Electronic Supplementary Information

An investigation on new infrared nonlinear optical material: $BaCdSnSe_4$, and three new related centrosymmetric compounds: Ba_2SnSe_4, Mg_2GeSe_4, and $Ba_2Ge_2S_6$

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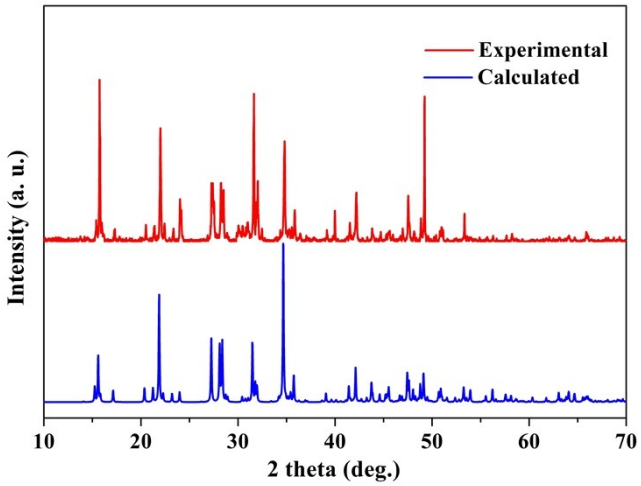
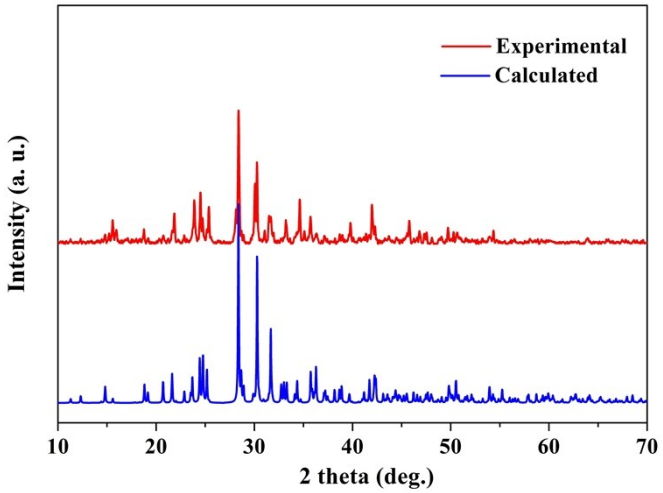
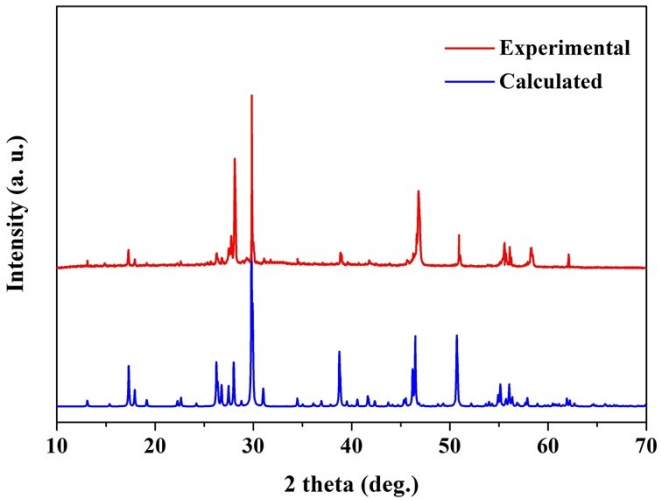


(a)



(b)



(c)

Figure S1. Powder XRD patterns of $BaCdSnSe_4$ (a), Ba_2SnSe_4 (b), and Mg_2GeSe_4 (c).

Table S1. (a) Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $BaCdSnSe_4$ U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Ba(1)	2500	2500	6255(3)	17(1)	2.245
Ba(2)	2515(1)	5022(1)	6264(2)	19(1)	2.249
Ba(3)	2500	7500	6294(3)	17(1)	2.247
Sn(1)	1136(1)	1245(1)	6294(1)	15(1)	4.026
Cd(1)	3876(1)	1244(1)	6302(2)	24(1)	2.071
Sn(2)	1822(1)	3754(1)	3376(1)	16(1)	4.033
Se(1)	2113(1)	3770(2)	5148(2)	16(1)	2.115
Cd(2)	1758(1)	6249(1)	4125(2)	25(1)	2.035
Se(2)	2182(1)	6255(2)	7465(2)	17(1)	2.245
Se(3)	1213(2)	5378(1)	5149(3)	18(1)	1.989
Se(4)	1201(2)	2117(1)	5140(3)	18(1)	1.949
Se(5)	2828(1)	6265(2)	5056(2)	19(1)	2.142
Se(6)	3720(2)	5378(1)	7618(3)	19(1)	2.014
Se(7)	3702(2)	2114(1)	7613(3)	18(1)	1.999
Se(8)	2094(1)	1243(2)	7308(2)	16(1)	2.214

Note: To provide a check on the consistency of the structure determination, the method of Bond-Valence Parameters was used to calculate the bond valences of elements (Refs 1, 2). The following equation is commonly used to calculate the bond valence (v_{ij}):

$$V_i = \sum_j v_{ij} = \sum_j \exp\left(\frac{r' - r_{ij}}{B}\right)$$

where r' is empirically determined bond valence parameter, r_{ij} is actual bond length, and B is commonly taken to be a universal constant equal to 0.37 Å. Bond valence v_{ij} is defined as sum of the bond valences between the atom i and j.

The calculated results have some deviations with oxidation states of elements, but they are still in the reasonable range. Therefore, we think that the calculated values are reasonable and can be acceptable.

Ref S1. I. D. Brown, and D. Altermatt, *Acta Crystallogr. Sect. B* 1985, **41**, 244.

Ref S2. N. E. Brese, and M. Okeeffe, *Acta Crystallogr. Sect. B* 1991, **47**, 192.

Table S1. (b) Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for Ba_2SnSe_4 U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Ba(1)	10945(1)	8828(1)	8441(1)	25(1)	1.924
Ba(2)	14663(1)	8469(1)	6592(1)	28(1)	1.995
Sn(1)	8065(1)	8139(1)	4933(1)	22(1)	4.108
Se(1)	7629(1)	8830(1)	2880(1)	25(1)	2.259
Se(2)	7623(1)	10213(1)	6092(1)	24(1)	2.109
Se(3)	10905(1)	6896(1)	6066(1)	23(1)	2.018
Se(4)	5776(1)	6291(1)	4567(1)	32(1)	1.641

Table S1. (c) Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for $Ba_2Ge_2S_6$ U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Ba(1)	1368(1)	2596(3)	6064(1)	23(1)	1.875
Ba(2)	3629(1)	-2460(3)	9695(1)	23(1)	1.870
Ge(1)	4252(2)	1591(4)	7333(2)	14(1)	4.000
Ge(2)	749(2)	6558(4)	3069(2)	15(1)	3.964
S(1)	3211(4)	2424(10)	5662(4)	17(1)	1.975
S(2)	1798(4)	-2381(10)	7441(4)	19(1)	1.963
S(3)	4238(4)	-2344(10)	7386(4)	17(1)	2.069
S(4)	756(4)	2563(10)	3143(4)	17(1)	2.038
S(5)	-1010(4)	2518(10)	5255(4)	22(1)	1.831
S(6)	3996(4)	-7486(10)	8754(4)	22(1)	1.833

Table S1. (d) Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Mg_2GeSe_4 U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Se(1)	929(1)	7500	7773(2)	11(1)	2.016
Se(2)	1683(1)	5155(1)	2458(1)	12(1)	1.825
Se(3)	-709(1)	7500	2525(2)	12(1)	1.991
Ge(1)	886(1)	7500	4107(2)	9(1)	3.853
Mg(1)	-2305(3)	7500	5052(6)	14(1)	1.845
Mg(2)	0	5000	0	15(1)	1.957

Table S2. (a) Selected bond distances (Å) and angles (deg) for $BaCdSnSe_4$.

Ba(1)-Se(8)#1	3.320(5)	Se(8)#1-Ba(1)-Se(8)	128.90(18)
Ba(1)-Se(8)	3.320(5)	Se(8)#1-Ba(1)-Se(1)#1	149.17(5)
Ba(1)-Se(1)#1	3.366(5)	Se(8)-Ba(1)-Se(1)#1	61.75(7)
Ba(1)-Se(1)	3.366(5)	Se(8)#1-Ba(1)-Se(1)	61.75(7)
Ba(1)-Se(7)	3.379(5)	Se(8)-Ba(1)-Se(1)	149.17(5)
Ba(1)-Se(7)#1	3.379(5)	Se(1)#1-Ba(1)-Se(1)	126.93(17)
Ba(1)-Se(4)	3.392(4)	Se(8)#1-Ba(1)-Se(7)	76.68(10)
Ba(1)-Se(4)#1	3.392(4)	Se(8)-Ba(1)-Se(7)	76.07(9)
Ba(2)-Se(8)#1	3.322(4)	Se(1)#1-Ba(1)-Se(7)	79.42(8)
Ba(2)-Se(2)	3.326(5)	Se(1)-Ba(1)-Se(7)	132.20(8)
Ba(2)-Se(5)	3.339(5)	Se(8)#1-Ba(1)-Se(7)#1	76.07(9)
Ba(2)-Se(1)	3.347(5)	Se(8)-Ba(1)-Se(7)#1	76.68(10)
Ba(2)-Se(6)	3.362(5)	Se(1)#1-Ba(1)-Se(7)#1	132.20(8)
Ba(2)-Se(3)	3.383(5)	Se(1)-Ba(1)-Se(7)#1	79.42(8)
Ba(2)-Se(7)#2	3.397(5)	Se(7)-Ba(1)-Se(7)#1	113.78(18)
Ba(2)-Se(4)#3	3.428(5)	Se(8)#1-Ba(1)-Se(4)	130.35(8)
Ba(3)-Se(2)#4	3.321(5)	Se(8)-Ba(1)-Se(4)	74.78(8)
Ba(3)-Se(2)	3.321(5)	Se(1)#1-Ba(1)-Se(4)	78.58(10)
Ba(3)-Se(5)	3.352(5)	Se(1)-Ba(1)-Se(4)	78.42(10)
Ba(3)-Se(5)#4	3.352(5)	Se(7)-Ba(1)-Se(4)	149.32(6)
Ba(3)-Se(3)#5	3.391(5)	Se(7)#1-Ba(1)-Se(4)	68.13(12)
Ba(3)-Se(3)#3	3.391(5)	Se(8)#1-Ba(1)-Se(4)#1	74.78(8)
Ba(3)-Se(6)#6	3.392(4)	Se(8)-Ba(1)-Se(4)#1	130.35(8)
Ba(3)-Se(6)#2	3.392(4)	Se(1)#1-Ba(1)-Se(4)#1	78.42(10)
Sn(1)-Se(5)#7	2.493(4)	Se(1)-Ba(1)-Se(4)#1	78.58(10)
Sn(1)-Se(7)#8	2.529(4)	Se(7)-Ba(1)-Se(4)#1	68.13(12)
Sn(1)-Se(4)	2.531(4)	Se(7)#1-Ba(1)-Se(4)#1	149.32(6)
Sn(1)-Se(8)	2.548(3)	Se(4)-Ba(1)-Se(4)#1	127.0(2)
Cd(1)-Se(2)#9	2.561(4)	Se(8)#1-Ba(2)-Se(2)	125.27(13)
Cd(1)-Se(7)	2.688(5)	Se(8)#1-Ba(2)-Se(5)	152.39(12)
Cd(1)-Se(4)#10	2.700(5)	Se(2)-Ba(2)-Se(5)	64.95(8)
Cd(1)-Se(1)#1	2.711(4)	Se(8)#1-Ba(2)-Se(1)	61.92(8)
Sn(2)-Se(1)	2.494(4)	Se(2)-Ba(2)-Se(1)	151.34(11)
Sn(2)-Se(3)#11	2.524(4)	Se(5)-Ba(2)-Se(1)	123.52(13)
Sn(2)-Se(6)#12	2.532(5)	Se(8)#1-Ba(2)-Se(6)	76.31(10)
Sn(2)-Se(2)#12	2.548(3)	Se(2)-Ba(2)-Se(6)	73.04(9)
Cd(2)-Se(8)#13	2.581(4)	Se(5)-Ba(2)-Se(6)	84.14(9)
Cd(2)-Se(6)#6	2.683(5)	Se(1)-Ba(2)-Se(6)	131.94(10)
Cd(2)-Se(3)	2.708(5)	Se(8)#1-Ba(2)-Se(3)	128.66(10)
Cd(2)-Se(5)	2.708(3)	Se(2)-Ba(2)-Se(3)	79.95(8)
Se(1)-Sn(2)-Se(2)#12	103.95(11)	Se(5)-Ba(2)-Se(3)	76.01(9)
Se(3)#11-Sn(2)-Se(2)#12	102.61(15)	Se(1)-Sn(2)-Se(6)#12	120.42(16)
Se(6)#12-Sn(2)-Se(2)#12	103.18(14)	Se(3)#11-Sn(2)-Se(6)#12	103.12(13)

Se(1)-Ba(2)-Se(3)	76.60(10)	Se(7)#2-Ba(2)-Se(4)#3	148.05(7)
Se(6)-Ba(2)-Se(3)	151.43(7)	Se(2)#4-Ba(3)-Se(2)	122.72(18)
Se(8)#1-Ba(2)-Se(7)#2	74.82(9)	Se(2)#4-Ba(3)-Se(5)	154.95(5)
Se(2)-Ba(2)-Se(7)#2	130.18(10)	Se(2)-Ba(3)-Se(5)	64.86(8)
Se(5)-Ba(2)-Se(7)#2	80.08(10)	Se(2)#4-Ba(3)-Se(5)#4	64.86(8)
Se(1)-Ba(2)-Se(7)#2	77.70(9)	Se(2)-Ba(3)-Se(5)#4	154.95(5)
Se(6)-Ba(2)-Se(7)#2	68.94(14)	Se(5)-Ba(3)-Se(5)#4	119.75(18)
Se(3)-Ba(2)-Se(7)#2	125.95(16)	Se(2)#4-Ba(3)-Se(3)#5	77.52(10)
Se(8)#1-Ba(2)-Se(4)#3	75.15(9)	Se(2)-Ba(3)-Se(3)#5	72.28(9)
Se(2)-Ba(2)-Se(4)#3	77.29(10)	Se(5)-Ba(3)-Se(3)#5	83.42(8)
Se(5)-Ba(2)-Se(4)#3	131.39(10)	Se(5)#4-Ba(3)-Se(3)#5	131.27(8)
Se(1)-Ba(2)-Se(4)#3	78.78(9)	Se(2)#4-Ba(3)-Se(3)#3	72.28(9)
Se(6)-Ba(2)-Se(4)#3	113.71(14)	Se(2)-Ba(3)-Se(3)#3	77.52(10)
Se(3)-Ba(2)-Se(4)#3	67.94(14)	Se(5)-Ba(3)-Se(3)#3	131.27(8)
Se(5)#4-Ba(3)-Se(6)#2	74.73(10)	Se(5)#4-Ba(3)-Se(3)#3	83.41(8)
Se(3)#5-Ba(3)-Se(6)#2	69.10(12)	Se(3)#5-Ba(3)-Se(3)#3	114.23(18)
Se(3)#3-Ba(3)-Se(6)#2	150.24(6)	Se(2)#4-Ba(3)-Se(6)#6	128.48(8)
Se(6)#6-Ba(3)-Se(6)#2	123.8(2)	Se(2)-Ba(3)-Se(6)#6	80.17(8)
Se(5)#7-Sn(1)-Se(7)#8	118.19(15)	Se(5)-Ba(3)-Se(6)#6	74.73(10)
Se(5)#7-Sn(1)-Se(4)	118.29(16)	Se(5)#4-Ba(3)-Se(6)#6	77.92(10)
Se(7)#8-Sn(1)-Se(4)	101.95(13)	Se(3)#5-Ba(3)-Se(6)#6	150.24(6)
Se(5)#7-Sn(1)-Se(8)	103.81(12)	Se(3)#3-Ba(3)-Se(6)#6	69.10(12)
Se(7)#8-Sn(1)-Se(8)	107.04(14)	Se(2)#4-Ba(3)-Se(6)#2	80.17(8)
Se(4)-Sn(1)-Se(8)	106.73(14)	Se(2)-Ba(3)-Se(6)#2	128.48(8)
Se(2)#9-Cd(1)-Se(7)	124.84(17)	Se(5)-Ba(3)-Se(6)#2	77.92(10)
Se(2)#9-Cd(1)-Se(4)#10	125.48(16)	Se(8)#13-Cd(2)-Se(6)#6	128.01(17)
Se(7)-Cd(1)-Se(4)#10	93.73(12)	Se(8)#13-Cd(2)-Se(3)	128.22(17)
Se(2)#9-Cd(1)-Se(1)#1	99.50(12)	Se(6)#6-Cd(2)-Se(3)	94.53(12)
Se(7)-Cd(1)-Se(1)#1	105.92(14)	Se(8)#13-Cd(2)-Se(5)	100.89(11)
Se(4)#10-Cd(1)-Se(1)#1	105.24(14)	Se(6)#6-Cd(2)-Se(5)	98.77(14)
Se(1)-Sn(2)-Se(3)#11	120.83(16)	Se(3)-Cd(2)-Se(5)	99.67(14)

Note. Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,z #2 -x+3/4,y+1/4,z-1/4
#3 -x+1/4,y+1/4,z+1/4 #4 -x+1/2,-y+3/2,z
#5 x+1/4,-y+5/4,z+1/4 #6 x-1/4,-y+5/4,z-1/4
#7 x-1/4,-y+3/4,z+1/4 #8 x-1/4,-y+1/4,z-1/4
#9 x+1/4,-y+3/4,z-1/4 #10 x+1/4,-y+1/4,z+1/4
#11 -x+1/4,y-1/4,z-1/4 #12 -x+1/2,-y+1,z-1/2
#13 x,y+1/2,z-1/2 #14 -x+1/2,-y+1,z+1/2
#15 -x+3/4,y-1/4,z+1/4 #16 x,y-1/2,z+1/2

Table S2. (b) Selected bond distances (Å) and angles (deg) for Ba_2SnSe_4.

Ba(1)-Se(1)#1	3.2501(12)	Se(2)-Ba(1)-Se(4)#5	137.23(3)
Ba(1)-Se(3)#2	3.3528(13)	Se(3)#3-Ba(1)-Se(4)#5	118.29(3)
Ba(1)-Se(2)	3.3878(13)	Se(3)-Ba(1)-Se(4)#5	85.76(3)
Ba(1)-Se(3)#3	3.4293(12)	Se(2)#4-Ba(1)-Se(4)#5	70.00(3)
Ba(1)-Se(3)	3.4454(12)	Se(1)#2-Ba(1)-Se(4)#5	135.02(3)
Ba(1)-Se(2)#4	3.5292(12)	Se(4)#3-Ba(1)-Se(4)#5	49.60(3)
Ba(1)-Se(1)#2	3.6054(13)	Se(1)#5-Ba(2)-Se(2)#6	84.47(3)
Ba(1)-Se(4)#3	3.6786(14)	Se(1)#5-Ba(2)-Se(2)#1	139.95(3)
Ba(1)-Se(4)#5	3.7929(15)	Se(2)#6-Ba(2)-Se(2)#1	79.16(3)
Ba(2)-Se(1)#5	3.1975(12)	Se(1)#5-Ba(2)-Se(3)	108.23(3)
Ba(2)-Se(2)#6	3.2784(13)	Se(2)#6-Ba(2)-Se(3)	159.43(3)
Ba(2)-Se(2)#1	3.3353(13)	Se(2)#1-Ba(2)-Se(3)	80.84(3)
Ba(2)-Se(3)	3.3490(13)	Se(1)#5-Ba(2)-Se(1)#1	142.62(2)
Ba(2)-Se(1)#1	3.4088(13)	Se(2)#6-Ba(2)-Se(1)#1	103.27(3)
Ba(2)-Se(4)#5	3.4348(14)	Se(2)#1-Ba(2)-Se(1)#1	77.11(3)
Ba(2)-Se(4)#6	3.6492(14)	Se(3)-Ba(2)-Se(1)#1	76.74(3)
Sn(1)-Se(4)	2.5010(13)	Se(1)#5-Ba(2)-Se(4)#5	71.96(3)
Sn(1)-Se(1)	2.5108(13)	Se(2)#6-Ba(2)-Se(4)#5	106.26(3)
Sn(1)-Se(2)	2.5226(12)	Se(2)#1-Ba(2)-Se(4)#5	147.83(3)
Sn(1)-Se(3)	2.5351(13)	Se(3)-Ba(2)-Se(4)#5	93.27(3)
Se(1)#1-Ba(1)-Se(3)#2	141.66(3)	Se(1)#1-Ba(2)-Se(4)#5	70.77(3)
Se(1)#1-Ba(1)-Se(2)	70.62(3)	Se(1)#5-Ba(2)-Se(4)#6	66.35(3)
Se(3)#2-Ba(1)-Se(2)	125.17(3)	Se(2)#6-Ba(2)-Se(4)#6	72.37(3)
Se(1)#1-Ba(1)-Se(3)#3	80.59(3)	Se(2)#1-Ba(2)-Se(4)#6	73.89(3)
Se(3)#2-Ba(1)-Se(3)#3	78.44(3)	Se(3)-Ba(2)-Se(4)#6	97.45(3)
Se(2)-Ba(1)-Se(3)#3	63.53(3)	Se(1)#1-Ba(2)-Se(4)#6	150.98(3)
Se(1)#1-Ba(1)-Se(3)	77.54(3)	Se(4)#5-Ba(2)-Se(4)#6	138.25(3)
Se(3)#2-Ba(1)-Se(3)	137.20(2)	Se(4)-Sn(1)-Se(1)	102.23(4)
Se(2)-Ba(1)-Se(3)	75.31(3)	Se(4)-Sn(1)-Se(2)	109.43(5)
Se(3)#3-Ba(1)-Se(3)	137.85(2)	Se(1)-Sn(1)-Se(2)	113.27(4)
Se(1)#1-Ba(1)-Se(2)#4	122.54(3)	Se(4)-Sn(1)-Se(3)	107.11(4)
Se(3)#2-Ba(1)-Se(2)#4	78.02(3)	Se(1)-Sn(1)-Se(3)	112.93(4)
Se(2)-Ba(1)-Se(2)#4	127.83(3)	Se(2)-Ba(1)-Se(4)#3	119.13(3)
Se(3)#3-Ba(1)-Se(2)#4	155.63(3)	Se(3)#3-Ba(1)-Se(4)#3	69.39(3)
Se(3)-Ba(1)-Se(2)#4	61.93(3)	Se(3)-Ba(1)-Se(4)#3	129.48(3)
Se(1)#1-Ba(1)-Se(1)#2	142.02(2)	Se(2)#4-Ba(1)-Se(4)#3	111.02(3)
Se(3)#2-Ba(1)-Se(1)#2	74.28(3)	Se(1)#2-Ba(1)-Se(4)#3	151.35(3)
Se(2)-Ba(1)-Se(1)#2	76.93(3)	Se(1)#1-Ba(1)-Se(4)#5	67.97(3)
Se(3)#3-Ba(1)-Se(1)#2	102.31(3)	Se(3)#2-Ba(1)-Se(4)#5	94.67(3)
Se(3)-Ba(1)-Se(1)#2	75.57(3)	Se(1)#1-Ba(1)-Se(4)#3	65.50(3)
Se(2)#4-Ba(1)-Se(1)#2	65.08(3)	Se(3)#2-Ba(1)-Se(4)#3	77.16(3)

Note. Symmetry transformations used to generate equivalent atoms:

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

Table S2. (c) Selected bond distances (Å) and angles (deg) for $Ba_2Ge_2S_6$.

Ba(1)-S(1)	3.106(6)	S(1)-Ba(1)-S(5)#1	83.36(15)
Ba(1)-S(5)#1	3.243(6)	S(1)-Ba(1)-S(4)#2	139.41(13)
Ba(1)-S(4)#2	3.311(5)	S(5)#1-Ba(1)-S(4)#2	116.19(15)
Ba(1)-S(2)	3.319(6)	S(1)-Ba(1)-S(2)	95.33(14)
Ba(1)-S(5)	3.332(6)	S(5)#1-Ba(1)-S(2)	178.45(15)
Ba(1)-S(2)#3	3.342(6)	S(4)#2-Ba(1)-S(2)	64.36(14)
Ba(1)-S(5)#4	3.357(6)	S(1)-Ba(1)-S(5)	153.83(12)
Ba(1)-S(4)	3.612(5)	S(5)#1-Ba(1)-S(5)	86.09(15)
Ba(2)-S(2)	3.113(5)	S(4)#2-Ba(1)-S(5)	66.49(12)
Ba(2)-S(6)#3	3.278(6)	S(2)-Ba(1)-S(5)	95.44(14)
Ba(2)-S(6)	3.304(6)	S(1)-Ba(1)-S(2)#3	98.46(15)
Ba(2)-S(3)#5	3.316(5)	S(5)#1-Ba(1)-S(2)#3	59.74(12)
Ba(2)-S(1)#5	3.317(6)	S(4)#2-Ba(1)-S(2)#3	67.55(14)
Ba(2)-S(6)#6	3.328(6)	S(2)-Ba(1)-S(2)#3	119.76(14)
Ba(2)-S(1)#2	3.352(6)	S(5)-Ba(1)-S(2)#3	96.75(14)
Ba(2)-S(3)	3.606(5)	S(1)-Ba(1)-S(5)#4	80.43(15)
Ge(1)-S(1)	2.169(5)	S(5)#1-Ba(1)-S(5)#4	121.59(14)
Ge(1)-S(6)#3	2.173(5)	S(4)#2-Ba(1)-S(5)#4	112.25(14)
Ge(1)-S(3)#7	2.270(6)	S(2)-Ba(1)-S(5)#4	58.86(12)
Ge(1)-S(3)	2.268(6)	S(5)-Ba(1)-S(5)#4	84.90(16)
Ge(2)-S(2)#8	2.172(6)	S(2)#3-Ba(1)-S(5)#4	178.02(14)
Ge(2)-S(5)#1	2.172(5)	S(1)-Ba(1)-S(4)	68.87(13)
Ge(2)-S(4)#9	2.251(6)	S(5)#1-Ba(1)-S(4)	60.63(13)
Ge(2)-S(4)	2.303(6)	S(4)#2-Ba(1)-S(4)	151.53(18)
S(2)-Ba(1)-S(4)	119.67(13)	S(1)#5-Ba(2)-S(6)#6	95.37(14)
S(5)-Ba(1)-S(4)	85.08(12)	S(2)-Ba(2)-S(1)#2	96.86(14)
S(2)#3-Ba(1)-S(4)	120.03(14)	S(6)#3-Ba(2)-S(1)#2	59.12(13)
S(5)#4-Ba(1)-S(4)	61.14(13)	S(6)-Ba(2)-S(1)#2	178.52(15)
S(2)-Ba(2)-S(6)#3	81.18(15)	S(3)#5-Ba(2)-S(1)#2	67.60(13)
S(2)-Ba(2)-S(6)	82.72(15)	S(1)#5-Ba(2)-S(1)#2	119.50(15)
S(6)#3-Ba(2)-S(6)	122.15(15)	S(6)#6-Ba(2)-S(1)#2	96.25(14)
S(2)-Ba(2)-S(3)#5	140.18(14)	S(2)-Ba(2)-S(3)	68.08(13)
S(6)#3-Ba(2)-S(3)#5	115.80(14)	S(6)#3-Ba(2)-S(3)	60.02(13)
S(6)-Ba(2)-S(3)#5	111.86(14)	S(6)-Ba(2)-S(3)	62.38(13)
S(2)-Ba(2)-S(1)#5	98.39(14)	S(3)#5-Ba(2)-S(3)	151.72(18)
S(6)#3-Ba(2)-S(1)#5	178.43(15)	S(1)#5-Ba(2)-S(3)	121.25(13)
S(6)-Ba(2)-S(1)#5	59.22(13)	S(6)#6-Ba(2)-S(3)	85.07(12)
S(3)#5-Ba(2)-S(1)#5	63.62(13)	S(1)#2-Ba(2)-S(3)	118.79(13)
S(2)-Ba(2)-S(6)#6	153.15(13)	S(1)-Ge(1)-S(6)#3	121.3(2)
S(6)#3-Ba(2)-S(6)#6	85.63(15)	S(1)-Ge(1)-S(3)#7	110.8(2)
S(6)-Ba(2)-S(6)#6	84.71(15)	S(6)#3-Ge(1)-S(3)#7	110.5(2)
S(3)#5-Ba(2)-S(6)#6	66.66(13)	S(1)-Ge(1)-S(3)	103.9(2)
S(2)#8-Ge(2)-S(4)	104.2(2)	S(6)#3-Ge(1)-S(3)	102.1(2)

S(5)#1-Ge(2)-S(4)	101.8(2)	S(3)#7-Ge(1)-S(3)	106.7(2)
S(4)#9-Ge(2)-S(4)	105.8(2)	S(2)#8-Ge(2)-S(5)#1	120.9(2)
S(5)#1-Ge(2)-S(4)#9	110.8(2)	S(2)#8-Ge(2)-S(4)#9	111.5(2)

Note. Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1 #2 x,-y+1/2,z+1/2
#3 x,y+1,z #4 -x,-y,-z+1 #5 x,-y-1/2,z+1/2
#6 -x+1,-y-1,-z+2 #7 -x+1,y+1/2,-z+3/2
#8 x,-y+1/2,z-1/2 #9 -x,y+1/2,-z+1/2
#10 x,-y-1/2,z-1/2 #11 x,y-1,z #12 -x+1,y-1/2,-z+3/2
#13 -x,y-1/2,-z+1/2

Table S2. (d) Selected bond distances (Å) and angles (deg) for Mg_2GeSe_4.

Ge(1)-Se(2)#7	2.376(3)	Se(1)#12-Mg(2)-Se(1)#4	180.00(4)
Mg(1)-Se(2)#1	2.750(4)	Se(3)#11-Mg(2)-Se(2)	94.44(11)
Mg(1)-Se(2)#4	2.750(4)	Se(3)-Mg(2)-Se(2)	85.56(11)
Mg(1)-Se(1)#8	2.758(6)	Se(1)#12-Mg(2)-Se(2)	83.38(11)
Mg(1)-Se(2)#9	2.795(4)	Se(1)#4-Mg(2)-Se(2)	96.62(11)
Mg(1)-Se(2)#10	2.795(4)	Se(3)#11-Mg(2)-Se(2)#11	85.56(11)
Mg(2)-Se(3)#11	2.711(3)	Se(3)-Mg(2)-Se(2)#11	94.44(11)
Mg(2)-Se(1)#12	2.726(3)	Se(1)#12-Mg(2)-Se(2)#11	96.62(11)
Mg(2)-Se(1)#4	2.726(3)	Se(1)#4-Mg(2)-Se(2)#11	83.38(11)
Mg(2)-Se(2)#11	2.761(5)	Se(2)-Mg(2)-Se(2)#11	180.000(19)
Se(1)-Ge(1)-Se(2)#7	115.50(7)	Se(2)#1-Mg(1)-Se(2)#10	88.83(14)
Se(1)-Ge(1)-Se(2)	115.50(7)	Se(2)#4-Mg(1)-Se(2)#10	168.02(13)
Se(2)#7-Ge(1)-Se(2)	101.56(15)	Se(1)#8-Mg(1)-Se(2)#10	82.19(15)
Se(1)-Ge(1)-Se(3)	116.46(9)	Se(2)#9-Mg(1)-Se(2)#10	82.41(17)
Se(2)#7-Ge(1)-Se(3)	102.87(10)	Se(3)#11-Mg(2)-Se(3)	180.00(4)
Se(2)-Ge(1)-Se(3)	102.87(10)	Se(3)#11-Mg(2)-Se(1)#12	92.90(14)
Se(3)-Mg(1)-Se(2)#1	95.76(14)	Se(3)-Mg(2)-Se(1)#12	87.10(14)
Se(3)-Mg(1)-Se(2)#4	95.76(14)	Se(3)#11-Mg(2)-Se(1)#4	87.10(14)
Se(2)#1-Mg(1)-Se(2)#4	98.58(19)	Se(3)-Mg(2)-Se(1)#4	92.90(14)
Se(3)-Mg(1)-Se(1)#8	173.38(16)	Se(2)#1-Mg(1)-Se(2)#9	168.02(13)
Se(2)#1-Mg(1)-Se(1)#8	88.55(13)	Se(2)#4-Mg(1)-Se(2)#9	88.83(14)
Se(2)#4-Mg(1)-Se(1)#8	88.55(13)	Se(1)#8-Mg(1)-Se(2)#9	82.19(15)
Se(3)-Mg(1)-Se(2)#9	92.84(16)	Se(3)-Mg(1)-Se(2)#10	92.84(16)

Note. Symmetry transformations used to generate equivalent atoms:

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

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

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

#9 x-1/2,y,-z+1/2 #10 x-1/2,-y+3/2,-z+1/2

#11 -x,-y+1,-z #12 x,y,z-1

Figure S2. IR spectra of title compounds: 1−$BaCdSnSe_4$; 2−Ba_2SnSe_4; 3−Mg_2GeSe_4; 4−$Ba_2Ge_2S_6$.

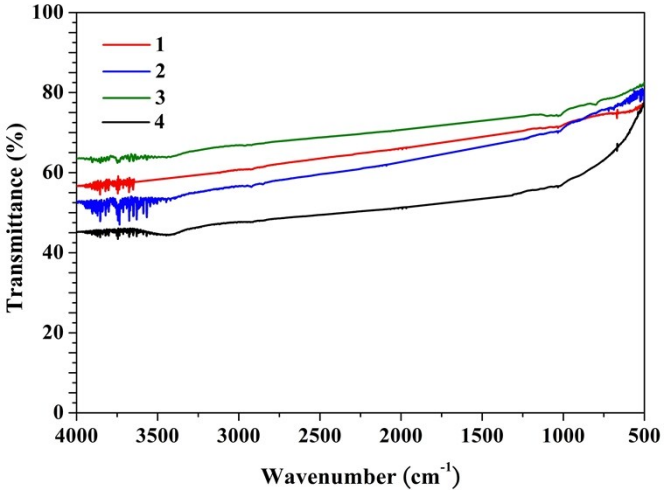


Figure S3. Particle size versus SHG intensity for compound 1.

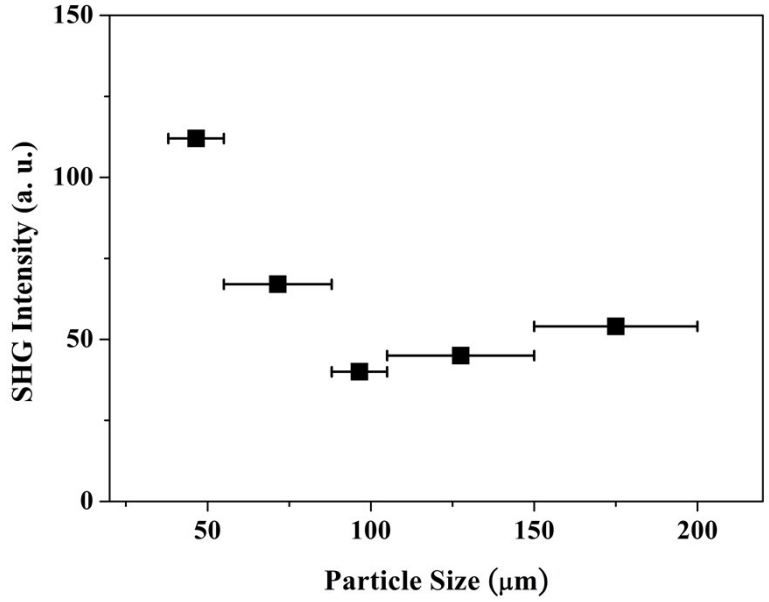


Figure S4. Band structures of (a) Ba_2SnSe_4, (b) Mg_2GeSe_4 and (c) $Ba_2Ge_2S_6$.

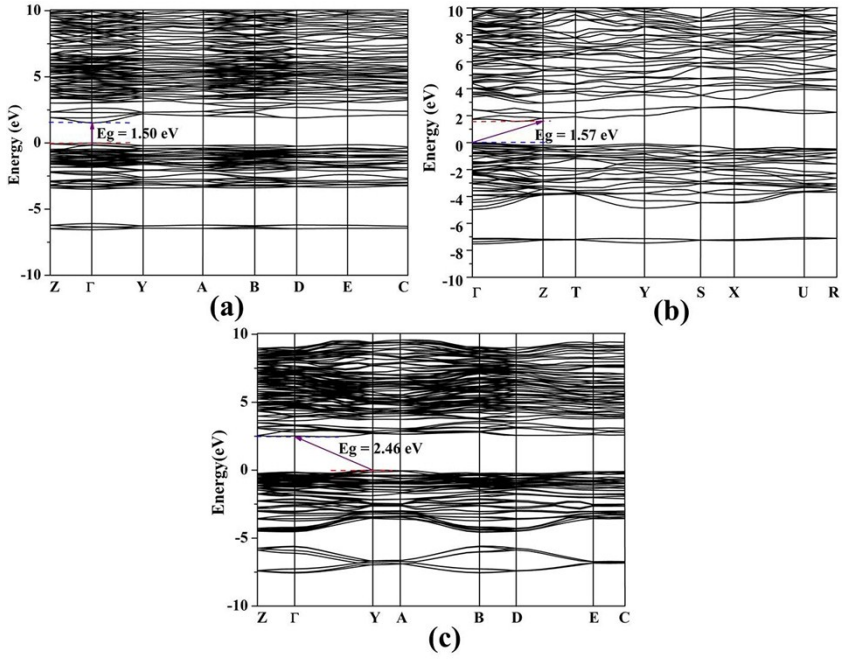


Figure S5. Total and partial densities of states (PDOS and TDOS) plots of (a) Ba_2SnSe_4, (b) $Ba_2Ge_2S_6$ and (c) Mg_2GeSe_4.

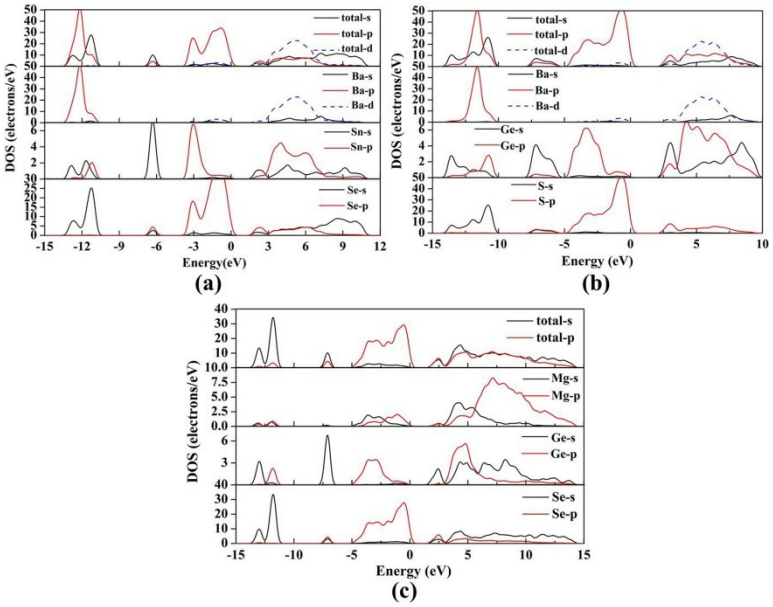


Figure S6. Calculated birefringences of title compounds: 1−$BaCdSnSe_4$; 2−Ba_2SnSe_4; 3− Mg_2GeSe_4; 4− $Ba_2Ge_2S_6$.