Supplementary Information

Simple Aliovalent Cation Substitution to Induce Strong Optical Anisotropy Enhancement in Rare Thioantimonates (V) Family

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Table S1. Crystal data and structure refinement for $Cs_4BaSb_2Se_8$ and $Rb_4BaSb_2Se_8$ (293K).

Empirical formula	**$Cs_4BaSb_2Se_8$**	**$Rb_4BaSb_2Se_8$**
Formula weight (Da)	1544.16	1354.40
Temperature (K)	293	293
Crystal system	Orthorhombic	Orthorhombic
Space group	*Ibam*	*Ibam*
a (Å)	20.2919(12)	20.1877(10)
b (Å)	9.9957(6)	9.7124(4)
c (Å)	11.0708(6)	10.7820(5)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å^3)	2245.5(2)	2114.04(17)
Z	4	4
Density (calc.) (g/cm^3)	4.568	4.255
Absorption coefficient (mm^{-1})	23.458	27.279
F (000)	2600.0	2312.0
Completeness to θ (%)	100	99.4
Theta range for data collection	4.014 to 54.984	6.942 to 54.958
Index ranges	$-26 \le h \le 26$, $-12 \le k \le 12$, $-14 \le l \le 14$	$-26 \le h \le 26$, $-10 \le k \le 12$, $-14 \le l \le 13$
Reflections collected	26206	11916
Independent reflections	1364 [R_{int} = 0.0654, R_{sigma} = 0.0228]	1270 [R_{int} = 0.0490, R_{sigma} = 0.0259]
Data / restraints / parameters	1364 / 0 / 43	1270 / 0 / 43
Goodness-of-fit on F^2	0.959	1.113
Final *R* indexes [$I \ge 2\sigma(I)$] [a]	R_1 = 0.0169, wR_2 = 0.0483	R_1 = 0.0234, wR_2 = 0.0495
Final *R* indexes [all data] [a]	R_1 = 0.0179, wR_2 = 0.0492	R_1 = 0.0253, wR_2 = 0.0501
Largest diff. peak / hole (e/Å^{-3})	0.96 / -0.64	1.04 / -0.85

[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 $F_o^2 > 2\sigma(F_o^2)$

Table S2. Fractional atomic coordinates ($\times 10^4$), equivalent isotropic displacement Parameters ($Å^2 \times 10^3$), and bond valence sun (BVS) for $Cs_4BaSb_2Se_8$ (293 K). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)	Wyckoff positions	BVS[a]
Cs1	5829.3(2)	1156.4(3)	5000	29.86(11)	8j	1.16
Cs2	7443.6(2)	5000	2500	43.46(13)	8f	0.72
Ba1	5000	5000	2500	20.55(11)	4a	1.66
Sb1	6293.4(2)	7031.4(3)	5000	16.69(10)	8j	5.39
Se1	5760.2(2)	7977.9(4)	3198.3(4)	30.45(12)	16k	2.13
Se2	6030.7(3)	4612.9(5)	5000	25.21(13)	8j	2.17
Se3	7478.4(3)	7529.7(6)	5000	30.50(15)	8j	2.15

[a] The bond valence sum is calculated by bond-valence theory ($S_{ij} = \exp[(R_0-R)/B$, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and $B = 0.37$).

Table S3. Anisotropic displacement parameters ($Å^2×10^3$) for $Cs_4BaSb_2Se_8$ (293K). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs1	37.00(19)	22.27(17)	30.32(19)	0	0	-3.85(13)
Cs2	58.8(3)	43.2(2)	28.4(2)	-4.93(16)	0	0
Ba1	21.72(19)	19.5(2)	20.4(2)	0	0	0
Sb1	17.45(16)	16.22(17)	16.39(16)	0	0	-1.11(10)
Se1	44.5(2)	26.7(2)	20.2(2)	3.53(14)	-9.43(15)	-1.60(15)
Se2	26.4(2)	15.6(2)	33.6(3)	0	0	-0.53(18)
Se3	19.2(2)	37.3(3)	34.9(3)	0	0	-6.2(2)

Table S4. Bond lengths for $Cs_4BaSb_2Se_8$ (293K).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cs1	Se2	3.4791(6)	Cs2	Se3[4]	3.7496(4)
Cs1	Se1[5]	3.6477(4)	Cs2	Se3[16]	3.7124(4)
Cs1	Se1[3]	3.8899(6)	Ba1	Se2[3]	3.4906(3)
Cs1	Se1[11]	3.6477(4)	Ba1	Se2[1]	3.4906(3)
Cs1	Se1[12]	3.7540(5)	Ba1	Se2[4]	3.4906(3)
Cs1	Se1[13]	3.7540(5)	Ba1	Se2	3.4905(3)
Cs1	Se1[2]	3.8899(6)	Ba1	Se1[1]	3.4405(4)
Cs1	Se3[14]	3.6980(7)	Ba1	Se1[5]	3.4405(4)
Cs2	Se2	4.0038(5)	Ba1	Se1	3.4405(4)
Cs2	Se2[4]	4.0038(5)	Ba1	Se1[2]	3.4405(4)
Cs2	Se1[15]	4.2388(6)	Sb1	Se2	2.4755(6)
Cs2	Se1[16]	4.2388(6)	Sb1	Se1	2.4585(4)
Cs2	Se3[14]	3.7124(4)	Sb1	Se1[7]	2.4585(4)
Cs2	Se3	3.7495(4)	Sb1	Se3	2.4557(6)

[1]1-X,+Y,1/2-Z;[2]1-X,1-Y,+Z;[3]1-X,1-Y,1-Z;[4]+X,1-Y,-1/2+Z;[5]+X,1-Y,1/2-Z;[6]+X,1+Y,+Z;[7]+X,+Y,1-Z;[8]1-X,-Y,1-Z;[9]3/2-X,1/2-Y,1/2+Z;[10]3/2-X,1/2-Y,1/2-Z;[11]+X,1-Y,1/2+Z;[12]+X,-1+Y,1-Z;[13]+X,-1+Y,+Z;[14]3/2-X,-1/2+Y,1-Z;[15]3/2-X,-1/2+Y,+Z;[16]3/2-X,3/2-Y,1/2-Z

Table S5. Bond angles for $Cs_4BaSb_2Se_8$ (293K).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
$Se1^{8}$	Cs1	$Se1^{3}$	115.452(11)	$Se3^{4}$	Cs2	$Se1^{16}$	78.278(11)
$Se1^{12}$	Cs1	$Se1^{2}$	114.398(11)	$Se3^{4}$	Cs2	$Se1^{17}$	99.831(13)
$Se1^{12}$	Cs1	$Se1^{13}$	71.554(10)	Se3	Cs2	$Se1^{17}$	78.279(11)
$Se1^{5}$	Cs1	$Se1^{13}$	135.653(11)	$Se3^{17}$	Cs2	$Se1^{17}$	60.677(10)
$Se1^{8}$	Cs1	$Se1^{13}$	64.192(14)	$Se3^{17}$	Cs2	$Se1^{16}$	114.614(14)
$Se1^{12}$	Cs1	$Se1^{8}$	135.653(11)	Se3	Cs2	$Se1^{16}$	99.832(13)
$Se1^{5}$	Cs1	$Se1^{2}$	54.379(12)	$Se3^{14}$	Cs2	$Se1^{16}$	60.677(10)
$Se1^{2}$	Cs1	$Se1^{3}$	61.698(13)	$Se3^{14}$	Cs2	$Se1^{17}$	114.614(14)
$Se1^{12}$	Cs1	$Se1^{5}$	152.186(16)	$Se3^{14}$	Cs2	Se3	84.113(4)
$Se1^{12}$	Cs1	$Se1^{3}$	54.379(12)	$Se3^{17}$	Cs2	Se3	95.794(5)
$Se1^{13}$	Cs1	$Se1^{2}$	115.452(11)	$Se3^{17}$	Cs2	$Se3^{4}$	84.114(5)
$Se1^{5}$	Cs1	$Se3^{14}$	86.999(9)	$Se3^{14}$	Cs2	$Se3^{17}$	175.12(2)
$Se1^{12}$	Cs1	$Se3^{14}$	86.999(9)	Se3	Cs2	$Se3^{4}$	177.84(2)
$Se3^{14}$	Cs1	$Se1^{2}$	133.421(12)	$Se3^{14}$	Cs2	$Se3^{4}$	95.794(5)
$Se3^{14}$	Cs1	$Se1^{13}$	110.419(13)	Se2	Ba1	$Se2^{4}$	106.378(14)
$Se3^{14}$	Cs1	$Se1^{3}$	133.421(11)	$Se2^{3}$	Ba1	$Se2^{4}$	167.273(17)
$Se3^{14}$	Cs1	$Se1^{8}$	110.419(13)	$Se2^{1}$	Ba1	$Se2^{4}$	75.085(14)
$Se1^{5}$	Cs1	$Se1^{3}$	114.398(11)	$Se2^{1}$	Ba1	$Se2^{3}$	106.377(14)
$Se1^{13}$	Cs1	$Se1^{3}$	83.387(11)	Se2	Ba1	$Se2^{3}$	75.084(14)
$Se1^{5}$	Cs1	$Se1^{8}$	71.554(11)	Se2	Ba1	$Se2^{1}$	167.273(17)
Se2	Cs1	$Se1^{12}$	76.639(8)	$Se1^{5}$	Ba1	$Se2^{3}$	122.867(10)
Se2	Cs1	$Se1^{5}$	76.639(8)	$Se1^{2}$	Ba1	$Se2^{1}$	79.259(11)
Se2	Cs1	$Se1^{2}$	82.902(12)	$Se1^{5}$	Ba1	$Se2^{1}$	89.690(11)
Se2	Cs1	$Se1^{3}$	82.902(12)	$Se1^{2}$	Ba1	$Se2^{4}$	122.867(10)
Se2	Cs1	$Se1^{8}$	147.658(7)	$Se1^{1}$	Ba1	$Se2^{1}$	69.457(11)
Se2	Cs1	$Se1^{13}$	147.658(7)	$Se1^{5}$	Ba1	$Se2^{4}$	69.457(11)
Se2	Cs1	$Se3^{14}$	61.466(14)	$Se1^{5}$	Ba1	Se2	79.259(11)
$Se1^{8}$	Cs1	$Se1^{2}$	83.387(11)	$Se1^{2}$	Ba1	Se2	89.689(11)
$Se2^{4}$	Cs2	Se2	88.532(15)	$Se1^{1}$	Ba1	$Se2^{3}$	79.259(11)
$Se2^{4}$	Cs2	$Se1^{16}$	141.989(9)	Se1	Ba1	$Se2^{3}$	89.690(11)
$Se2^{4}$	Cs2	$Se1^{17}$	116.334(9)	Se1	Ba1	$Se2^{1}$	122.868(10)
Se2	Cs2	$Se1^{16}$	116.334(9)	Se1	Ba1	$Se2^{4}$	79.259(11)
Se2	Cs2	$Se1^{17}$	141.990(9)	$Se1^{1}$	Ba1	$Se2^{4}$	89.690(11)
$Se1^{17}$	Cs2	$Se1^{16}$	61.398(13)	$Se1^{2}$	Ba1	$Se2^{3}$	69.457(11)
$Se3^{14}$	Cs2	$Se2^{4}$	127.599(15)	Se1	Ba1	Se2	69.457(11)
$Se3^{17}$	Cs2	Se2	127.599(15)	$Se1^{1}$	Ba1	Se2	122.867(10)
$Se3^{4}$	Cs2	$Se2^{4}$	64.431(10)	$Se1^{2}$	Ba1	$Se1^{5}$	60.199(14)
$Se3^{14}$	Cs2	Se2	56.693(11)	$Se1^{5}$	Ba1	$Se1^{1}$	154.030(13)
Se3	Cs2	$Se2^{4}$	117.296(13)	$Se1^{2}$	Ba1	$Se1^{1}$	126.724(15)
Se3	Cs2	Se2	64.431(10)	$Se1^{5}$	Ba1	Se1	126.724(15)
$Se3^{17}$	Cs2	$Se2^{4}$	56.692(11)	$Se1^{2}$	Ba1	Se1	154.030(14)
$Se3^{4}$	Cs2	Se2	117.296(13)	$Se1^{1}$	Ba1	Se1	60.199(14)

Se1	Sb1	Se2	106.322(14)	Se3	Sb1	Se2	114.14(2)
Se1[7]	Sb1	Se2	106.321(14)	Se3	Sb1	Se1	110.663(15)
Se1	Sb1	Se1[7]	108.45(2)	Se3	Sb1	Se1[7]	110.663(15)

[1]1-X,+Y,1/2-Z;[2]1-X,1-Y,+Z;[3]1-X,1-Y,1-Z;[4]+X,1-Y,-1/2+Z;[5]+X,1-Y,1/2-Z;[6]+X,1+Y,+Z;[7]+X,+Y,1-Z;[8]+X,-1+Y,+Z;[9]3/2-X,1/2-Y,1/2+Z;[10]3/2-X,1/2-Y,1/2-Z;[11]1-X,-Y,1-Z;[12]+X,1-Y,1/2+Z;[13]+X,-1+Y,1-Z;[14]3/2-X,-1/2+Y,1-Z;[15]3/2-X,1/2+Y,1-Z;[16]3/2-X,-1/2+Y,+Z;[17]3/2-X,3/2-Y,1/2-Z;[18]3/2-X,3/2-Y,1/2+Z

Table S6. Fractional atomic coordinates ($\times 10^4$), equivalent isotropic displacement Parameters ($Å^2 \times 10^3$), and bond valence sun (BVS) for $Rb_4BaSb_2Se_8$ (293 K). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)	Wyckoff positions	BVS[a]
Rb1	4201.3(4)	1170.0(7)	5000	32.93(18)	8j	1.03
Rb2	2477.5(5)	10000	7500	50.5(2)	8f	0.58
Ba1	5000	5000	7500	20.53(13)	4a	1.73
Sb1	3686.8(2)	7057.2(4)	5000	16.18(11)	8j	5.38
Se1	4226.4(3)	8085.2(5)	6817.7(5)	32.66(15)	16k	1.95
Se2	3967.1(3)	4578.4(7)	5000	25.14(16)	8j	2.06
Se3	2489.2(4)	7505.5(8)	5000	33.07(18)	8j	1.89

[a] The bond valence sum is calculated by bond-valence theory ($S_{ij} = \exp[(R_0-R)/B$, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and $B = 0.37$).

Table S7. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_4BaSb_2Se_8$ (293K). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb1	45.9(4)	22.0(3)	30.9(4)	0	0	3.9(3)
Rb2	69.6(6)	47.6(5)	34.2(4)	7.6(4)	0	0
Ba1	21.7(3)	20.1(3)	19.8(3)	0	0	0
Sb1	16.8(2)	15.4(2)	16.3(2)	0	0	1.16(14)
Se1	51.8(3)	26.3(3)	19.8(3)	-3.98(19)	-11.1(2)	0.8(2)
Se2	25.1(3)	14.6(3)	35.8(4)	0	0	-0.5(2)
Se3	19.1(3)	38.9(4)	41.2(4)	0	0	6.4(3)

Table S8. Bond lengths for $Rb_4BaSb_2Se_8$ (293K)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Rb1	Se3[9]	3.6509(11)	Rb2	Se1	4.0578(11)
Rb1	Se2	3.3440(10)	Rb2	Se1[6]	4.0578(11)
Rb1	Se1[8]	3.5806(8)	Ba1	Se2[15]	3.4323(4)
Rb1	Se1[10]	3.5069(5)	Ba1	Se2[2]	3.4323(4)
Rb1	Se1[11]	3.5069(5)	Ba1	Se2[13]	3.4323(4)
Rb1	Se1[12]	3.5806(8)	Ba1	Se2	3.4324(4)
Rb1	Se1[13]	3.7999(9)	Ba1	Se1[15]	3.4581(5)
Rb1	Se1[14]	3.7999(9)	Ba1	Se1[10]	3.4581(5)
Rb2	Se3[5]	3.6244(6)	Ba1	Se1[14]	3.4581(5)
Rb2	Se3	3.6243(6)	Ba1	Se1	3.4582(5)
Rb2	Se3[4]	3.6321(6)	Sb1	Se3	2.4565(8)
Rb2	Se3[3]	3.6321(6)	Sb1	Se2	2.4732(7)
Rb2	Se2[4]	3.9923(9)	Sb1	Se1[16]	2.4545(5)
Rb2	Se2[3]	3.9923(9)	Sb1	Se1	2.4545(5)

[1]+X,1+Y,+Z;[2]+X,1-Y,1/2+Z;[3]1/2-X,3/2-Y,3/2-Z;[4]1/2-X,1/2+Y,1-Z;[5]+X,2-Y,1/2+Z;[6]+X,2-Y,3/2-Z;[7]1-X,-Y,1-Z;[8]+X,-1+Y,+Z;[9]1/2-X,-1/2+Y,1-Z;[10]+X,1-Y,3/2-Z;[11]+X,1-Y,-1/2+Z;[12]+X,-1+Y,1-Z;[13]1-X,1-Y,1-Z;[14]1-X,1-Y,+Z;[15]1-X,+Y,3/2-Z;[16]+X,+Y,1-Z

Table S9. Bond angles for $Rb_4BaSb_2Se_8$ (293K).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
$Se3^{10}$	Rb1	$Se1^{11}$	135.494(19)	$Se3^{4}$	Rb2	$Se1^{6}$	99.00(2)
$Se3^{10}$	Rb1	$Se1^{12}$	135.494(19)	$Se3^{3}$	Rb2	$Se1^{6}$	79.126(18)
Se2	Rb1	$Se3^{10}$	61.06(2)	$Se3^{5}$	Rb2	Se1	115.82(3)
Se2	Rb1	$Se1^{11}$	85.96(2)	$Se3^{5}$	Rb2	$Se1^{6}$	63.456(16)
Se2	Rb1	$Se1^{12}$	85.96(2)	$Se3^{4}$	Rb2	Se1	79.126(18)
Se2	Rb1	$Se1^{8}$	146.137(11)	Se3	Rb2	Se1	63.456(16)
Se2	Rb1	$Se1^{13}$	78.337(14)	$Se2^{3}$	Rb2	$Se2^{4}$	86.14(2)
Se2	Rb1	$Se1^{14}$	78.337(14)	$Se2^{4}$	Rb2	Se1	143.612(12)
Se2	Rb1	$Se1^{7}$	146.137(11)	$Se2^{4}$	Rb2	$Se1^{6}$	117.788(11)
$Se1^{13}$	Rb1	$Se3^{10}$	86.573(16)	$Se2^{3}$	Rb2	$Se1^{6}$	143.612(12)
$Se1^{14}$	Rb1	$Se3^{10}$	86.573(16)	$Se2^{3}$	Rb2	Se1	117.788(11)
$Se1^{7}$	Rb1	$Se3^{10}$	108.09(2)	$Se1^{6}$	Rb2	Se1	59.06(2)
$Se1^{8}$	Rb1	$Se3^{10}$	108.09(2)	$Se3^{3}$	Rb2	Se1	99.00(2)
$Se1^{13}$	Rb1	$Se1^{7}$	68.708(14)	Se3	Rb2	$Se1^{6}$	115.82(3)
$Se1^{13}$	Rb1	$Se1^{12}$	56.224(17)	$Se2^{1}$	Ba1	$Se2^{12}$	166.30(2)
$Se1^{11}$	Rb1	$Se1^{12}$	62.10(2)	$Se2^{15}$	Ba1	Se2	166.30(2)
$Se1^{7}$	Rb1	$Se1^{11}$	115.45(2)	$Se2^{12}$	Ba1	Se2	76.499(18)
$Se1^{8}$	Rb1	$Se1^{12}$	115.45(2)	$Se2^{15}$	Ba1	$Se2^{12}$	105.185(19)
$Se1^{7}$	Rb1	$Se1^{8}$	66.37(2)	$Se2^{1}$	Ba1	Se2	105.184(19)
$Se1^{13}$	Rb1	$Se1^{8}$	135.067(19)	$Se2^{15}$	Ba1	$Se2^{1}$	76.499(18)
$Se1^{8}$	Rb1	$Se1^{11}$	82.251(17)	Se2	Ba1	$Se1^{15}$	123.009(13)
$Se1^{14}$	Rb1	$Se1^{12}$	116.95(2)	$Se2^{1}$	Ba1	$Se1^{11}$	123.009(13)
$Se1^{7}$	Rb1	$Se1^{12}$	82.251(17)	$Se2^{12}$	Ba1	$Se1^{14}$	123.009(13)
$Se1^{14}$	Rb1	$Se1^{7}$	135.067(19)	$Se2^{15}$	Ba1	$Se1^{14}$	90.225(14)
$Se1^{14}$	Rb1	$Se1^{8}$	68.708(14)	Se2	Ba1	Se1	70.243(13)
$Se1^{14}$	Rb1	$Se1^{11}$	56.224(17)	$Se2^{1}$	Ba1	$Se1^{14}$	70.243(14)
$Se1^{13}$	Rb1	$Se1^{11}$	116.95(2)	$Se2^{12}$	Ba1	$Se1^{11}$	70.243(14)
$Se1^{14}$	Rb1	$Se1^{13}$	156.13(3)	$Se2^{15}$	Ba1	$Se1^{15}$	70.243(14)
Se3	Rb2	$Se3^{5}$	179.25(4)	$Se2^{15}$	Ba1	Se1	123.009(13)
$Se3^{5}$	Rb2	$Se3^{3}$	95.967(4)	$Se2^{15}$	Ba1	$Se1^{11}$	77.839(14)
Se3	Rb2	$Se3^{3}$	84.019(4)	$Se2^{12}$	Ba1	Se1	90.224(14)
$Se3^{5}$	Rb2	$Se3^{4}$	84.019(4)	$Se2^{1}$	Ba1	Se1	77.840(14)
Se3	Rb2	$Se3^{4}$	95.967(4)	Se2	Ba1	$Se1^{14}$	77.839(14)
$Se3^{3}$	Rb2	$Se3^{4}$	177.88(4)	$Se2^{1}$	Ba1	$Se1^{15}$	90.225(14)
$Se3^{3}$	Rb2	$Se2^{4}$	116.48(2)	$Se2^{12}$	Ba1	$Se1^{15}$	77.839(14)
$Se3^{3}$	Rb2	$Se2^{3}$	65.240(15)	Se2	Ba1	$Se1^{11}$	90.225(14)
$Se3^{5}$	Rb2	$Se2^{3}$	125.13(3)	$Se1^{15}$	Ba1	$Se1^{11}$	126.31(2)
Se3	Rb2	$Se2^{4}$	125.13(3)	$Se1^{11}$	Ba1	Se1	155.436(17)
Se3	Rb2	$Se2^{3}$	55.534(15)	$Se1^{15}$	Ba1	Se1	59.894(18)
$Se3^{4}$	Rb2	$Se2^{3}$	116.48(2)	$Se1^{15}$	Ba1	$Se1^{14}$	155.436(17)
$Se3^{4}$	Rb2	$Se2^{4}$	65.240(15)	$Se1^{14}$	Ba1	Se1	126.31(2)
$Se3^{5}$	Rb2	$Se2^{4}$	55.533(16)	$Se1^{14}$	Ba1	$Se1^{11}$	59.895(18)

Se3	Sb1	Se2	113.44(3)	Se1[17]	Sb1	Se3	111.39(2)
Se1	Sb1	Se3	111.39(2)	Se1[17]	Sb1	Se2	107.121(18)

[1]+X,1-Y,1/2+Z;[2]+X,1+Y,+Z;[3]1/2-X,1/2+Y,1-Z;[4]1/2-X,3/2-Y,3/2-Z;[5]+X,2-Y,1/2+Z;[6]+X,2-Y,3/2-Z;[7]+X,-1+Y,1-Z;[8]+X,-1+Y,+Z;[9]1-X,-Y,1-Z;[10]1/2-X,-1/2+Y,1-Z;[11]1-X,1-Y,+Z;[12]1-X,1-Y,1-Z;[13]+X,1-Y,-1/2+Z;[14]+X,1-Y,3/2-Z;[15]1-X,+Y,3/2-Z;[16]1/2-X,3/2-Y,-1/2+Z;[17]+X,+Y,1-Z

Table S10. Crystal data and structure refinement for Rb_2BaSb_4SCl (293 K).

Empirical formula	**Rb_2BaSbS_4Cl**
Formula weight (Da)	593.72
Temperature (K)	273.15
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.1114(15)
b (Å)	9.0493(13)
c (Å)	12.3826(16)
α (°)	90
β (°)	90.382(6)
γ (°)	90
Volume (Å^3)	1133.0(3)
Z	4
Density (calc.) (g/cm^3)	3.481
Absorption coefficient /mm^{-1}	15.278
F (000)	1048.0
Completeness to θ (%)	99.7
Theta range for data collection	4.028 to 50.054
Index ranges	$-12 \le h \le 12$, $-10 \le k \le 10$, $-14 \le l \le 14$
Reflections collected	49877
Independent reflections	1995 [R_{int} = 0.1184, R_{sigma} = 0.0356]
Data / restraints / parameters	1995 / 0 / 83
Goodness-of-fit on F^2	1.052
Final R indexes [$I \ge 2\sigma(I)$] [a]	R_1 = 0.0339, wR_2 = 0.0777
Final R indexes [all data] [a]	R_1 = 0.0420, wR_2 = 0.0822
Largest diff. peak / hole / e Å^{-3}	1.60/-1.01

[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 $F_o^2 > 2\sigma(F_o^2)$

Table S11. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Rb_2BaSb_4SCl (293K). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)	Wyckoff positions	BVS[a]
Rb1	7430.5(8)	1150.2(9)	5263.6(7)	22.6(2)	4e	1.42
Rb2	4761.0(12)	802.8(15)	8259.1(9)	50.5(3)	4e	0.64
Ba1	153.1(6)	939.6(7)	8181.3(5)	29.2(2)	4e	1.66
Sb1	2412.7(5)	3038.0(6)	5961.3(4)	16.74(19)	4e	5.80
S1	2241(3)	5239(3)	5012.5(19)	30.7(6)	4e	2.26
S2	588(2)	1636(3)	5504.7(19)	28.2(5)	4e	2.15
S3	4377(2)	1879(3)	5607(2)	38.8(6)	4e	2.18
S4	2248(3)	3581(3)	7797.3(18)	30.7(6)	4e	2.11
Cl1	-2086(3)	3285(3)	7664(2)	46.5(7)	4e	0.93

[a] The bond valence sum is calculated by bond-valence theory ($S_{ij} = \exp[(R_0-R)/B$, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and $B = 0.37$).

Table S12. Anisotropic displacement parameters ($Å^2×10^3$) for Rb_2BaSb_4SCl (293K). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb1	15.0(4)	19.2(4)	33.6(5)	4.2(4)	3.3(3)	3.1(3)
Rb2	49.3(7)	70.6(8)	31.6(6)	7.9(5)	1.8(5)	27.5(6)
Ba1	26.5(3)	33.0(3)	28.1(3)	2.9(2)	1.9(2)	-3.9(2)
Sb1	16.2(3)	16.7(3)	17.3(3)	0.0(2)	-0.3(2)	-0.6(2)
S1	46.8(15)	17.8(11)	27.3(12)	3.7(9)	-1.4(10)	-1.5(10)
S2	15.6(11)	35.7(13)	33.2(13)	-4.3(10)	-0.8(9)	-6.4(10)
S3	17.0(12)	57.5(17)	42.0(15)	9.8(13)	4.9(10)	11.0(12)
S4	45.6(15)	28.0(12)	18.4(11)	-2.9(10)	-2.3(10)	-4.9(11)
Cl1	59.3(18)	44.6(16)	35.6(14)	7.2(12)	0.8(12)	9.9(13)

Table S13. Bond lengths for Rb_2BaSb_4SCl (293K).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Rb1	S1[5]	3.303(2)	Rb2	S4[6]	3.867(3)
Rb1	S2[3]	3.235(2)	Rb2	Cl1[9]	3.712(3)
Rb1	S2[4]	3.362(3)	Ba1	S1[8]	3.267(3)
Rb1	S3[4]	3.462(3)	Ba1	S1[9]	3.367(3)
Rb1	S3	3.188(2)	Ba1	S2[8]	3.642(3)
Rb1	S4[6]	3.357(2)	Ba1	S2	3.405(3)
Rb1	Cl1[2]	3.299(3)	Ba1	S4	3.231(3)
Rb1	Cl1[3]	3.576(3)	Ba1	S4[9]	3.447(3)
Rb2	S1[8]	3.488(3)	Ba1	Cl1[9]	3.273(3)
Rb2	S1[6]	3.734(3)	Ba1	Cl1	3.165(3)
Rb2	S3	3.445(3)	Sb1	S1	2.318(2)
Rb2	S3[8]	3.608(3)	Sb1	S2	2.306(2)
Rb2	S3[6]	3.915(3)	Sb1	S3	2.291(2)
Rb2	S4	3.617(3)	Sb1	S4	2.333(2)

[1]+X,1/2-Y,-1/2+Z; [2]1+X,1/2-Y,-1/2+Z; [3]1+X,+Y,+Z; [4]1-X,-Y,1-Z; [5]1-X,1-Y,1-Z; [6]1-X,-1/2+Y,3/2-Z; [7]1-X,-Y,2-Z; [8]+X,1/2-Y,1/2+Z; [9]-X,-1/2+Y,3/2-Z

Table S14. Bond angles for Rb_2BaSb_4SCl (293K).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
$S1^5$	Rb1	$S2^4$	130.72(7)	S3	Rb2	$S3^6$	128.44(7)
$S1^5$	Rb1	$S3^4$	143.53(7)	$S3^8$	Rb2	S4	69.15(6)
$S1^5$	Rb1	$S4^6$	138.61(7)	S3	Rb2	$S4^6$	84.72(6)
$S1^5$	Rb1	$Cl1^3$	62.51(6)	$S3^8$	Rb2	$S4^6$	131.57(6)
$S2^3$	Rb1	$S1^5$	77.01(7)	S3	Rb2	S4	65.06(6)
$S2^3$	Rb1	$S2^4$	62.51(7)	$S3^8$	Rb2	$Cl1^9$	121.54(7)
$S2^4$	Rb1	$S3^4$	68.44(6)	S3	Rb2	$Cl1^9$	78.61(7)
$S2^3$	Rb1	$S3^4$	130.92(6)	S4	Rb2	$S1^6$	138.79(6)
$S2^3$	Rb1	$S4^6$	86.41(7)	S4	Rb2	$S3^6$	147.31(7)
$S2^3$	Rb1	$Cl1^3$	73.76(7)	$S4^6$	Rb2	$S3^6$	58.46(5)
$S2^3$	Rb1	$Cl1^2$	85.19(7)	S4	Rb2	$S4^6$	149.10(4)
$S2^4$	Rb1	$Cl1^3$	124.18(7)	S4	Rb2	$Cl1^9$	82.43(7)
S3	Rb1	$S1^5$	84.68(7)	$Cl1^9$	Rb2	$S1^6$	132.83(7)
S3	Rb1	$S2^3$	156.30(8)	$Cl1^9$	Rb2	$S3^6$	73.36(7)
S3	Rb1	$S2^4$	140.56(7)	$Cl1^9$	Rb2	$S4^6$	98.43(7)
S3	Rb1	$S3^4$	72.28(8)	$S1^8$	Ba1	$S1^9$	86.66(7)
S3	Rb1	$S4^6$	97.87(7)	$S1^9$	Ba1	S2	141.21(6)
S3	Rb1	$Cl1^3$	84.53(8)	$S1^9$	Ba1	$S2^8$	70.87(6)
S3	Rb1	$Cl1^2$	104.37(8)	$S1^8$	Ba1	S2	130.46(6)
$S3^4$	Rb1	$Cl1^3$	139.06(7)	$S1^8$	Ba1	$S2^8$	64.80(5)
$S4^6$	Rb1	$S2^4$	68.15(6)	$S1^8$	Ba1	$S4^9$	119.50(6)
$S4^6$	Rb1	$S3^4$	73.90(6)	$S1^9$	Ba1	$S4^9$	66.98(6)
$S4^6$	Rb1	$Cl1^3$	76.55(6)	$S1^8$	Ba1	$Cl1^9$	66.30(7)
$Cl1^2$	Rb1	$S1^5$	74.33(7)	S2	Ba1	$S2^8$	129.92(3)
$Cl1^2$	Rb1	$S2^4$	75.38(7)	S2	Ba1	$S4^9$	82.40(6)
$Cl1^2$	Rb1	$S3^4$	84.28(7)	S4	Ba1	$S1^9$	135.41(6)
$Cl1^2$	Rb1	$S4^6$	142.29(7)	S4	Ba1	$S1^8$	85.54(6)
$Cl1^2$	Rb1	$Cl1^3$	134.99(5)	$S4^9$	Ba1	$S2^8$	137.03(6)
$Sb1^6$	Rb2	$S3^6$	34.03(4)	S4	Ba1	$S2^8$	66.10(6)
$S1^8$	Rb2	$S1^6$	101.52(6)	S4	Ba1	S2	68.33(6)
$S1^8$	Rb2	$S3^8$	64.70(6)	S4	Ba1	$S4^9$	150.16(3)
$S1^8$	Rb2	$S3^6$	72.15(6)	S4	Ba1	$Cl1^9$	95.88(7)
$S1^6$	Rb2	$S3^6$	59.50(5)	Cl1	Ba1	$S1^8$	144.81(7)
$S1^8$	Rb2	S4	76.76(6)	$Cl1^9$	Ba1	$S1^9$	120.51(7)
$S1^6$	Rb2	$S4^6$	59.28(5)	Cl1	Ba1	$S1^9$	75.18(7)
$S1^8$	Rb2	$S4^6$	130.25(6)	$Cl1^9$	Ba1	$S2^8$	128.73(6)
$S1^8$	Rb2	$Cl1^9$	59.47(6)	Cl1	Ba1	$S2^8$	80.69(6)
S3	Rb2	$S1^8$	126.27(7)	$Cl1^9$	Ba1	S2	75.12(7)
$S3^8$	Rb2	$S1^6$	73.08(6)	Cl1	Ba1	S2	77.05(6)
S3	Rb2	$S1^6$	132.14(7)	Cl1	Ba1	S4	86.73(8)
S3	Rb2	$S3^8$	126.28(4)	$Cl1^9$	Ba1	$S4^9$	81.58(7)
$S3^8$	Rb2	$S3^6$	105.27(6)	Cl1	Ba1	$S4^9$	80.97(7)

Cl1	Ba1	Cl1[9]	148.77(3)	S3	Sb1	S1	110.99(10)
S1	Sb1	S4	107.91(9)	S3	Sb1	S2	113.22(10)
S2	Sb1	S1	106.94(9)	S3	Sb1	S4	110.51(10)
S2	Sb1	S4	107.01(9)				

[1]+X,1/2-Y,-1/2+Z; [2]1+X,1/2-Y,-1/2+Z; [3]1+X,+Y,+Z; [4]1-X,-Y,1-Z; [5]1-X,1-Y,1-Z; [6]1-X,-1/2+Y,3/2-Z; [7]1-X,-Y,2-Z; [8]+X,1/2-Y,1/2+Z; [9]-X,-1/2+Y,3/2-Z; [10]-1+X,+Y,+Z; [11]-1+X, 1/2-Y,1/2+Z; [12]1-X,1/2+Y,3/2-Z; [13]-X,1/2+Y,3/2-Z

Table S15. Structural features of thioantimonates.

	Compound	Crystal System	Space Group	Structural units
1	Cs_3SbS_4	Orthorhombic	*Pnma*	[a]**[SbS_4]**
2	Cs_3SbSe_4	Orthorhombic	*Pnma*	[a]**[SbS_4]**
3	K_3SbS_4	Orthorhombic	$Cmc2_1$	[a]**[SbS_4]**
4	K_3SbSe_4	Trigonal	R3*c*	[a]**[SbS_4]**
5	Na_3SbS_4	Tetragonal	$P\bar{4}2_1c$	[a]**[SbS_4]**
6	Na_3SbSe_4	Tetragonal	$P\bar{4}2_1c$	[a]**[SbS_4]**
7	Rb_3SbS_4	Orthorhombic	*Pnma*	[a]**[SbS_4]**
8	Rb_3SbSe_4	Orthorhombic	*Pnma*	[a]**[SbS_4]**
9	Cu_3SbS_4	Tetragonal	$I\bar{4}2m$	[a]**[SbS_4]**
10	Cu_3SbSe_4	Tetragonal	$I\bar{4}2m$	[a]**[SbS_4]**
11	Ag_2KSbS_4	Tetragonal	$I\bar{4}2m$	[a]**[SbS_4]**
12	K_2AgSbS_4	Orthorhombic	*Pnn*2	[a]**[SbS_4]**
13	Cs_2AgSbS_4	Triclinic	$P\bar{1}$	[a]**[SbS_4]**
14	Ag_2RbSbS_4	Trigonal	$P3_221$	[a]**[SbS_4]**
15	Rb_2AgSbS_4	Monoclinic	*P*21/*c*	[a]**[SbS_4]**
16	Rb_2AuSbS_4	Orthorhombic	*Pbcm*	[a]**[SbS_4]**
17	$Cs_3Ag_2Sb_3S_8$	Monoclinic	$P2_1/m$	[a]**[SbS_4]** [SbS_3]
18	$K_2Sb_4S_7$	Monoclinic	*C*2/*c*	[b][SbS_4] [SbS_3]
19	$NaSbS_2$	Cubic	$Fm\bar{3}m$	[b][SbS_4]
20	$KSbS_2$	Monoclinic	*C*2/*c*	[b][SbS_4]
21	$RbSbS_2$	Triclinic	$P\bar{1}$	[b][SbS_4] [SbS_3]
22	K_3SbS_3	Cubic	$P2_13$	[SbS_3]
23	Na_3SbS_3	Cubic	$P2_13$	[SbS_3]
24	$Cs_2Sb_4S_7$	Monoclinic	$P2_1$/c	[b][SbS_4] [SbS_3]
25	$Rb_2Sb_4S_7$	Cubic	$P2_13$	[b][SbS_4] [SbS_3]
26	$CsSbS_2$	Monoclinic	$P2_1$/c	[SbS_3]
27	$Cs_4Sb_{14}S_{23}$	Triclinic	$P\bar{1}$	[b][SbS_4] [SbS_3]
28	$Cs_2Sb_8S_{13}$	Triclinic	$P\bar{1}$	[b][SbS_4] [SbS_3]
29	$Ba_8Sb_6S_{17}$	Monoclinic	*P*2/*c*	[b][SbS_4] [SbS_3]
30	$Ca_2Sb_2S_5$	Monoclinic	$P2_1$/c	[SbS_3]
31	$Sr_3Sb_4S_9$	Orthorhombic	$Pna2_1$	[SbS_3] [SbS_5]
32	$Li_{1.5}Sb_{5.5}S_9$	Triclinic	$P\bar{1}$	[b][SbS_4] [SbS_5]
33	$LiSbS_2$	Trigonal	$R\bar{3}$	[b][SbS_4]
34	$BaSb_2S_4$	Monoclinic	$P2_1$/c	[b][SbS_4] [SbS_3]
35	$KHgSbS_3$	Monoclinic	*C*2/*c*	[SbS_3]
36	$Cs_3Sb_5S_9$	Monoclinic	*C*2/*m*	[SbS_3] [SbS_6]
37	Na_2CuSbS_3	Monoclinic	$P2_1$/c	[SbS_3]
38	$Rb_2Au_6Sb4S_{10}$	Orthorhombic	*Pnnm*	[b][SbS_4] [SbS_3]
39	RbU_2SbS_8	Monoclinic	*Cm*	[b][SbS_4]
40	KSb_5S_8	Monoclinic	*Pc*	[b][SbS_4] [SbS_5] [SbS_3]

41	$Sr_6Sb_6S_{17}$	Orthorhombic	$P2_12_12_1$	$[SbS_3]$
42	$Ba_{2.605}Pb_{1.39}Sb4S_{10}$	Monoclinic	$P2_1$	$^{b}[SbS_4]$ $[SbS_3]$
43	$Na_9Gd_5Sb_8S_{26}$	Orthorhombic	*Pnma*	$^{b}[SbS_4]$ $[SbS_3]$
44	$KSbP_2S_6$	Monoclinic	$P2_1$	$^{b}[SbS_4]$
45	$KLa_2Sb_3S_9$	Orthorhombic	$P2_12_12_1$	$[SbS_5]$
46	$Li_5SbS_3I_2$	Orthorhombic	*Pnnm*	$[SbS_3]$
47	$CsAgSb_4S_7$	Monoclinic	$C2/c$	$^{b}[SbS_4]$ $[SbS_3]$
48	K_2CuSbS_3	Monoclinic	$P2_1/c$	$[SbS_3]$
49	$NaSbP_2S_6$	Monoclinic	$P2_1/c$	$[SbS_5]$
50	KAg_2SbS_3	Triclinic	$P\bar{1}$	$[SbS_3]$
51	$K_2Ag_3Sb_3S_7$	Orthorhombic	$Cmc2_1$	$[SbS_3]$
52	$BaSbBS_4$	Orthorhombic	*Pnma*	$[SbS_3]$
53	$K_3Ag_9Sb_4S_{12}$	Tetragonal	$P4_2/n$	$[SbS_3]$
54	$Cs_3Ag_9Sb_4S_{12}$	Tetragonal	$P4_2/n$	$[SbS_3]$
55	$Rb_3Ag_9Sb_4S_{12}$	Tetragonal	$P4_2/n$	$[SbS_3]$
56	Ba_2SbFeS_5	Orthorhombic	*Pnma*	$[SbS_3]$
57	$NaCdSbS_3$	Monoclinic	$C2/c$	$[SbS_3]$
58	$Ba_{23}Ga_8Sb_2S_{38}$	Orthorhombic	$Cmc2_1$	$[SbS_3]$
59	Li_3SbS_3	Orthorhombic	$Pna2_1$	$[SbS_3]$
60	$Ba_2Sb_4GeS_{10}$	Tetragonal	$P4_2/mbc$	$[SbS_3]$ $[SbS_5]$
61	Ba_2SbGaS_5	Orthorhombic	*Pnma*	$[SbS_3]$
62	Cs_3SbS_3	Cubic	$P2_13$	$[SbS_3]$
63	Rb_3SbS_3	Cubic	$P2_13$	$[SbS_3]$
64	$Rb_6U_3Sb_2P_8S_{32}$	Trigonal	$R\bar{3}c$	$[SbS_3]$
65	$Cs_6U_3Sb_2P_8S_{32}$	Trigonal	$R\bar{3}c$	$[SbS_3]$
66	$Cs_2Cu_2Sb_2S_5$	Triclinic	$P\bar{1}$	$[SbS_3]$
67	$Ba_6B_3SbS_{12}$	Monoclinic	$P2_1/c$	$[SbS_3]$
68	Ba_3BSbS_6	Hexagonal	$P\bar{6}2m$	$[SbS_3]$
69	$BaAgSbS_3$	Monoclinic	$C2/c$	$[SbS_3]$
70	$K_2Sb_2Sn_3S_{10}$	Monoclinic	$P2_1/c$	$[SbS_3]$
71	$Rb_2Sb_2Sn_3S_{10}$	Monoclinic	$P2_1/c$	$[SbS_3]$
72	$Cs_2Sb_2Sn_3S_{10}$	Monoclinic	$P2_1/c$	$[SbS_3]$
73	$Ba_3Sb_2S_7$	Monoclinic	$C2/c$	$[SbS_3]$
74	$Li_{17}Sb_{13}S_{28}$	Monoclinic	$C2/m$	$[SbS_3]$ $[SbS_5]$
75	$RbCuSb_2S_4$	Monoclinic	$C2/c$	$^{b}[SbS_4]$
76	$CsCuSb_2S_4$	Monoclinic	$C2/c$	$^{b}[SbS_4]$
77	KCu_2SbS_3	Triclinic	$P\bar{1}$	$[SbS_3]$
78	Ba_2AlSbS_5	Orthorhombic	Pnma	$[SbS_3]$
79	$Cs_2HgSb_4S_8$	Triclinic	$P\bar{1}$	$[SbS_3]$
80	$Na_7HgSb_5S_{12}$	Trigonal	$R\bar{3}$	$b[SbS_4]$
81	$Li_3Sb_{11}S_{18}$	Triclinic	$P\bar{1}$	$[SbS_3]$
82	$NaBaSbS_3$	Monoclinic	$P2_1/c$	$[SbS_3]$
83	$LiBaSbS_3$	Orthorhombic	*Pbam*	$[SbS_3]$
84	$Rb_2Ag_3Sb_3S_7$	Orthorhombic	$Cmc2_1$	$[SbS_3]$

85	$Cs_2Ag_3Sb_3S_7$	Orthorhombic	$Cmc2_1$	$[SbS_3]$
86	$Na_6CdSb_4S_{10}$	Monoclinic	$C2/c$	$^b[SbS_4]$ $[SbS_3]$
87	$K_2Ba_3Cu_2Sb_2S_{10}$	Monoclinic	$C2/m$	$[SbS_3]$
88	$Cs_2Ba_3Cu_2Sb_2S_{10}$	Monoclinic	$C2/m$	$[SbS_3]$
89	$Rb_2Ba_3Cu_2Sb2S_{10}$	Monoclinic	$C2/m$	$[SbS_3]$
90	$CsAg_2SbS_3$	Triclinic	$P\bar{1}$	$[SbS_3]$
91	$CsSb_5S_8$	Monoclinic	$P2_1/c$	$^b[SbS_4]$ $[SbS_3]$
92	$Cs_4Sb_4S_8$	Orthorhombic	$Pnma$	$[SbS_3]$
93	$RbSb_5S_8$	Monoclinic	Pc	$^b[SbS_4]$ $[SbS_3]$
94	$Rb_2CuSb_7S_{12}$	Triclinic	$P\bar{1}$	$^b[SbS_4]$ $[SbS_3]$
95	$Rb_2ZnSb_4S_8$	Triclinic	$P\bar{1}$	$[SbS_3]$
96	$LiSrSbS_3$	Monoclinic	$P2_1/c$	$[SbS_3]$
97	$Rb_2HgSb_4S_8$	Triclinic	$P\bar{1}$	$[SbS_3]$
98	$Cs_2ZnSb_2S_5$	Monoclinic	$C2/c$	$[SbS_3]$
99	$LiSbSe_2$	Cubic	$Fm\bar{3}m$	$[SbS_6]$
100	$NaSbSe_2$	Cubic	$Fm\bar{3}m$	$[SbS_6]$
101	$KSbSe_2$	Triclinic	$P\bar{1}$	$^b[SbS_4]$ $[SbS_3]$
102	$RbSb3Se_5$	Orthorhombic	$Pnma$	$[SbS_5]$ $[SbS_6]$
103	$BaSb_2Se_4$	Monoclinic	$P2_1/c$	$^b[SbS_4]$ $[SbS_3]$
104	$RbSbSe_2$	Orthorhombic	$Pnnm$	$^b[SbS_4]$ $[SbS_3]$
105	$Ba_4Sb_4Se_{11}$	Triclinic	$P\bar{1}$	$[SbS_3]$
106	$CsSb_2Se_4$	Triclinic	$P\bar{1}$	$^b[SbS_4]$ $[SbS_3]$
107	$Cs_3Sb_5Se_9$	Monoclinic	$C2/m$	$[SbS_3]$ $[SbS_6]$
108	$K_2Sb_4Se_8$	Triclinic	$P\bar{1}$	$^b[SbS_4]$ $[SbS_3]$
109	$Rb_2Sb_4Se_8$	Triclinic	$P\bar{1}$	$^b[SbS_4]$ $[SbS_3]$
110	KU_2SbSe_8	Monoclinic	Cm	$^b[SbS_4]$
111	$Cs_2Cu_2Sb_2Se_5$	Triclinic	$P\bar{1}$	$[SbS_3]$
112	$K_2Gd_2Sb_2Se_9$	Orthorhombic	$Pbam$	$[SbS_5]$
113	$K_2Gd_2Sb_2Se_9$	Monoclinic	$C2/m$	$[SbS_3]$
114	$RbHgSbSe_3$	Monoclinic	$P21/c$	$[SbS_3]$
115	$CsHgSbSe_3$	Orthorhombic	$Cmcm$	$[SbS_3]$
116	K_3SbSe_3	Cubic	$P2_13$	$[SbS_3]$
117	Rb_3SbSe_3	Cubic	$P2_13$	$[SbS_3]$
118	Cs_3SbSe_3	Cubic	$P2_13$	$[SbS_3]$
119	$KHgSbSe_3$	Orthorhombic	$Pnma$	$[SbS_3]$
120	$KSbP_2Se_6$	Monoclinic	$P2_1$	$[SbS_3]$
121	$KSm_2Sb_3Se_8$	Orthorhombic	$Pnma$	$[SbS_3]$ $[SbS_5]$
122	$Ba_4LaGe_3SbSe_{13}$	Monoclinic	$P2_1/c$	$[SbS_3]$
123	$BaLaSb_2Se_6$	Monoclinic	$P2_1/c$	$[SbS_3]$
124	KCu_2SbSe_3	Monoclinic	$P2_1/c$	$[SbS_3]$
125	$Ba_3SnSb_2Se_8$	Orthorhombic	$Pnma$	$[SbS_5]$
126	Na_3SbSe_3	Cubic	$P2_13$	$[SbS_3]$
127	$Ba_2GaSbSe_5$	Orthorhombic	$Pnma$	$[SbS_3]$
128	$Ba_2InSbSe_5$	Orthorhombic	$Cmc2_1$	$[SbS_5]$

129	$KBaSbSe_3$	Monoclinic	$P2_1/c$	$[SbS_3]$
130	Ba_3BSbSe_6	Hexagonal	$P\bar{6}2m$	[b]$[SbS_4]$ $[SbS_3]$
131	$Ba_3Sb_2Se_7$	Monoclinic	$C2/c$	$[SbS_3]$
132	$Ba_2Sb_2Se_5$	Orthorhombic	$Pbam$	$[SbS_5]$
133	$Ba_2FeSbSe_5$	Orthorhombic	$Pnma$	$[SbS_3]$
134	$Ba_{23}Ga_8Sb_2Se_{38}$	Orthorhombic	$Cmc2_1$	$[SbS_3]$
135	$NaBaSbSe_3$	Monoclinic	$P2_1/c$	$[SbS_3]$
136	$LiBaSbSe_3$	Orthorhombic	$Pbam$	$[SbS_3]$
137	$Na_3CdSbSe_4$	Monoclinic	$P2_1/c$	$[SbS_3]$
138	$Ba_4NbSbSe_{12}$	Triclinic	$P\bar{1}$	$[SbS_3]$
139	$Ba_4TaSbSe_{12}$	Triclinic	$P\bar{1}$	$[SbS_3]$
140	$Ba_{10}Fe_3Sb_7Se_{24}$	Orthorhombic	$Cmc2_1$	[b]$[SbS_4]$ $[SbS_3]$
141	$Ba_4GeSb_2Se_{11}$	Orthorhombic	$Cmc2_1$	$[SbS_3]$
142	$Ba_2AsSbSe_5$	Monoclinic	$P2_1$	$[SbS_3]$ $[SbS_5]$
143	$Ba_3KSb_4S_9Cl$	Orthorhombic	$Pnnm$	$[SbS_3]$ $[SbS_5]$
144	$Ba_4Sb_3S_8Cl$	Monoclinic	$P2_1/c$	[b]$[SbS_4]$ $[SbS_3]$
145	Ba_2SbS_3I	Orthorhombic	$Pnma$	$[SbS_3]$
146	$LiBa_3SbS_6C_{l2}$	Monoclinic	$C2/m$	$[SbS_3]$
147	$Ba_2Sb_2Se_4F_2$	Triclinic	$P\bar{1}$	$[SbS_3]$
148	$Sr_2Sb_2Se_4F_2$	Tetragonal	$P4/nmm$	$[SbS_5]$

[a]$[SbS_4]$: Regular tetrahedron, [b]$[SbS_4]$: Seesaw tetrahedron.

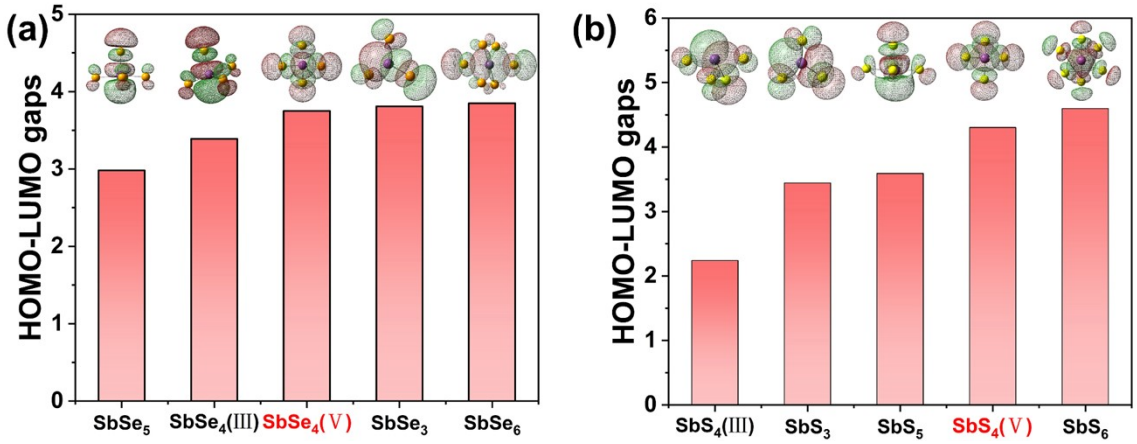

Figure S1. The calculated HOMO-LUMO gaps.

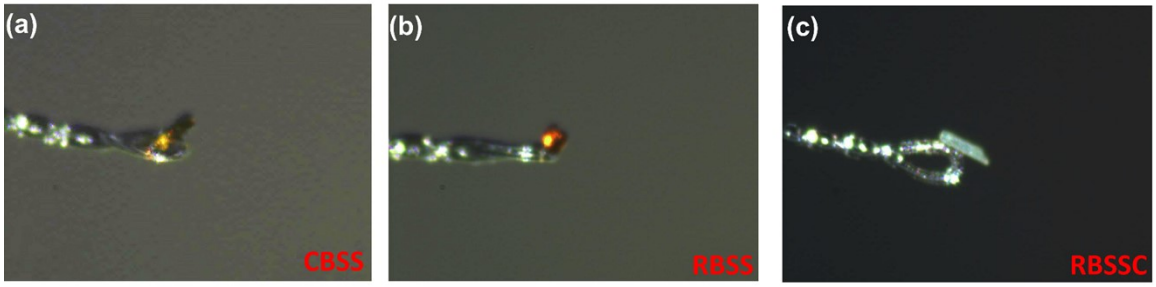

Figure S2. (a-c) They are used respectively to collect crystal photographs of CBSS, RBSS, and RBSSC single crystal X-ray data.

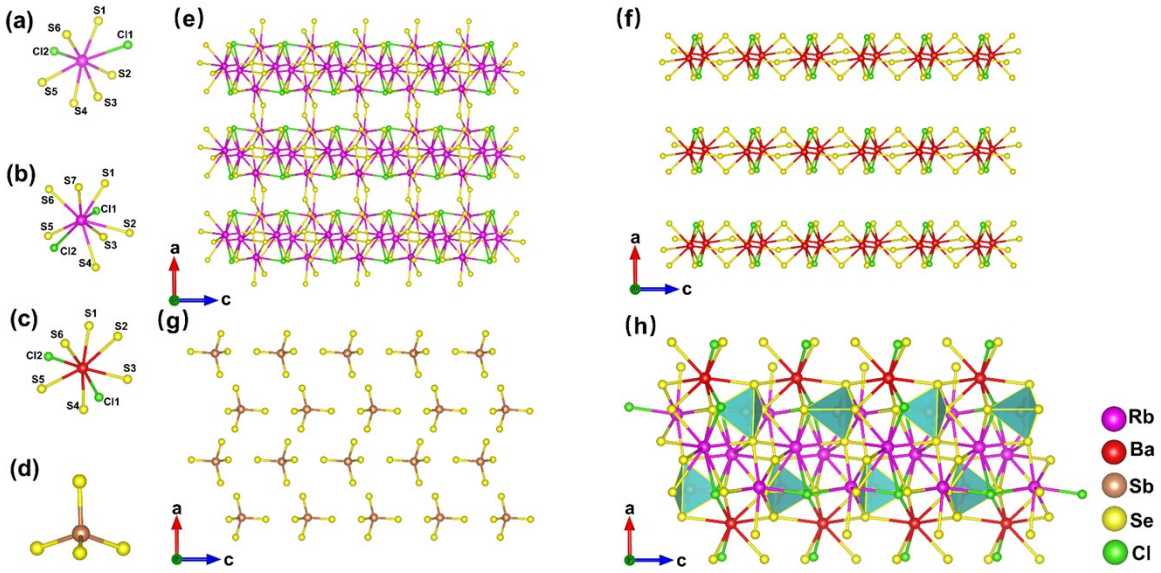

Figure S3. (a-d) Coordination patterns among Rb atoms, Ba atoms, and Sb atoms. (e) The two-dimensional layer formed by the sharing of S atoms between $[RbS_6Cl_2]$ and $[RbS_7Cl_2]$ units. (f) Two opposing infinite chains of $[BaS_5Cl_2]$. (g) The RBSSC structures contain isolated $[SbS_4]$ tetrahedra. (h) Crystal structure of RBSSC along the b-axis.

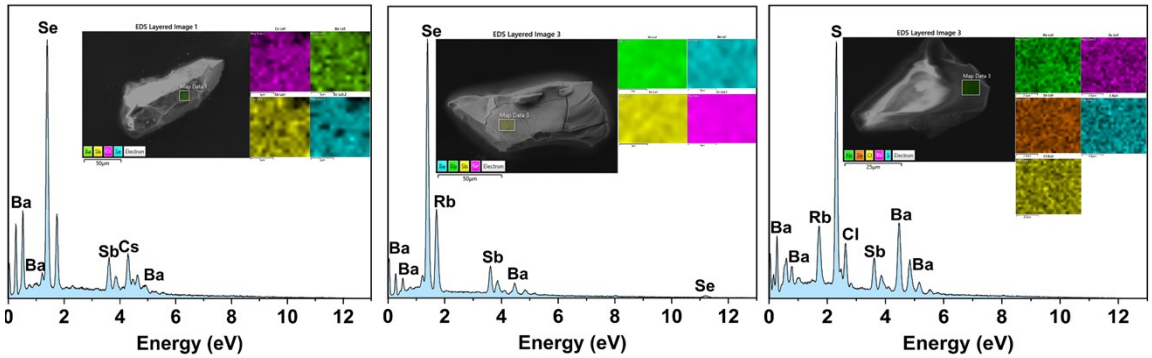

Figure S4. X-ray energy dispersive spectrum of CBSS, RBSS and RBSSC crystals.

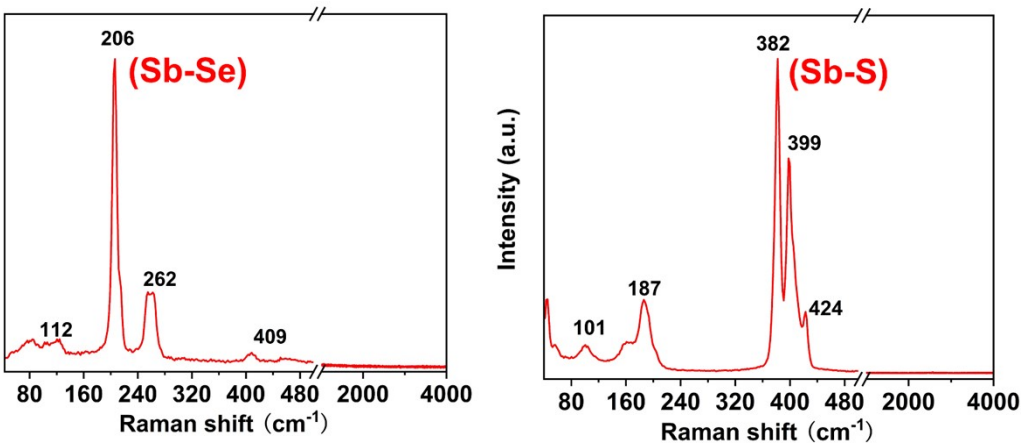

Figure S5. The Raman spectroscopy of RBSS and RBSSC.

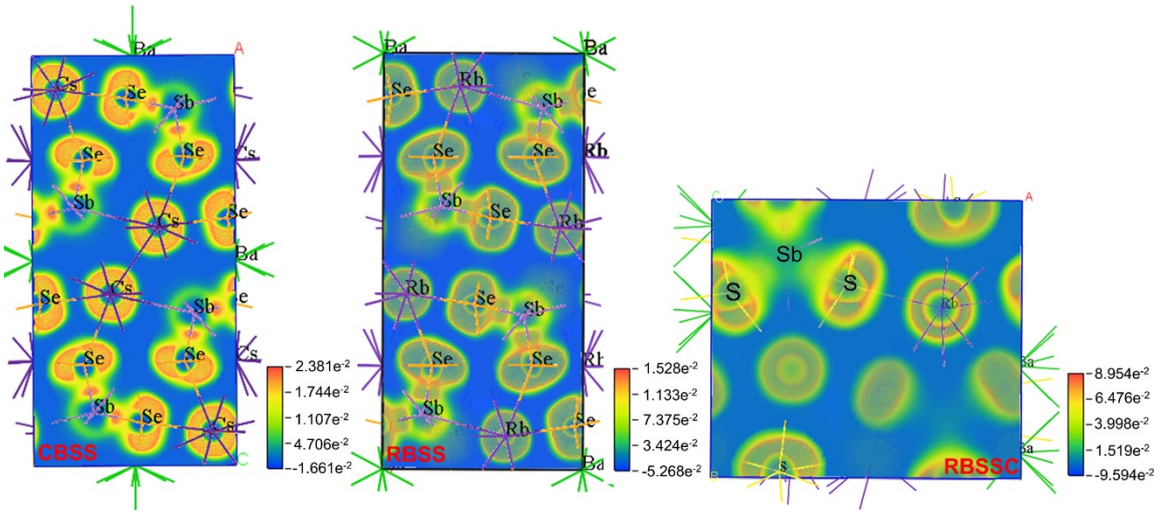

Figure S6. The electron localization function (ELF) for RBSS, RBSS and RBSSC.

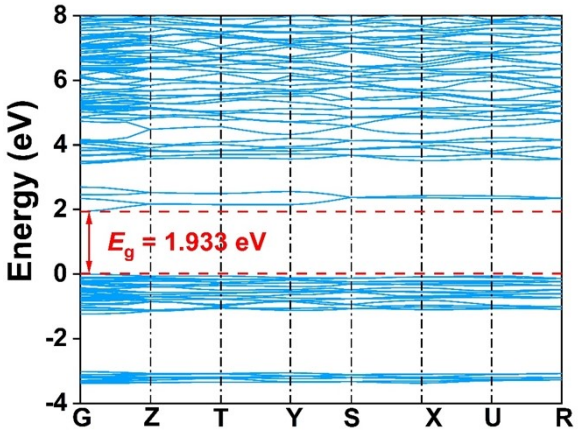

Figure S7. Calculate the GGA band gap of Cs_3SbSe_4 compound.

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