Supporting Information

$BaCdSnS_4$ and $Ba_3CdSn_2S_8$: Syntheses, Structures, Nonlinear Optical and Photoluminescence Properties

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Table S1. (a) Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $BaCdSnS_4$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	**X**	**Y**	**Z**	**U_{eq}**	**BVS**	**Wyckoff position**
Ba(1)	10000	10000	135(2)	15(1)	2.215	8a
Ba(2)	9990(1)	7477(1)	113(2)	14(1)	2.187	16b
Ba(3)	10000	10000	5097(2)	16(1)	2.189	8a
Cd(1)	8884(1)	8757(1)	2586(1)	22(1)	2.040	16b
Cd(2)	9249(1)	8749(1)	7286(1)	22(1)	2.030	16b
Sn(1)	8182(1)	8752(1)	5486(1)	13(1)	4.144	16b
Sn(2)	8621(1)	8746(1)	86(1)	13(1)	4.149	16b
S(1)	2070(5)	-2599(9)	6455(4)	7(1)	2.138	16b
S(2)	6024(4)	2715(7)	5585(3)	8(1)	2.252	16b
S(3)	9564(2)	8745(3)	-913(3)	14(1)	2.231	16b
S(4)	7820(2)	8736(3)	-1132(3)	17(1)	2.145	16b
S(5)	8710(3)	7894(2)	6215(4)	17(1)	1.990	16b
S(6)	8715(3)	9601(2)	6242(4)	14(1)	2.024	16b
S(7)	8694(3)	9602(2)	1222(4)	13(1)	1.965	16b
S(8)	8694(3)	7905(2)	1244(4)	16(1)	2.006	16b

Table S1. (b) Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ba_3CdSn_2S_8$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	**X**	**Y**	**Z**	**U_{eq}**	**BVS**	**Wyckoff position**
Ba(1)	10000	7500	-177(1)	36(1)	2.13	24d
Cd(1)	10000	2500	-1250	26(1)	1.97	12b
Sn(1)	9785(1)	4785(1)	215(1)	17(1)	4.18	16c
S(1)	10850(1)	3910(1)	-662(1)	20(1)	2.19	48e
S(2)	8865(1)	3865(1)	1135(1)	28(1)	2.29	16c

Table S2. (a) Selected bond distances (Å) and angles (deg) for $BaCdSnS_4$.

Cd(1)-S(2)	2.453(4)	S(2)-Cd(1)-S(7)	126.19(19)
Cd(1)-S(8)	2.588(5)	S(8)-Cd(1)-S(7)	90.83(11)
Cd(1)-S(1)	2.596(4)	S(1)-Cd(1)-S(7)	105.77(18)
Cd(1)-S(7)	2.597(5)	S(8)-Sn(2)-S(3)	106.84(19)
Cd(2)-S(3)	2.456(4)	S(7)-Sn(2)-S(3)	106.39(18)
Cd(2)-S(6)	2.577(6)	S(1)-Sn(1)-S(5)	121.0(2)
Cd(2)-S(4)	2.604(4)	S(1)-Sn(1)-S(6)	120.9(2)
Cd(2)-S(5)	2.604(6)	S(5)-Sn(1)-S(6)	102.06(13)
Sn(1)-S(1)	2.356(4)	S(1)-Sn(1)-S(2)#2	104.65(13)
Sn(1)-S(5)	2.387(5)	S(5)-Sn(1)-S(2)#2	102.4(2)
Sn(1)-S(6)	2.390(5)	S(6)-Sn(1)-S(2)#2	102.99(18)
Sn(1)-S(2)	2.413(4)	S(4)-Sn(2)-S(8)	118.3(2)
Sn(2)-S(4)	2.353(4)	S(4)-Sn(2)-S(7)	118.5(2)
Sn(2)-S(8)	2.381(5)	S(8)-Sn(2)-S(7)	101.37(12)
Sn(2)-S(7)	2.392(5)	S(4)-Sn(2)-S(3)	104.45(14)
Sn(2)-S(3)	2.419(4)	S(7)#12-Ba(1)-S(8)#5	68.73(16)
Ba(1)-S(1)	3.234(7)	S(3)-Ba(1)-S(3)#12	129.12(16)
Ba(2)-S(1)	3.246(6)	S(3)-Ba(1)-S(1)#5	63.11(10)
Ba(2)-S(2)	3.202(6)	S(3)#12-Ba(1)-S(1)#5	147.05(7)
Ba(3)-S(2)	3.202(6	S(3)-Ba(1)-S(1)#9	147.05(7)
Ba(1)-S(3)	3.199(6)	S(3)#12-Ba(1)-S(1)#9	63.11(10)
Ba(2)-S(3)	3.205(6)	S(1)#5-Ba(1)-S(1)#9	126.47(18)
Ba(2)-S(4) #9	3.232(7)	S(3)-Ba(1)-S(7)#12	131.75(11)
Ba(2)-S(4)#1	3.232(6)	S(3)#12-Ba(1)-S(7)	73.04(11)
Ba(3)-S(4)	3.238(6)	S(1)#5-Ba(1)-S(7)	78.11(13)
Ba(2)-S(5)	3.255(6)	S(1)#9-Ba(1)-S(7)	79.27(12)
Ba(3)-S(5)	3.291(6)	S(3)-Ba(1)-S(7)	73.04(11)
Ba(2)-S(6)	3.263(6)	S(3)#12-Ba(1)-S(7)	131.75(11)
Ba(3)-S(6)	3.270(6)	S(1)#5-Ba(1)-S(7)	79.27(12)
Ba(1)-S(7)	3.273(6)	S(1)#9-Ba(1)-S(7)	78.11(13)
Ba(2)-S(7)	3.302(6)	S(7)#12-Ba(1)-S(7)	128.4(2)
Ba(1)-S(8)	3.276(6)	S(3)-Ba(1)-S(8)#9	76.09(12)
Ba(2)-S(8)	3.300(6)	S(3)#12-Ba(1)-S(8)#9	76.24(12)
S(3)#3-Cd(2)-S(6)	129.53(19)	S(1)#5-Ba(1)-S(8)#9	133.94(12)
S(3)#3-Cd(2)-S(4)#4	101.52(11)	S(1)#9-Ba(1)-S(8)#9	78.89(11)
S(6)-Cd(2)-S(4)#4	98.17(18)	S(7)#12-Ba(1)-S(8)#9	147.94(8)
S(3)#3-Cd(2)-S(5)	129.73(19)	S(7)-Ba(1)-S(8)#9	68.73(16)
S(6)-Cd(2)-S(5)	91.57(11)	S(3)-Ba(1)-S(8)#5	76.24(12)
S(4)#4-Cd(2)-S(5)	98.94(19)	S(3)#12-Ba(1)-S(8)#5	76.09(12)
S(2)-Cd(1)-S(8)	125.82(19)	S(1)#5-Ba(1)-S(8)#5	78.89(11)
S(2)-Cd(1)-S(1)	100.28(13)	S(1)#9-Ba(1)-S(8)#5	133.94(12)
S(8)-Cd(1)-S(1)	105.85(19)	S(8)-Ba(2)-S(7)#5	146.73(8)

S(7)-Ba(1)-S(8)#5	147.94(8)	S(2)-Ba(3)-S(2)#12	120.32(18)
S(8)#9-Ba(1)-S(8)#5	112.4(2)	S(2)-Ba(3)-S(4)#4	66.24(11)
S(3)-Ba(2)-S(1)#5	62.91(10)	S(2)#12-Ba(3)-S(4)#4	156.19(7)
S(4)#1-Ba(2)-S(1)#5	122.01(15)	S(2)-Ba(3)-S(4)#11	156.19(7)
S(2)#13-Ba(2)-S(5)#13	80.72(11)	S(2)#12-Ba(3)-S(4)#11	66.24(11)
S(2)#13-Ba(2)-S(3)	124.74(14)	S(4)#4-Ba(3)-S(4)#11	118.06(19)
S(2)#13-Ba(2)-S(4)#1	66.32(11)	S(2)-Ba(3)-S(6)#12	128.41(12)
S(3)-Ba(2)-S(4)#1	150.88(12)	S(2)#12-Ba(3)-S(6)#12	80.54(11)
S(2)#13-Ba(2)-S(1)#5	151.88(10)	S(4)#4-Ba(3)-S(6)#12	78.67(13)
S(3)-Ba(2)-S(5)#13	130.32(12)	S(4)#11-Ba(3)-S(6)#12	73.97(12)
S(4)#1-Ba(2)-S(5)#13	75.22(12)	S(2)-Ba(3)-S(6)	80.54(11)
S(1)#5-Ba(2)-S(5)#13	76.52(13)	S(2)#12-Ba(3)-S(6)	128.41(12)
S(2)#13-Ba(2)-S(6)#10	71.09(11)	S(4)#4-Ba(3)-S(6)	73.97(12)
S(3)-Ba(2)-S(6)#10	75.88(12)	S(4)#11-Ba(3)-S(6)	78.67(13)
S(4)#1-Ba(2)-S(6)#10	84.62(12)	S(6)#12-Ba(3)-S(6)	125.3(2)
S(1)#5-Ba(2)-S(6)#10	133.23(12)	S(2)-Ba(3)-S(5)#9	77.79(12)
S(5)#13-Ba(2)-S(6)#10	150.22(8)	S(2)#12-Ba(3)-S(5)#9	70.35(12)
S(2)#13-Ba(2)-S(8)	129.64(12)	S(4)#4-Ba(3)-S(5)#9	131.97(12)
S(3)-Ba(2)-S(8)	72.66(11)	S(4)#11-Ba(3)-S(5)#9	84.13(11)
S(4)#1-Ba(2)-S(8)	80.32(13)	S(6)#12-Ba(3)-S(5)#9	148.86(8)
S(1)#5-Ba(2)-S(8)	77.95(11)	S(6)-Ba(3)-S(5)#9	69.49(16)
S(5)#13-Ba(2)-S(8)	126.88(18)	S(2)-Ba(3)-S(5)#5	70.35(12)
S(6)#10-Ba(2)-S(8)	69.12(17)	S(2)#12-Ba(3)-S(5)#5	77.79(12)
S(2)#13-Ba(2)-S(7)#5	78.04(12)	S(4)#4-Ba(3)-S(5)#5	84.13(11)
S(3)-Ba(2)-S(7)#5	75.83(11)	S(4)#11-Ba(3)-S(5)#5	131.97(12)
S(4)#1-Ba(2)-S(7)#5	132.50(12)	S(6)#12-Ba(3)-S(5)#5	69.49(16)
S(1)#5-Ba(2)-S(7)#5	78.45(11)	S(6)-Ba(3)-S(5)#5	148.86(8)
S(5)#13-Ba(2)-S(7)#5	68.71(17)	S(5)#9-Ba(3)-S(5)#5	113.2(2)
S(6)#10-Ba(2)-S(7)#5	113.05(17)		

Note. Symmetry transformations used to generate equivalent atoms:

#1 -x+7/4,y-1/4,z+1/4 #2 x-1/4,-y+7/4,z+1/4#3 x,y,z+1

#4 x+1/4,-y+7/4,z+3/4 #5 x+1/4,-y+7/4,z-1/4

#6 -x+2,-y+3/2,z+1/2 #7 x,y,z-1 #8 x-1/4,-y+7/4,z-3/4

#9 -x+7/4,y+1/4,z-1/4 #10 -x+7/4,y-1/4,z-3/4

#11 -x+7/4,y+1/4,z+3/4 #12 -x+2,-y+2,z

#13 -x+2,-y+3/2,z-1/2

Table S2. (b) Selected bond distances (Å) and angles (deg) for $Ba_3CdSn_2S_8$.

Cd(1)-S(1)	2.5654(18)	S(2)#4-Ba(1)-S(2)#5	112.43(5)
Cd(1)-S(1)#12	2.5654(18)	S(2)#4-Ba(1)-S(1)#6	74.17(5)
Cd(1)-S(1)#13	2.5654(18)	S(2)#5-Ba(1)-S(1)#6	156.66(5)
Cd(1)-S(1)#14	2.5654(18)	S(2)#4-Ba(1)-S(1)#1	156.66(5)
Sn(1)-S(2)	2.340(3)	S(2)#5-Ba(1)-S(1)#1	74.17(5)
Sn(1)-S(1)#1	2.3977(18)	S(1)#6-Ba(1)-S(1)#1	109.04(7)
Sn(1)-S(1)#2	2.3977(18)	S(2)#4-Ba(1)-S(1)#2	87.60(6)
Sn(1)-S(1)	2.3977(18)	S(2)#5-Ba(1)-S(1)#2	73.03(5)
Ba(1)-S(2)#4	3.1352(14)	S(1)#6-Ba(1)-S(1)#2	130.29(5)
Ba(1)-S(2)#5	3.1352(14)	S(1)#1-Ba(1)-S(1)#2	72.64(6)
Ba(1)-S(1)#6	3.2057(19)	S(2)#4-Ba(1)-S(1)#7	73.03(5)
Ba(1)-S(1)#1	3.2057(19)	S(2)#5-Ba(1)-S(1)#7	87.60(6)
Ba(1)-S(1)#2	3.2885(19)	S(1)#6-Ba(1)-S(1)#7	72.64(6)
Ba(1)-S(1)#7	3.2885(19)	S(1)#1-Ba(1)-S(1)#7	130.29(5)
Ba(1)-S(1)#8	3.499(2)	S(1)#2-Ba(1)-S(1)#7	145.07(6)
Ba(1)-S(1)#9	3.499(2)	S(2)#4-Ba(1)-S(1)#8	131.69(6)
S(2)-Sn(1)-S(1)#1	112.12(4)	S(2)#5-Ba(1)-S(1)#8	94.32(3)
S(2)-Sn(1)-S(1)#2	112.12(4)	S(1)#6-Ba(1)-S(1)#8	67.27(2)
S(1)#1-Sn(1)-S(1)#2	106.70(5)	S(1)#1-Ba(1)-S(1)#8	67.27(2)
S(2)-Sn(1)-S(1)	112.12(4)	S(1)#2-Ba(1)-S(1)#8	139.89(5)
S(1)#1-Sn(1)-S(1)	106.70(5)	S(1)#7-Ba(1)-S(1)#8	68.58(5)
S(1)#2-Sn(1)-S(1)	106.70(5)	S(2)#4-Ba(1)-S(1)#9	94.32(3)
S(1)-Cd(1)-S(1)#12	96.50(2)	S(2)#5-Ba(1)-S(1)#9	131.69(6)
S(1)-Cd(1)-S(1)#13	140.69(8)	S(1)#6-Ba(1)-S(1)#9	67.27(2)
S(1)#12-Cd(1)-S(1)#13	96.50(2)	S(1)#1-Ba(1)-S(1)#9	67.27(2)
S(1)-Cd(1)-S(1)#14	96.50(2)	S(1)#2-Ba(1)-S(1)#9	68.58(5)
S(1)#12-Cd(1)-S(1)#14	140.69(8)	S(1)#7-Ba(1)-S(1)#9	139.89(5)
S(1)#13-Cd(1)-S(1)#14	96.50(2)	S(1)#8-Ba(1)-S(1)#9	96.52(6)

Note. Symmetry transformations used to generate equivalent atoms:

#1-z+1,x-1/2,-y+1/2#2y+1/2,-z+1/2,-x+1#3-z+1,-x+3/2,y-1#4-y+5/4,-x+7/4,z-1/4#5y+3/4,x-1/4,z-1/4 #6 z+1,-x+2,-y+1/2

#7-y+3/2,z+1,-x+1 #8-x+9/4,-z+3/4,y-1/4#9x-1/4,z+3/4,y-1/4

#10 -x+2,-y+3/2,z+0#11 y+1,z+1,x-1 #12 -y+5/4,x-3/4,-z-1/4

#13 -x+2,-y+1/2,z+0 #14 y+3/4,-x+5/4,-z-1/4#15 z+1,x-1,y-1#16

#x+1/4,z+1/4,y-3/4#17 -x+7/4,-z+1/4,y-3/4

#18 -z+3/4,y-1/4,-x+5/4#19 y+1/4,x-3/4,z+1/4

Table S3. Space groups of compounds following the formula of A_2MNS_4 (A = alkali metal, M=Cd and N=Sn).

quaternary		ternary	
compounds	space group	compounds	space group
Li_2CdSnS_4[1]	*P*mn2_1-NCS	$LiInS_2$[2]	*P*na2_1–NCS
Na_2CdSnS_4[3]	C2-NCS	$NaInS_2$[4]	R$\bar{3}$m–CS
Ag_2CdSnS_4[5]	*C*mc2_1-NCS	$AgInS_2$[6]	*I*$\bar{4}$2d–NCS
Cu_2CdSnS_4[7]	I$\bar{4}$2m- NCS	$CuInS_2$[8]	I$\bar{4}$2d–NCS

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Table S4. The local dipole moments for the CdS_4 and SnS_4 tetrahedra, and the net dipole moment of a unit cell for $BaCdSnS_4$.

$BaCdSnS_4$				
Units	Dipole moment (D)			
	x-component	y-component	z-component	debye
$Cd(1)S_4$	0.00	0.00	-1.43	1.43
$Cd(2)S_4$	0.00	0.00	-77.23	77.23
$Sn(1)S_4$	0.00	0.00	97.93	97.93
$Sn(2)S_4$	0.00	0.00	14.08	14.08
Total CdS_4	0.00	0.00	-78.66	78.66
Total SnS_4	0.00	0.00	112.01	112.01
Net dipole moment (a unit cell)	0.00	0.00	33.35	33.35

Figure S1. Powder X-ray diffraction patterns of $BaCdSnS_4$ and $Ba_3CdSn_2S_8$.

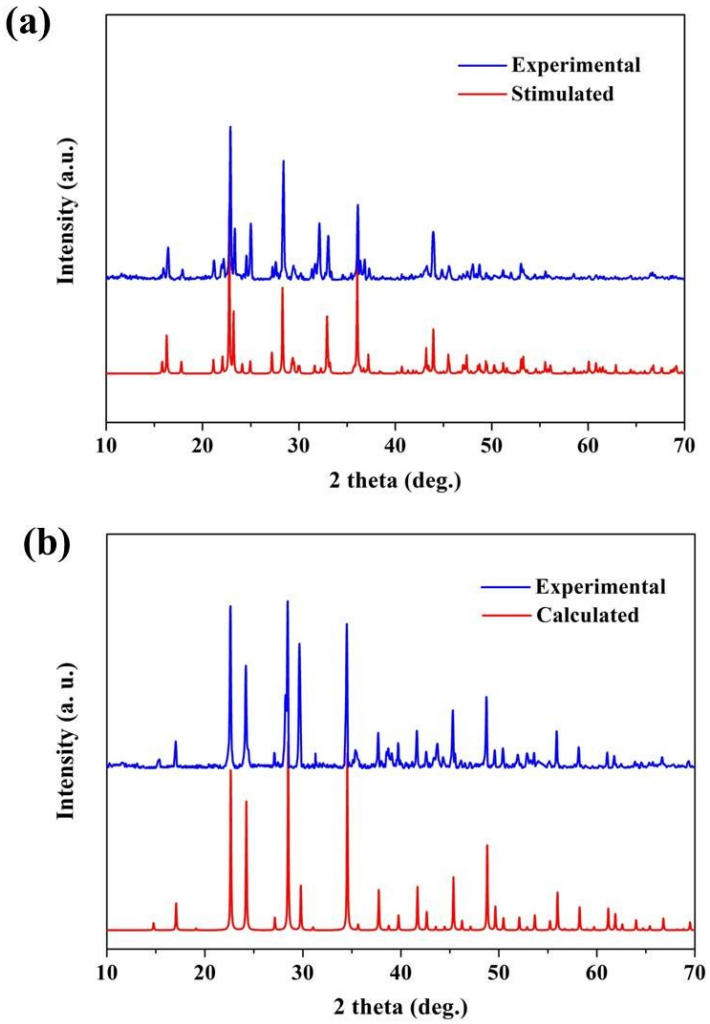


Figure S2. The $BaIn_2S_4$ structure. (a) and (b) 2D $_\infty$[In-S] layers formed by the InS_4 tetrahedra interweave with a 3D framework constituted by BaS_8 polyhedra, the In−S bonds were omitted for the sake of clarity; (c) 2D $_\infty$[In-S] layer. (d) the In_2S_6 dimer.

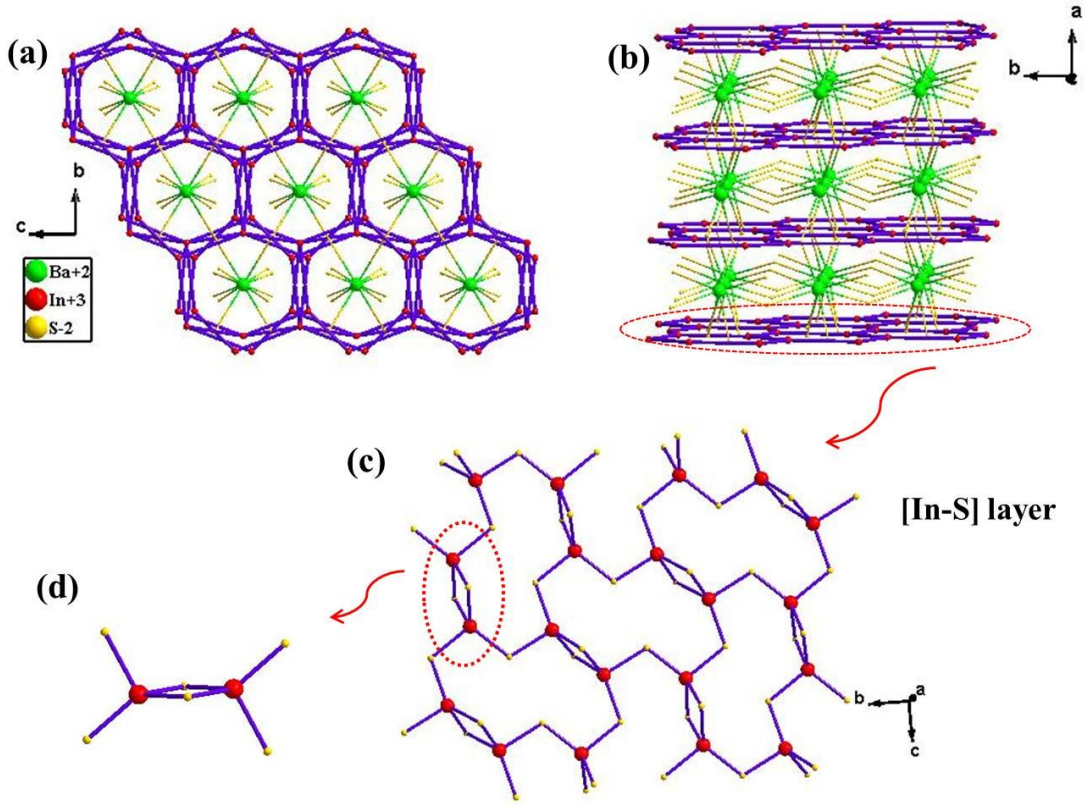
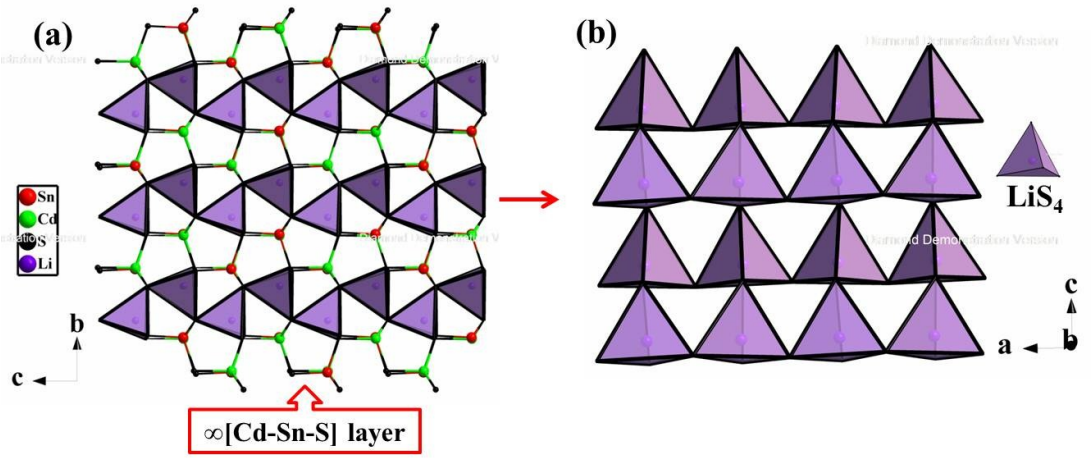


Figure S3. The 2D layers of LiS_4 tetrahedra in the structure of Li_2CdSnS_4.



(a) 3D framework showing alternate stacking of the LiS_4 and [Cd-Sn-S] tetrahedral layers; (b) the LiS_4 tetrahedra connect with each other to build a 2D layer in the *a*-*c* plane. The purple tetrahedra: LiS_4 tetrahedron.

Figure S4. The 3D framework built by BaS_8 polyhedra in the two structures $BaCdSnS_4$ and $BaHgSnS_4$.

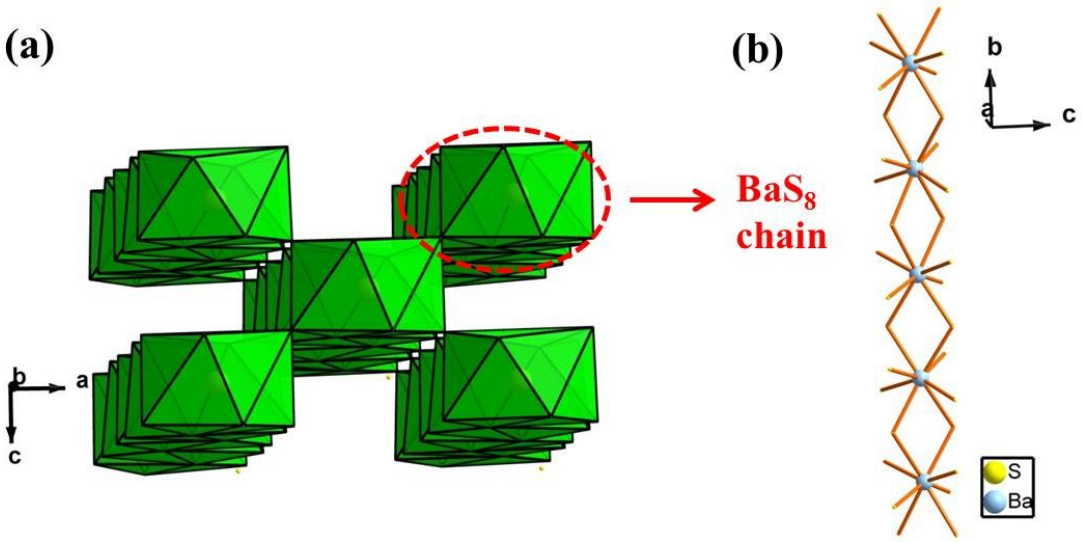
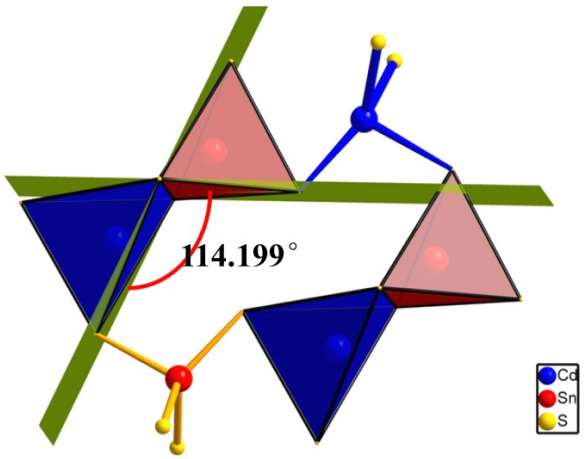


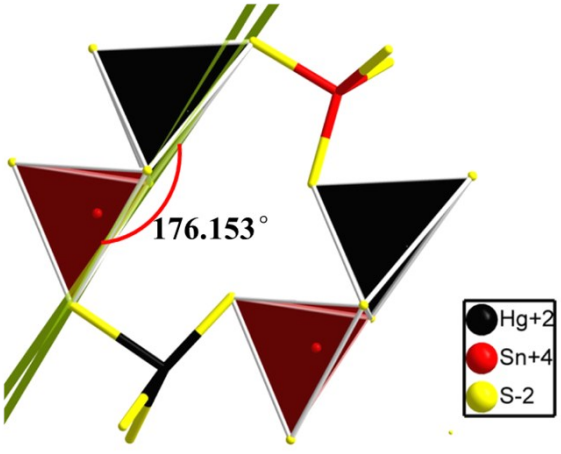
Figure S5. The different dihedral angles formed by edge-sharing of CdS_4/HgS_4 and SnS_4 tetrahedra in the structure of $BaCdSnS_4$ (a) and $BaHgSnS_4$ (b).

(a)



a dihedral angles 114.199° formed by edge-sharing of CdS_4 and SnS_4 tetrahedra in $BaCdSnS_4$, blue, CdS_4; red, SnS_4.

(b)



a dihedral angles 176.153° formed by edge-sharing of HgS_4 and SnS_4 tetrahedra in $BaHgSnS_4$, black, HgS_4; red, SnS_4.

Figure S6. The CdS_4 and SnS_4 tetrahedra of $Ba_3CdSn_2S_8$ are connected each other via corner-sharing (S1).

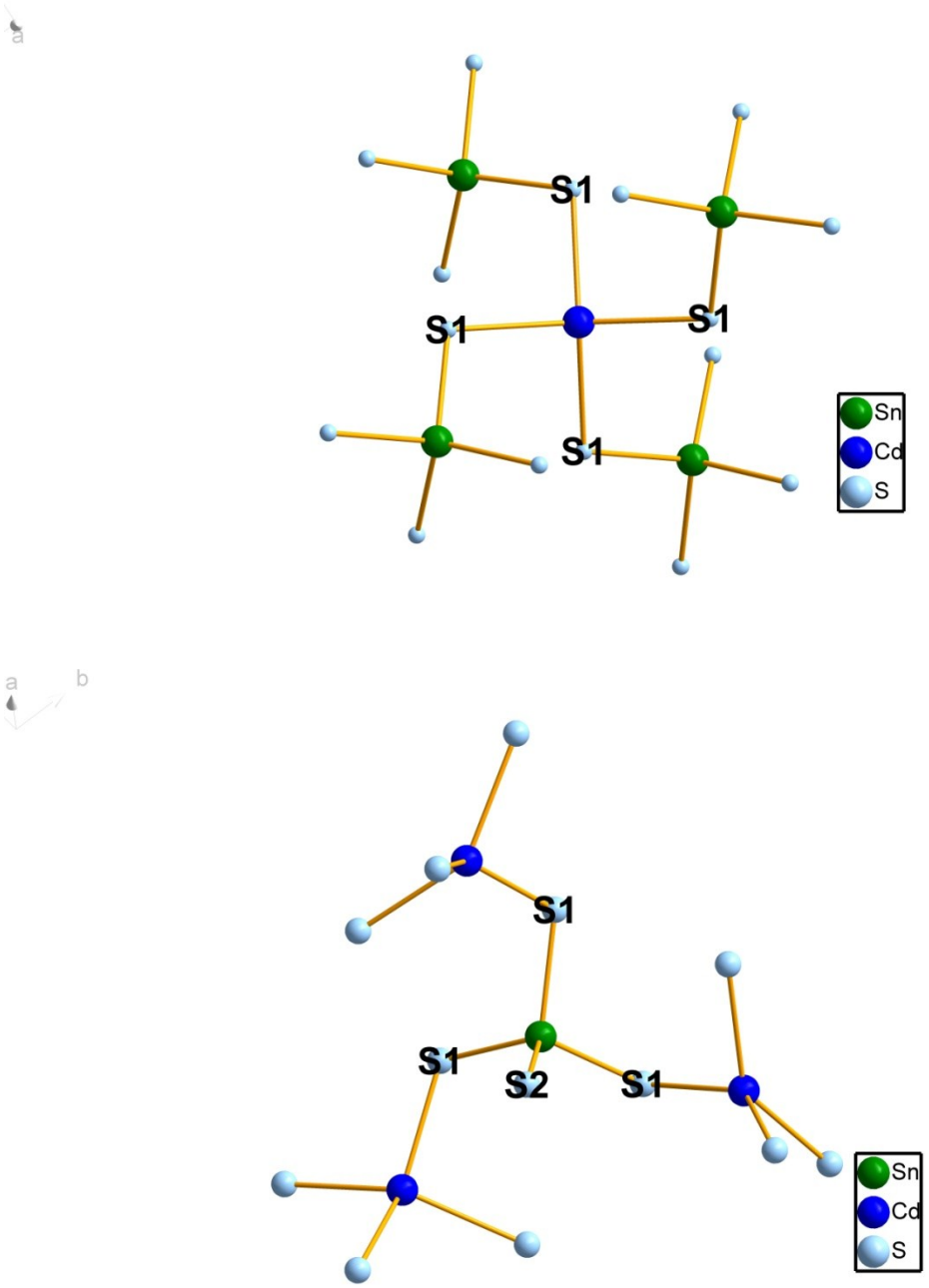


Figure S7. Mirror symmetry for the CdS_4 tetrahedron in $Ba_3CdSn_2S_8$.

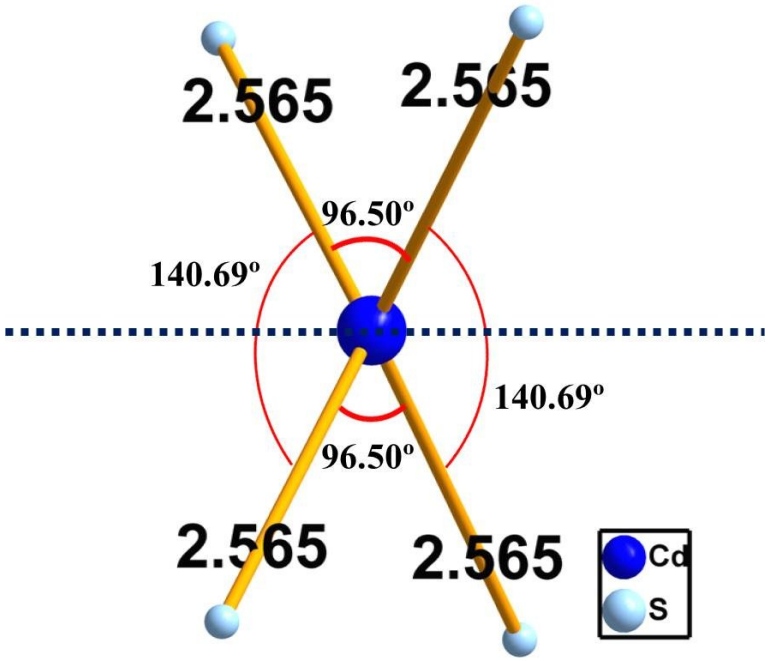


Figure S8. The GeS_4 tetrahedra are arranged along the [111] direction in $Na_{0.5}Pb_{1.75}GeS_4$.

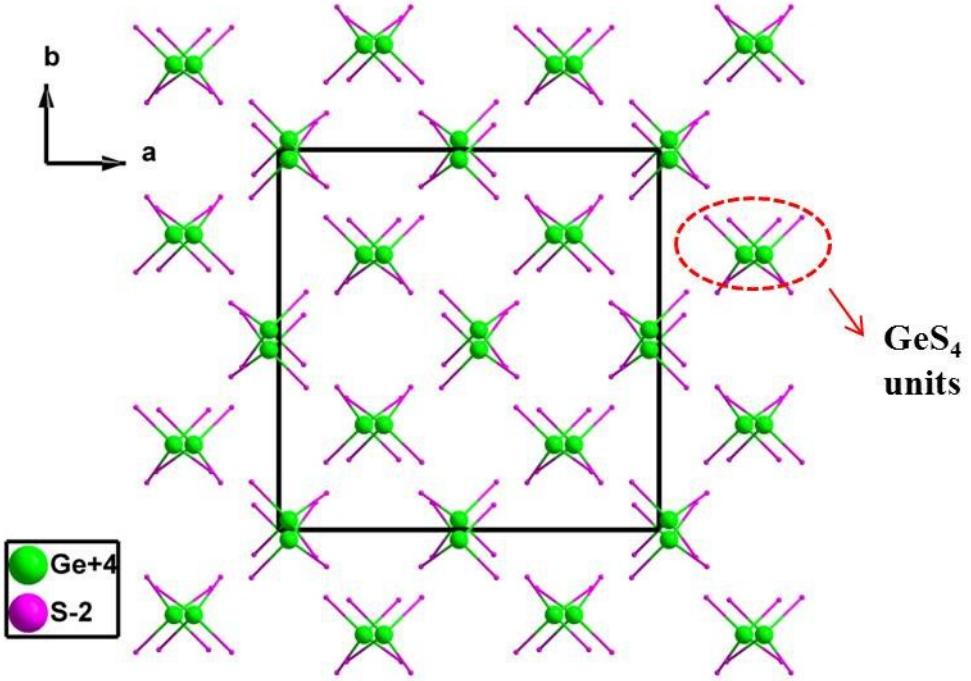


Figure S9. The IR spectra of $BaCdSnS_4$ and $Ba_3CdSn_2S_8$.

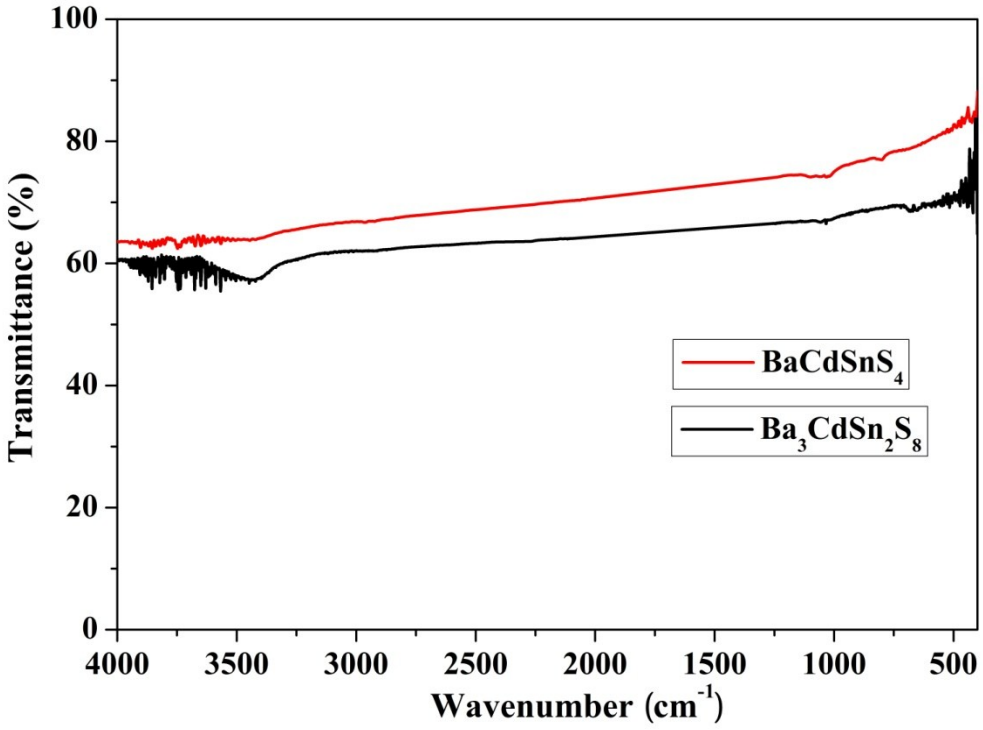


Figure S10. The SHG intensity as a function of particle size for $BaCdSnS_4$ and $Ba_3CdSn_2S_8$, AGS serves as the reference.

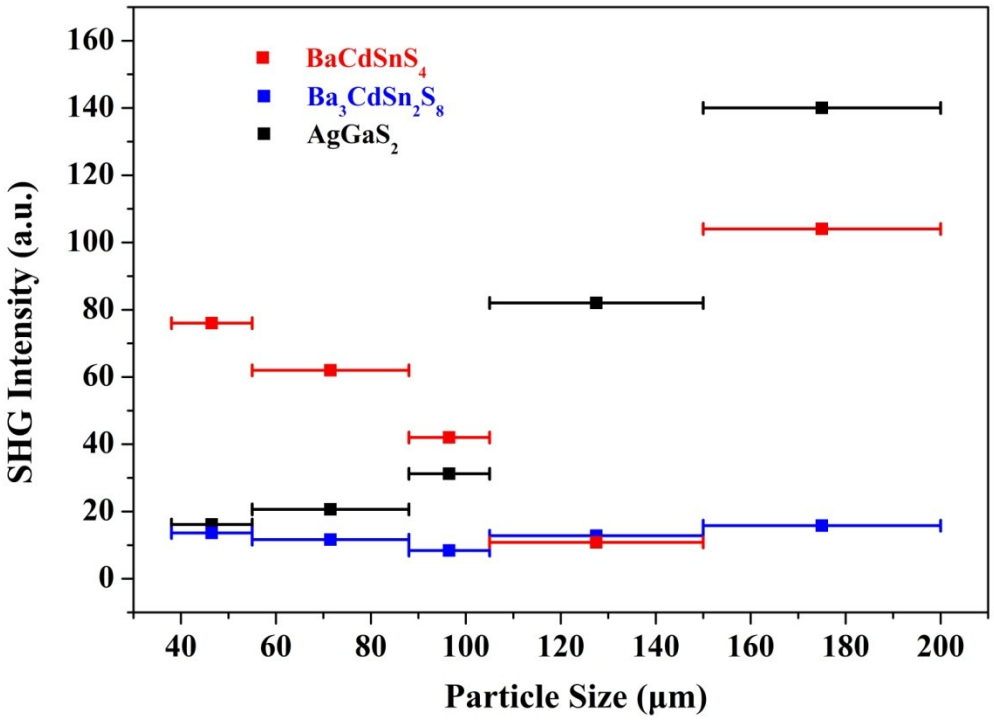


Figure S11. (a) Purple arrows represent the approximate direction of the local dipole moments and the net dipole moments for CdS_4tetrahedra. (b) Red arrows represent the approximate direction of the local dipole moments and the net dipole moments for SnS_4 tetrahedra, respectively. The green arrow represents the direction of the net dipole moment for $BaCdSnS_4$.