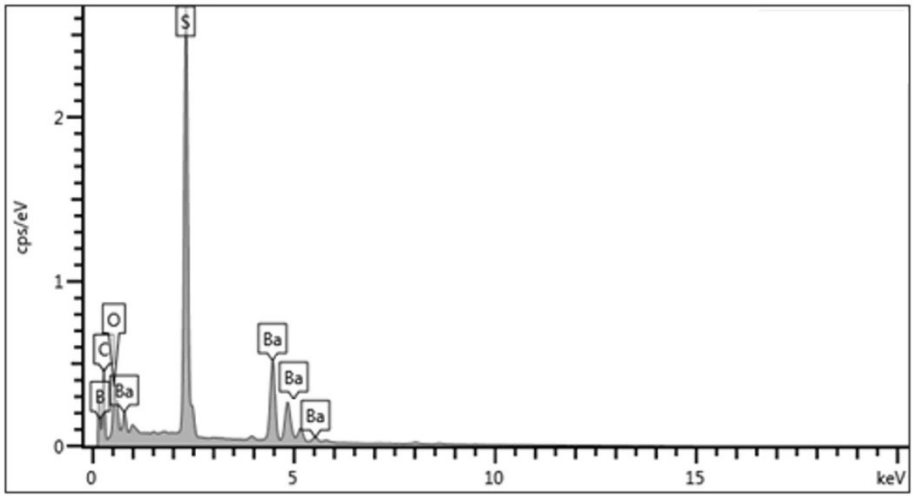

Fig. S1. The energy dispersive X-ray spectroscopy of $Ba_4(BS_3S)_2S_4$. The results confirm the existence of the Ba, B and S elements in the compounds.

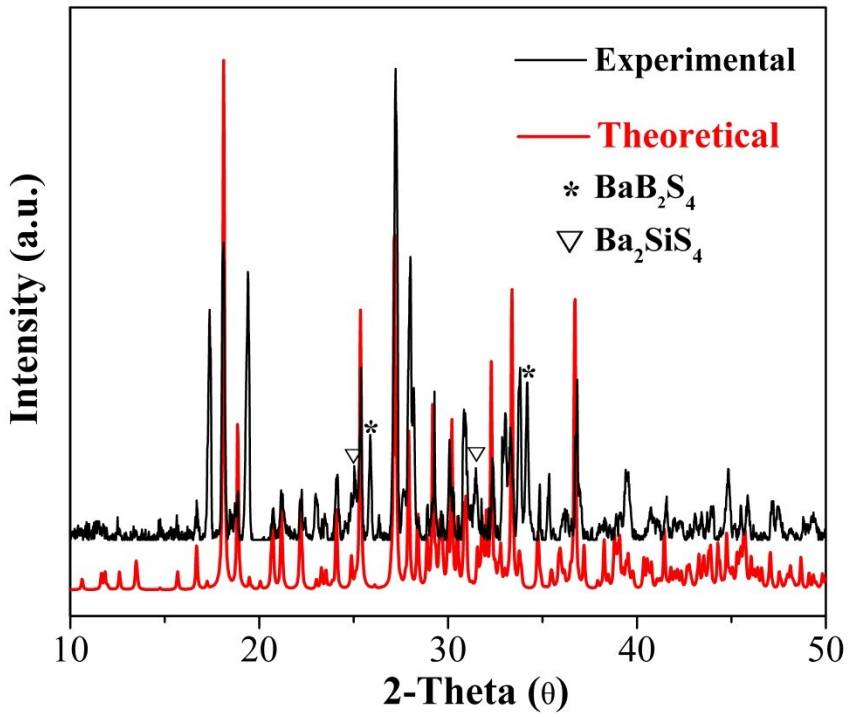

Fig. S2. Experimental and theoretical X-ray diffraction patterns of $Ba_4(BS_3S)_2S_4$.

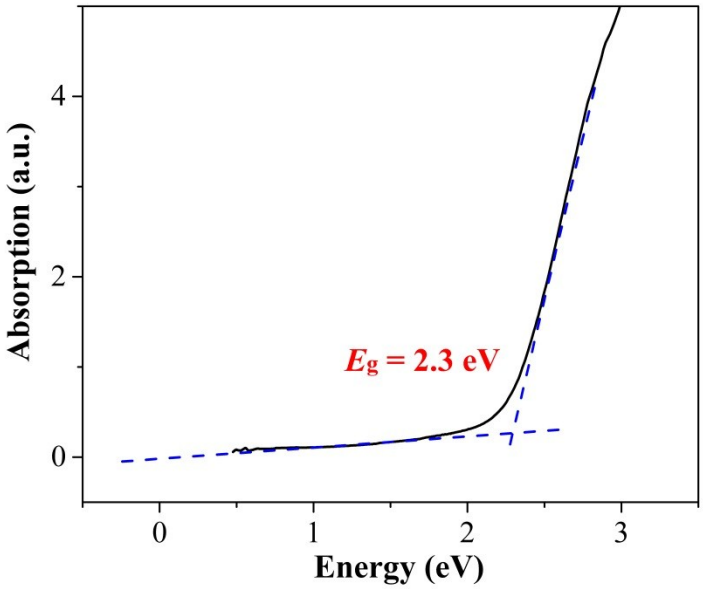

Fig. S3. The experimental bandgap of $Ba_4(BS_3S)_2S_4$.

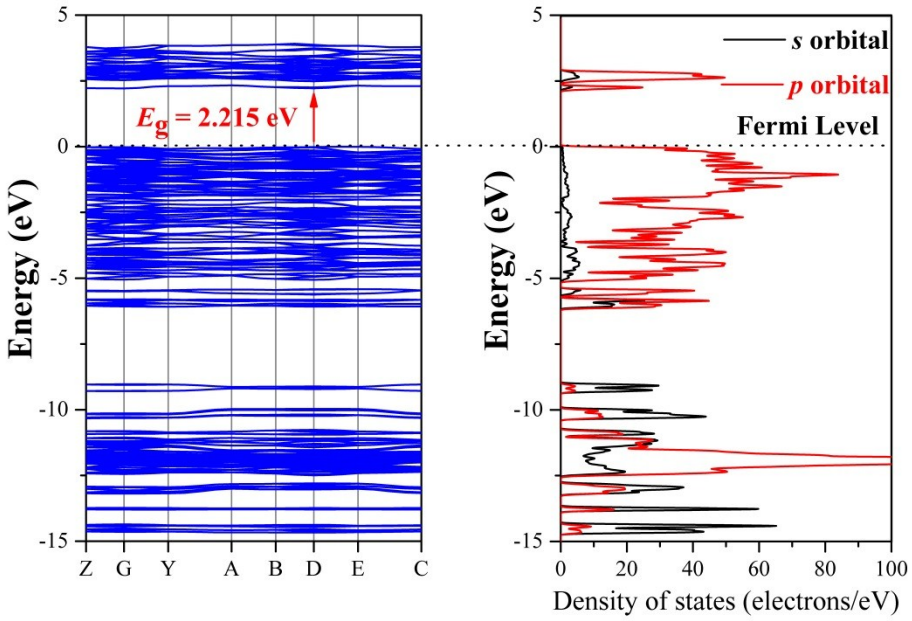

Fig. S4. Band structure and density of states of $Ba_4(BS_3S)_2S_4$.

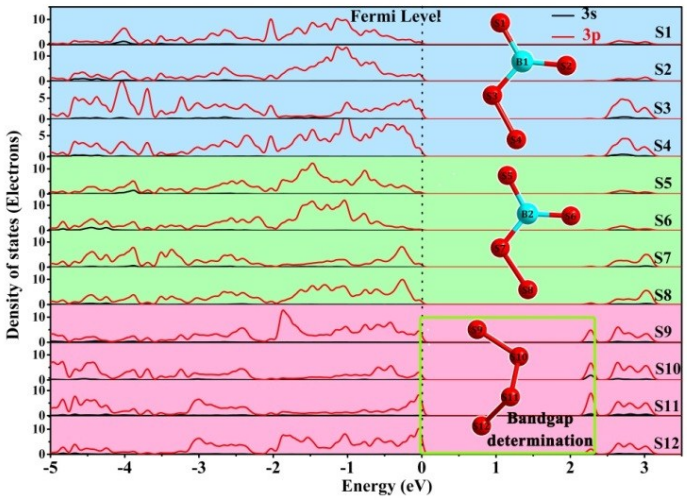

Fig. S5. PDOSs for S(1)-S(12) corresponding to [B(1)S_3-S], [B(2)S_3-S] and $[S_4]^{2-}$.

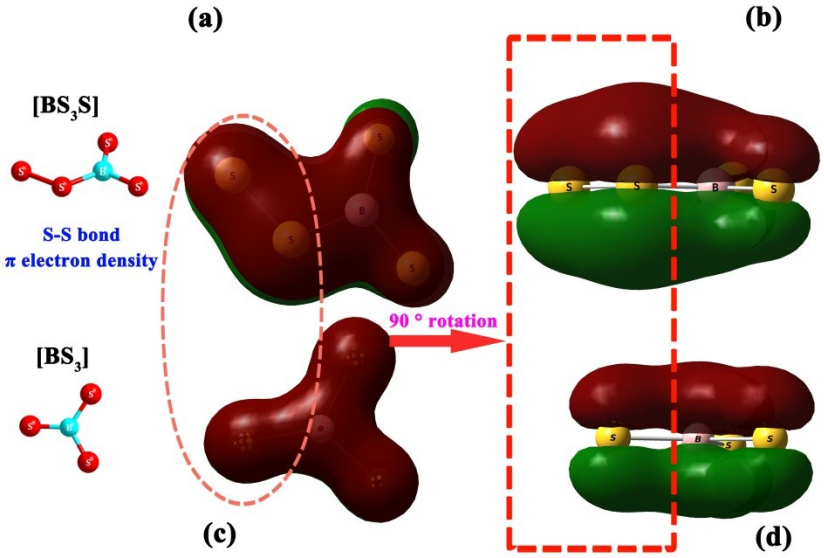

Fig. S6. The visualized π-configuration for [BS_3-S] (a-b) and [BS_3] groups (c-d) in vertical and horizontal directions.

Table S1. Crystal data and refinement parameters of $Ba_4(BS_3S)_2S_4$.

Empirical formula	$Ba_4(BS_3S)_2S_4$
Formula weight	955.7
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 9.191(4) Å
	b = 13.066(6) Å
	c = 15.321(7) Å
	β = 97.757(9) º
Volume	1823.1(15) $Å^3$
Z, Calculated density	4, 3.482 mg/m^3
Absorption coefficient	9.872 mm^{-1}
F(000)	1704
Crystal size	0.113 × 0.089 × 0.080 mm^3
Theta range for data collection	2.06 to 27.36 º
Limiting indices	-11⩽h⩽11,-9⩽k⩽16,-18⩽l⩽19
Reflections collected / unique	11300 / 4090 [$R_{(int)}$ = 0.0679]
Completeness to theta = 27.36 º	99.10%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7546 and 0.4423
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4090 / 0 / 164
Goodness-of-fit on F^2	0.973
Final R indices [I > 2sigma(I)]	R_1 = 0.0427, wR_2 = 0.0750
R indices (all data)	R_1 = 0.0707, wR_2 = 0.0853
Extinction coefficient	0.00039(4)
Largest diff. peak and hole	1.259 and -1.271 $e.Å^{-3}$

Table S2. The atomic coordinates, equivalent isotropic displacement parameters and BVS in $Ba_4(BS_3S)_2S_4$.

Atom	x	y	z	U(eq)	BVS
Ba(1)	4468(1)	9714(1)	1254(1)	19(1)	2.13
Ba(2)	1713(1)	9730(1)	3419(1)	21(1)	2.45
Ba(3)	7215(1)	7125(1)	2233(1)	23(1)	1.85
Ba(4)	446(1)	7509(1)	108(1)	19(1)	1.85
B(1)	2016(12)	9839(8)	-839(7)	21(2)	0.22
B(2)	3401(10)	7507(7)	2431(7)	15(2)	0.72
S(1)	3182(2)	8707(2)	-744(2)	18(1)	3.03
S(2)	2603(3)	11108(2)	-500(2)	22(1)	3.05
S(3)	-139(2)	10548(2)	1262(2)	18(1)	1.97
S(4)	1205(2)	9276(2)	1420(2)	20(1)	1.75
S(5)	4610(3)	8373(2)	3103(2)	18(1)	1.37
S(6)	3748(2)	7166(2)	1334(2)	20(1)	1.26
S(7)	3168(3)	12090(2)	2044(2)	20(1)	1.99
S(8)	4532(3)	11213(2)	2965(2)	19(1)	1.93
S(9)	2375(3)	8618(2)	5218(2)	24(1)	1.22
S(10)	3352(3)	10034(2)	5417(2)	22(1)	0.89
S(11)	-1810(3)	9007(2)	4179(2)	24(1)	0.98
S(12)	-1702(3)	9407(2)	2889(2)	30(1)	0.44

Table S3. Selected bond lengths [Å] and angles [°] in $Ba_4(BS_3S)_2S_4$.

Ba(1)-S(4)	3.098(3)	S(2)#1-Ba(1)-S(6)	82.19(6)	S(1)#8-Ba(3)-S(6)	121.44(6)
Ba(1)-S(1)#1	3.160(2)	S(8)-Ba(1)-S(6)	122.72(6)	S(12)#5-Ba(3)-S(5)	68.52(6)
Ba(1)-S(2)#1	3.252(3)	S(5)-Ba(1)-S(6)	55.77(6)	S(11)#6-Ba(3)-S(5)	130.79(6)
Ba(1)-S(8)	3.267(3)	S(1)-Ba(1)-S(6)	66.88(6)	S(8)#7-Ba(3)-S(5)	159.04(6)
Ba(1)-S(5)	3.318(3)	S(4)-Ba(1)-S(2)	77.28(6)	S(1)#8-Ba(3)-S(5)	84.38(6)
Ba(1)-S(1)	3.394(3)	S(1)#1-Ba(1)-S(2)	75.57(6)	S(6)-Ba(3)-S(5)	56.69(6)
Ba(1)-S(6)	3.399(3)	S(2)#1-Ba(1)-S(2)	104.05(6)	S(12)#5-Ba(3)-S(2)#1	65.89(7)
Ba(1)-S(2)	3.498(3)	S(8)-Ba(1)-S(2)	104.94(7)	S(11)#6-Ba(3)-S(2)#1	58.05(6)
Ba(1)-S(7)	3.595(3)	S(5)-Ba(1)-S(2)	152.78(6)	S(8)#7-Ba(3)-S(2)#1	91.82(6)
Ba(2)-S(4)	3.092(3)	S(1)-Ba(1)-S(2)	55.54(6)	S(1)#8-Ba(3)-S(2)#1	152.59(6)
Ba(2)-S(11)	3.103(3)	S(6)-Ba(1)-S(2)	117.40(6)	S(6)-Ba(3)-S(2)#1	79.45(6)
Ba(2)-S(12)	3.163(3)	S(4)-Ba(1)-S(7)	76.24(6)	S(5)-Ba(3)-S(2)#1	95.19(6)
Ba(2)-S(6)#3	3.240(3)	S(1)#1-Ba(1)-S(7)	77.80(6)	S(12)#5-Ba(3)-S(12)#4	162.78(3)
Ba(2)-S(9)	3.248(3)	S(2)#1-Ba(1)-S(7)	137.19(6)	S(11)#6-Ba(3)-S(12)#4	71.19(6)
Ba(2)-S(5)	3.289(3)	S(8)-Ba(1)-S(7)	35.17(6)	S(8)#7-Ba(3)-S(12)#4	75.50(6)
Ba(2)-S(8)	3.382(3)	S(5)-Ba(1)-S(7)	98.32(6)	S(1)#8-Ba(3)-S(12)#4	74.86(6)
Ba(2)-S(7)#4	3.527(3)	S(1)-Ba(1)-S(7)	123.18(6)	S(6)-Ba(3)-S(12)#4	83.18(6)
Ba(2)-S(3)	3.666(3)	S(6)-Ba(1)-S(7)	139.30(6)	S(5)-Ba(3)-S(12)#4	114.23(6)
Ba(3)-S(12)#5	3.258(3)	S(2)-Ba(1)-S(7)	70.01(6)	S(2)#1-Ba(3)-S(12)#4	128.77(6)
Ba(3)-S(11)#6	3.259(3)	S(4)-Ba(2)-S(11)	140.81(7)	S(4)-Ba(4)-S(11)#9	115.69(6)
Ba(3)-S(8)#7	3.270(3)	S(4)-Ba(2)-S(12)	73.04(7)	S(4)-Ba(4)-S(5)#9	151.71(6)
Ba(3)-S(1)#8	3.291(3)	S(11)-Ba(2)-S(12)	103.52(7)	S(11)#9-Ba(4)-S(5)#9	77.94(6)
Ba(3)-S(6)	3.297(3)	S(4)-Ba(2)-S(6)#3	107.45(6)	S(4)-Ba(4)-S(3)#10	80.21(7)
Ba(3)-S(5)	3.321(3)	S(11)-Ba(2)-S(6)#3	111.67(7)	S(11)#9-Ba(4)-S(3)#10	112.87(6)
Ba(3)-S(2)#1	3.540(3)	S(12)-Ba(2)-S(6)#3	91.16(6)	S(5)#9-Ba(4)-S(3)#10	71.53(6)
Ba(3)-S(12)#4	3.585(3)	S(4)-Ba(2)-S(9)	161.01(6)	S(4)-Ba(4)-S(1)	77.86(6)
Ba(4)-S(4)	3.079(3)	S(11)-Ba(2)-S(9)	37.77(6)	S(11)#9-Ba(4)-S(1)	160.23(7)
Ba(4)-S(11)#9	3.208(3)	S(12)-Ba(2)-S(9)	125.15(7)	S(5)#9-Ba(4)-S(1)	83.85(6)
Ba(4)-S(5)#9	3.274(3)	S(6)#3-Ba(2)-S(9)	79.72(6)	S(3)#10-Ba(4)-S(1)	52.94(6)
Ba(4)-S(3)#10	3.282(3)	S(4)-Ba(2)-S(5)	76.56(6)	S(4)-Ba(4)-S(6)	68.19(6)
Ba(4)-S(1)	3.372(2)	S(11)-Ba(2)-S(5)	79.21(6)	S(11)#9-Ba(4)-S(6)	129.87(7)
Ba(4)-S(6)	3.377(3)	S(12)-Ba(2)-S(5)	133.25(7)	S(5)#9-Ba(4)-S(6)	123.70(6)
Ba(4)-S(8)#4	3.402(3)	S(6)#3-Ba(2)-S(5)	131.94(6)	S(3)#10-Ba(4)-S(6)	116.83(6)
Ba(4)-S(2)#10	3.454(3)	S(9)-Ba(2)-S(5)	85.59(6)	S(1)-Ba(4)-S(6)	67.38(6)
Ba(4)-S(9)#4	3.546(3)	S(4)-Ba(2)-S(8)	85.64(6)	S(4)-Ba(4)-S(8)#4	80.32(7)
Ba(4)-S(10)#6	3.644(3)	S(11)-Ba(2)-S(8)	112.79(7)	S(11)#9-Ba(4)-S(8)#4	68.18(6)
B(1)-S(1)	1.820(11)	S(12)-Ba(2)-S(8)	141.75(7)	S(5)#9-Ba(4)-S(8)#4	127.77(6)
B(1)-S(2)	1.799(11)	S(6)#3-Ba(2)-S(8)	64.99(6)	S(3)#10-Ba(4)-S(8)#4	158.46(6)
B(1)-S(3)#10	1.830(12)	S(9)-Ba(2)-S(8)	81.57(6)	S(1)-Ba(4)-S(8)#4	130.52(6)
B(2)-S(5)	1.806(10)	S(5)-Ba(2)-S(8)	67.72(6)	S(6)-Ba(4)-S(8)#4	63.34(6)
B(2)-S(6)	1.809(11)	S(4)-Ba(2)-S(7)#4	67.52(6)	S(4)-Ba(4)-S(2)#10	67.17(6)

B(2)-S(7)#4	1.826(10)	S(11)-Ba(2)-S(7)#4	73.31(6)	S(11)#9-Ba(4)-S(2)#10	59.40(6)
S(2)-B(1)-S(1)	125.1(7)	S(12)-Ba(2)-S(7)#4	82.77(6)	S(5)#9-Ba(4)-S(2)#10	104.72(6)
S(2)-B(1)-S(3)#10	126.0(6)	S(6)#3-Ba(2)-S(7)#4	173.02(6)	S(3)#10-Ba(4)-S(2)#10	72.84(6)
S(1)-B(1)-S(3)#10	108.7(6)	S(9)-Ba(2)-S(7)#4	106.60(6)	S(1)-Ba(4)-S(2)#10	119.32(6)
S(5)-B(2)-S(6)	120.7(5)	S(5)-Ba(2)-S(7)#4	52.78(6)	S(6)-Ba(4)-S(2)#10	131.45(6)
S(5)-B(2)-S(7)#4	113.5(6)	S(8)-Ba(2)-S(7)#4	118.28(6)	S(8)#4-Ba(4)-S(2)#10	91.12(6)
S(6)-B(2)-S(7)#4	125.8(6)	S(4)-Ba(2)-S(3)	34.28(6)	S(4)-Ba(4)-S(9)#4	141.43(6)
S(4)-Ba(1)-S(1)#1	147.41(6)	S(11)-Ba(2)-S(3)	161.56(6)	S(11)#9-Ba(4)-S(9)#4	84.07(6)
S(4)-Ba(1)-S(2)#1	145.65(6)	S(12)-Ba(2)-S(3)	58.91(6)	S(5)#9-Ba(4)-S(9)#4	60.46(6)
S(1)#1-Ba(1)-S(2)#1	60.12(6)	S(6)#3-Ba(2)-S(3)	76.52(6)	S(3)#10-Ba(4)-S(9)#4	124.28(6)
S(4)-Ba(1)-S(8)	87.55(6)	S(9)-Ba(2)-S(3)	156.04(6)	S(1)-Ba(4)-S(9)#4	93.66(6)
S(1)#1-Ba(1)-S(8)	82.40(6)	S(5)-Ba(2)-S(3)	108.12(6)	S(6)-Ba(4)-S(9)#4	73.78(6)
S(2)#1-Ba(1)-S(8)	123.85(6)	S(8)-Ba(2)-S(3)	85.60(6)	S(8)#4-Ba(4)-S(9)#4	77.13(6)
S(4)-Ba(1)-S(5)	76.04(6)	S(7)#4-Ba(2)-S(3)	97.29(6)	S(2)#10-Ba(4)-S(9)#4	143.30(6)
S(1)#1-Ba(1)-S(5)	127.32(6)	S(12)#5-Ba(3)-S(11)#6	120.94(6)	S(4)-Ba(4)-S(10)#6	123.68(6)
S(2)#1-Ba(1)-S(5)	100.96(6)	S(12)#5-Ba(3)-S(8)#7	96.72(7)	S(11)#9-Ba(4)-S(10)#6	115.55(6)
S(8)-Ba(1)-S(5)	68.72(7)	S(11)#6-Ba(3)-S(8)#7	69.21(6)	S(5)#9-Ba(4)-S(10)#6	61.94(6)
S(4)-Ba(1)-S(1)	77.26(6)	S(12)#5-Ba(3)-S(1)#8	88.81(7)	S(3)#10-Ba(4)-S(10)#6	100.08(6)
S(1)#1-Ba(1)-S(1)	101.35(6)	S(11)#6-Ba(3)-S(1)#8	138.83(6)	S(1)-Ba(4)-S(10)#6	60.61(6)
S(2)#1-Ba(1)-S(1)	75.88(6)	S(8)#7-Ba(3)-S(1)#8	80.38(6)	S(6)-Ba(4)-S(10)#6	61.80(6)
S(8)-Ba(1)-S(1)	157.28(6)	S(12)#5-Ba(3)-S(6)	110.59(7)	S(8)#4-Ba(4)-S(10)#6	98.33(6)
S(5)-Ba(1)-S(1)	122.28(6)	S(11)#6-Ba(3)-S(6)	76.91(6)	S(2)#10-Ba(4)-S(10)#6	166.60(6)
S(4)-Ba(1)-S(6)	67.71(6)	S(8)#7-Ba(3)-S(6)	144.23(6)	S(9)#4-Ba(4)-S(10)#6	33.08(5)
S(1)#1-Ba(1)-S(6)	142.31(6)				

Symmetry transformations used to generate equivalent atoms:

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

5. References

[1] G. M. Sheldrick, *Bruker Analytical X-Ray Instruments*, Inc.: Madison, WI, **2003**.

[2] A. Spek, *J. Appl. Crystallogr.*, **2003**, *36*, 7-13.

[3] K. Gustav, *Experimental Testing of the "Kubelka-Munk" Theory*, Springer, Berlin, Heidelberg, **1969**.

[4] J. C. Stewart, D. S. Matthew, J. P. Chris, J. H. Phil, I. J. P. Matt, R. Keith, C. P. Mike, *Z. Kristallogr.-Cryst. Mater.*, **2005**, *220*, 2194-4946.

[5] E. P. Blöchl, O. Jepsen, O. K. Andersen, *Phys. Rew. B*, **1994**, *49*, 16223-16233.

[6] M. J. T. Frisch, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G. , *Gaussian, Inc.*, Wallingford CT, **2009**.