Supporting Information

$BaCu_2M^{IV}Q_4$ (M^{IV} = Si, Ge, and Sn; Q = S, Se): synthesis, crystal structures, optical performances and theoretical calculations

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Fig. S6(a) The PDOS of $BaCu_2SiSe_4$.

Fig. S6(b) The PDOS of $BaCu_2GeS_4$.

Fig. S6(c) The PDOS of $BaCu_2GeSe_4$.

Fig. S6(d) The PDOS of $BaCu_2SnSe_4$.

Fig. S7(a) SHG density of $BaCu_2GeS_4$.

Fig. S7(b) SHG density of $BaCu_2GeSe_4$.

Fig. S7(c) SHG density of $BaCu_2SiSe_4$.

Fig. S7(d) SHG density of $BaCu_2SnSe_4$.

Table S1(a) Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $BaCu_2SiSe_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	*x*	*y*	*z*	*U*(eq)	BVS
Ba(1)	3a	5496(1)	10000	6667	14(1)	2.46
Cu(1)	6c	9203(2)	5863(2)	5767(1)	23(1)	0.85
Se(1)	6c	6748(1)	7671(1)	8276(1)	12(1)	1.99
Se(2)	6c	10283(1)	5168(1)	7220(1)	12(1)	2.06
Si(1)	3b	10000	7165(5)	8333	9(1)	3.94

Table S1(b) Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $BaCu_2GeS_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	*x*	*y*	*z*	*U*(eq)	BVS
Ba(1)	3b	0	4361(1)	1667	12(1)	2.49
Cu(1)	6c	4104(1)	749(1)	766(1)	21(1)	1.11
Ge(1)	3a	7142(1)	7142(1)	0	9(1)	4.01
S(1)	6c	5178(2)	4805(2)	1131(1)	11(1)	2.13
S(2)	6c	7628(2)	10930(2)	35(1)	11(1)	2.23

Table S1(c) Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $BaCu_2GeSe_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	*x*	*y*	*z*	*U*(eq)	BVS
Ba(1)	3a	4497.2(12)	4497.2(12)	0	12(2)	2.30
Cu(1)	6c	6608.(2)	797.(2)	8999(7)	21(3)	0.86
Ge(1)	3b	10000	7149(2)	1666.7	8(3)	3.92
Se(1)	6c	9669.4(16)	4781.8(15)	523.9(5)	10(2)	1.95
Se(2)	6c	6662.5(15)	7675.0(16)	1710.5(5)	10(3)	2.02

Table S1(d) Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $BaCu_2SnS_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	*x*	*y*	*z*	*U*(eq)	BVS
Ba(1)	3a	4324(1)	4324(1)	0	14(1)	2.24
Cu(1)	6c	728(2)	6536(2)	893(1)	23(1)	1.12
S(1)	6c	4575(4)	9522(4)	478(1)	13(1)	2.12
S(2)	6c	7650(4)	6548(4)	1670(1)	13(1)	2.20
Sn(1)	3b	7095(1)	10000	1667	11(1)	4.13

Table S1(e) Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $BaCu_2SnSe_4$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	*x*	*y*	*z*	*U*(eq)	BVS
Ba(1)	4a	0	5000	4992(1)	15(1)	2.23
Cu(1)	8c	1285(1)	2853(1)	862(2)	23(1)	0.84
Se(1)	4b	2500	1096(1)	2189(2)	13(1)	1.88
Se(2)	4b	2500	-588(1)	7456(2)	13(1)	1.97
Se(3)	8c	717(1)	2525(1)	7415(2)	13(1)	1.95
Sn(1)	4b	2500	1476(1)	5865(1)	12(1)	3.82

Table S2(a) Bond lengths (Å) and angles (°) for $BaCu_2SiSe_4$.

Ba(1)-Se(1)	3.2843(15)	Se(1)#3-Ba(1)-Se(2)#5	82.26(2)
Ba(1)-Se(1)#1	3.2843(15)	Se(2)#4-Ba(1)-Se(2)#5	129.61(3)
Ba(1)-Se(1)#2	3.3108(16)	Se(1)-Ba(1)-Se(2)#6	74.20(2)
Ba(1)-Se(1)#3	3.3108(17)	Se(1)#1-Ba(1)-Se(2)#6	141.103(18)
Ba(1)-Se(2)#4	3.3232(12)	Se(1)#2-Ba(1)-Se(2)#6	67.74(2)
Ba(1)-Se(2)#5	3.3232(12)	Se(1)#3-Ba(1)-Se(2)#6	79.46(3)
Ba(1)-Se(2)#6	3.3508(12)	Se(2)#4-Ba(1)-Se(2)#6	148.21(3)
Ba(1)-Se(2)#7	3.3508(12)	Se(2)#5-Ba(1)-Se(2)#6	66.799(13)
Cu(1)-Se(2)#5	2.4285(14)	Se(1)-Ba(1)-Se(2)#7	141.103(18)
Cu(1)-Se(1)#8	2.4286(15)	Se(1)#1-Ba(1)-Se(2)#7	74.20(2)
Cu(1)-Se(1)#9	2.5045(14)	Se(1)#2-Ba(1)-Se(2)#7	79.46(3)
Cu(1)-Se(2)	2.5391(18)	Se(1)#3-Ba(1)-Se(2)#7	67.738(19)
Si(1)-Se(2)#14	2.263(2)	Se(2)#4-Ba(1)-Se(2)#7	66.799(13)
Si(1)-Se(1)#14	2.269(2)	Se(2)#5-Ba(1)-Se(2)#7	148.21(3)
Se(1)-Ba(1)-Se(1)#1	123.62(4)	Se(2)#6-Ba(1)-Se(2)#7	115.23(3)
Se(1)-Ba(1)-Se(1)#2	69.44(4)	Se(2)#5-Cu(1)-Se(1)#8	132.69(5)
Se(1)#1-Ba(1)-Se(1)#2	147.85(2)	Se(2)#5-Cu(1)-Se(1)#9	108.47(5)
Se(1)-Ba(1)-Se(1)#3	147.85(2)	Se(1)#8-Cu(1)-Se(1)#9	99.17(4)
Se(1)#1-Ba(1)-Se(1)#3	69.44(4)	Se(2)#5-Cu(1)-Se(2)	95.36(4)
Se(1)#2-Ba(1)-Se(1)#3	116.75(5)	Se(1)#8-Cu(1)-Se(2)	117.98(5)
Se(1)-Ba(1)-Se(2)#4	85.92(2)	Se(1)#9-Cu(1)-Se(2)	98.53(5)
Se(1)#1-Ba(1)-Se(2)#4	70.67(3)	Se(2)-Si(1)-Se(1)#14	110.03(3)
Se(1)#2-Ba(1)-Se(2)#4	82.26(2)	Se(2)#14-Si(1)-Se(1)#14	112.92(3)
Se(1)#3-Ba(1)-Se(2)#4	125.534(17)	Se(2)-Si(1)-Se(1)	112.92(3)
Se(1)-Ba(1)-Se(2)#5	70.67(3)	Se(2)#14-Si(1)-Se(1)	110.03(3)
Se(1)#1-Ba(1)-Se(2)#5	85.92(2)	Se(1)#14-Si(1)-Se(1)	105.84(13)
Se(1)#2-Ba(1)-Se(2)#5	125.534(17)		

Symmetry transformations used to generate equivalent atoms:

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

Table S2(b) Bond lengths (Å) and angles (°) for $BaCu_2GeS_4$.

Ba(1)-S(2)#1	3.1597(13)	S(1)#3-Ba(1)-S(2)#5	125.23(3)
Ba(1)-S(2)#2	3.1597(13)	S(1)-Ba(1)-S(2)#5	82.87(3)
Ba(1)-S(1)#3	3.1967(14)	S(2)#4-Ba(1)-S(2)#5	114.17(5)
Ba(1)-S(1)	3.1967(13)	S(2)#1-Ba(1)-S(1)#6	73.35(3)
Ba(1)-S(2)#4	3.2017(13)	S(2)#2-Ba(1)-S(1)#6	140.17(3)
Ba(1)-S(2)#5	3.2017(13)	S(1)#3-Ba(1)-S(1)#6	148.87(4)
Ba(1)-S(1)#6	3.2489(14)	S(1)-Ba(1)-S(1)#6	66.340(16)
Ba(1)-S(1)#7	3.2489(14)	S(2)#4-Ba(1)-S(1)#6	67.49(3)
Cu(1)-S(2)#10	2.3162(13)	S(2)#5-Ba(1)-S(1)#6	77.87(3)
Cu(1)-S(1)	2.3300(13)	S(2)#1-Ba(1)-S(1)#7	140.17(3)
Cu(1)-S(2)#11	2.4164(13)	S(2)#2-Ba(1)-S(1)#7	73.35(3)
Cu(1)-S(1)#1	2.4426(14)	S(1)#3-Ba(1)-S(1)#7	66.340(16)
Ge(1)-S(1)#14	2.2147(12)	S(1)-Ba(1)-S(1)#7	148.87(4)
Ge(1)-S(1)	2.2147(12)	S(2)#4-Ba(1)-S(1)#7	77.87(3)
Ge(1)-S(2)	2.2173(13)	S(2)#5-Ba(1)-S(1)#7	67.49(3)
Ge(1)-S(2)#14	2.2173(13)	S(1)#6-Ba(1)-S(1)#7	113.87(4)
S(2)#1-Ba(1)-S(2)#2	127.65(5)	S(2)#10-Cu(1)-S(1)	134.35(5)
S(2)#1-Ba(1)-S(1)#3	87.68(3)	S(2)#10-Cu(1)-S(2)#11	99.15(3)
S(2)#2-Ba(1)-S(1)#3	70.91(3)	S(1)-Cu(1)-S(2)#11	107.51(5)
S(2)#1-Ba(1)-S(1)	70.91(3)	S(2)#10-Cu(1)-S(1)#1	116.81(5)
S(2)#2-Ba(1)-S(1)	87.68(3)	S(1)-Cu(1)-S(1)#1	95.26(3)
S(1)#3-Ba(1)-S(1)	130.75(4)	S(2)#11-Cu(1)-S(1)#1	98.72(5)
S(2)#1-Ba(1)-S(2)#4	69.00(2)	S(1)#14-Ge(1)-S(1)	105.85(7)
S(2)#2-Ba(1)-S(2)#4	146.90(3)	S(1)#14-Ge(1)-S(2)	107.91(5)
S(1)#3-Ba(1)-S(2)#4	82.87(3)	S(1)-Ge(1)-S(2)	114.46(4)
S(1)-Ba(1)-S(2)#4	125.23(3)	S(1)#14-Ge(1)-S(2)#14	114.46(4)
S(2)#1-Ba(1)-S(2)#5	146.90(3)	S(1)-Ge(1)-S(2)#14	107.91(5)
S(2)#2-Ba(1)-S(2)#5	69.00(2)	S(2)-Ge(1)-S(2)#14	106.49(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-x+y,-z+1/3	#2 x-1,y-1,z	#3 -x,-x+y,-z+1/3
#4 -y+1,x-y+1,z+1/3	#5 y-1,x,-z	#6 -x+1,-x+y+1,-z+1/3
#7 x-1,y,z	#8 -x,-x+y+1,-z+1/3	#9 x,y+1,z
#10 y-1,x-1,-z	#11 x,y-1,z	#12 x+1,y,z
#13 -x+y,-x,z-1/3	#14 y,x,-z	#15 y+1,x+1,-z
#16 x+1,y+1,z	#17 -x+y,-x+1,z-1/3	

Table S2(c) Bond lengths (Å) and angles (°) for $BaCu_2GeSe_4$.

Ba(1)-Se(4)	3.3096(13)	Se(3)#1-Ba(1)-Se(2)#4	86.32(3)
Ba(1)-Se(3)#1	3.3118(13)	Se(3)-Ba(1)-Se(2)#4	126.17(3)
Ba(1)-Se(3)	3.3281(13)	Se(4)#2-Ba(1)-Se(2)#4	82.51(3)
Ba(1)-Se(4)#2	3.3303(13)	Se(1)#3-Ba(1)-Se(2)#4	127.61(3)
Ba(1)-Se(1)#3	3.3441(13)	Se(4)-Ba(1)-Se(2)	139.63(3)
Ba(1)-Se(2)#4	3.3472(13)	Se(3)#1-Ba(1)-Se(2)	73.53(3)
Ba(1)-Se(2)	3.3818(12)	Se(3)-Ba(1)-Se(2)	78.36(3)
Ba(1)-Se(1)#5	3.3845(12)	Se(4)#2-Ba(1)-Se(2)	69.83(3)
Ba(1)-Cu(2)#3	3.6200(16)	Se(1)#3-Ba(1)-Se(2)	66.17(3)
Ba(1)-Cu(1)#4	3.6240(16)	Se(2)#4-Ba(1)-Se(2)	150.11(4)
Ba(1)-Cu(2)#5	3.8959(16)	Se(4)-Ba(1)-Se(1)#5	73.53(3)
Ba(1)-Cu(1)	3.8971(17)	Se(3)#1-Ba(1)-Se(1)#5	139.59(3)
Cu(1)-Se(1)#6	2.4269(18)	Se(3)-Ba(1)-Se(1)#5	69.81(3)
Cu(1)-Se(3)	2.4342(17)	Se(4)#2-Ba(1)-Se(1)#5	78.31(3)
Cu(1)-Se(4)#7	2.4944(18)	Se(1)#3-Ba(1)-Se(1)#5	150.14(4)
Cu(1)-Se(2)	2.541(2)	Se(2)#4-Ba(1)-Se(1)#5	66.15(3)
Cu(2)-Se(2)#1	2.4266(18)	Se(2)-Ba(1)-Se(1)#5	116.75(3)
Cu(2)-Se(4)#8	2.4363(18)	Se(1)#6-Cu(1)-Se(3)	132.96(7)
Cu(2)-Se(3)#8	2.4944(18)	Se(1)#6-Cu(1)-Se(4)#7	109.02(6)
Cu(2)-Se(1)	2.536(2)	Se(3)-Cu(1)-Se(4)#7	99.27(6)
Ge(1)-Se(1)	2.3519(16)	Se(1)#6-Cu(1)-Se(2)	95.34(6)
Ge(1)-Se(2)	2.3550(16)	Se(3)-Cu(1)-Se(2)	116.84(7)
Ge(1)-Se(3)#9	2.3605(15)	Se(4)#7-Cu(1)-Se(2)	98.97(6)
Ge(1)-Se(4)#2	2.3605(15)	Se(2)#1-Cu(2)-Se(4)#8	132.82(7)
Se(4)-Ba(1)-Se(3)#1	125.75(3)	Se(2)#1-Cu(2)-Se(3)#8	109.01(6)
Se(4)-Ba(1)-Se(3)	68.85(3)	Se(4)#8-Cu(2)-Se(3)#8	99.11(6)
Se(3)#1-Ba(1)-Se(3)	146.81(3)	Se(2)#1-Cu(2)-Se(1)	95.42(6)
Se(4)-Ba(1)-Se(4)#2	146.75(3)	Se(4)#8-Cu(2)-Se(1)	117.01(7)
Se(3)#1-Ba(1)-Se(4)#2	68.86(3)	Se(3)#8-Cu(2)-Se(1)	99.11(6)
Se(3)-Ba(1)-Se(4)#2	117.10(3)	Se(1)-Ge(1)-Se(2)	105.07(5)
Se(4)-Ba(1)-Se(1)#3	86.33(3)	Se(1)-Ge(1)-Se(3)#9	109.21(6)
Se(3)#1-Ba(1)-Se(1)#3	70.22(3)	Se(2)-Ge(1)-Se(3)#9	113.93(6)
Se(3)-Ba(1)-Se(1)#3	82.56(3)	Se(1)-Ge(1)-Se(4)#2	114.08(6)
Se(4)#2-Ba(1)-Se(1)#3	126.21(3)	Se(2)-Ge(1)-Se(4)#2	109.14(6)
Se(4)-Ba(1)-Se(2)#4	70.21(3)	Se(3)#9-Ge(1)-Se(4)#2	105.63(5)

Symmetry transformations used to generate equivalent atoms:

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

Table S2(d) Bond lengths (Å) and angles (°) for $BaCu_2SnS_4$.

Ba(1)-S(2)#1	3.203(3)	S(1)#4-Ba(1)-S(2)#5	126.73(5)
Ba(1)-S(2)#2	3.203(3)	S(2)-Ba(1)-S(2)#5	113.81(9)
Ba(1)-S(1)#3	3.223(3)	S(2)#1-Ba(1)-S(1)	136.92(5)
Ba(1)-S(1)#4	3.223(3)	S(2)#2-Ba(1)-S(1)	72.17(5)
Ba(1)-S(2)	3.229(3)	S(1)#3-Ba(1)-S(1)	65.09(3)
Ba(1)-S(2)#5	3.229(3)	S(1)#4-Ba(1)-S(1)	152.85(7)
Ba(1)-S(1)	3.313(3)	S(2)-Ba(1)-S(1)	71.53(5)
Ba(1)-S(1)#5	3.313(3)	S(2)#5-Ba(1)-S(1)	75.30(6)
Cu(1)-S(2)#9	2.311(2)	S(2)#1-Ba(1)-S(1)#5	72.17(5)
Cu(1)-S(1)	2.316(2)	S(2)#2-Ba(1)-S(1)#5	136.92(5)
Cu(1)-S(2)#2	2.416(2)	S(1)#3-Ba(1)-S(1)#5	152.85(7)
Cu(1)-S(1)#3	2.423(3)	S(1)#4-Ba(1)-S(1)#5	65.09(3)
Sn(1)-S(1)#14	2.386(2)	S(2)-Ba(1)-S(1)#5	75.30(6)
Sn(1)-S(2)#14	2.389(2)	S(2)#5-Ba(1)-S(1)#5	71.53(5)
S(2)#1-Ba(1)-S(2)#2	132.11(8)	S(1)-Ba(1)-S(1)#5	116.99(7)
S(2)#1-Ba(1)-S(1)#3	88.53(6)	S(2)#9-Cu(1)-S(1)	134.06(9)
S(2)#2-Ba(1)-S(1)#3	70.23(6)	S(2)#9-Cu(1)-S(2)#2	99.33(6)
S(2)#1-Ba(1)-S(1)#4	70.23(6)	S(1)-Cu(1)-S(2)#2	108.39(8)
S(2)#2-Ba(1)-S(1)#4	88.53(6)	S(2)#9-Cu(1)-S(1)#3	115.15(9)
S(1)#3-Ba(1)-S(1)#4	126.71(7)	S(1)-Cu(1)-S(1)#3	95.79(6)
S(2)#1-Ba(1)-S(2)	144.61(5)	S(2)#2-Cu(1)-S(1)#3	99.60(9)
S(2)#2-Ba(1)-S(2)	68.16(6)	S(1)#14-Sn(1)-S(1)	105.19(12)
S(1)#3-Ba(1)-S(2)	126.73(5)	S(1)#14-Sn(1)-S(2)#14	106.41(8)
S(1)#4-Ba(1)-S(2)	83.79(5)	S(1)-Sn(1)-S(2)#14	117.03(7)
S(2)#1-Ba(1)-S(2)#5	68.16(6)	S(1)#14-Sn(1)-S(2)	117.03(7)
S(2)#2-Ba(1)-S(2)#5	144.61(5)	S(1)-Sn(1)-S(2)	106.41(8)
S(1)#3-Ba(1)-S(2)#5	83.79(5)	S(2)#14-Sn(1)-S(2)	105.32(11)

Symmetry transformations used to generate equivalent atoms:

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

Table S2(e) Bond lengths (Å) and angles (°) for $BaCu_2SnSe_4$.

Ba(1)-Se(3)#1	3.311(2)	Se(2)#3-Ba(1)-Se(1)#5	147.11(4)
Ba(1)-Se(3)	3.311(2)	Se(1)#4-Ba(1)-Se(1)#5	128.05(7)
Ba(1)-Se(2)#2	3.323(2)	Se(3)#1-Ba(1)-Se(3)#2	152.57(4)
Ba(1)-Se(2)#3	3.323(2)	Se(3)-Ba(1)-Se(3)#2	67.25(6)
Ba(1)-Se(1)#4	3.375(2)	Se(2)#2-Ba(1)-Se(3)#2	73.02(4)
Ba(1)-Se(1)#5	3.375(2)	Se(2)#3-Ba(1)-Se(3)#2	76.70(4)
Ba(1)-Se(3)#2	3.409(2)	Se(1)#4-Ba(1)-Se(3)#2	135.70(2)
Ba(1)-Se(3)#3	3.409(2)	Se(1)#5-Ba(1)-Se(3)#2	74.32(4)
Cu(1)-Se(3)#6	2.431(3)	Se(3)#1-Ba(1)-Se(3)#3	67.25(6)
Cu(1)-Se(2)#3	2.4528(19)	Se(3)-Ba(1)-Se(3)#3	152.57(4)
Cu(1)-Se(3)#2	2.492(2)	Se(2)#2-Ba(1)-Se(3)#3	76.70(4)
Cu(1)-Se(1)	2.546(2)	Se(2)#3-Ba(1)-Se(3)#3	73.02(4)
Sn(1)-Se(3)#7	2.5266(18)	Se(1)#4-Ba(1)-Se(3)#3	74.32(4)
Sn(1)- Se(2)	2.545(2)	Se(1)#5-Ba(1)-Se(3)#3	135.70(2)
Sn(1)- Se(1)	2.509(3)	Se(3)#6-Cu(1)-Se(3)#2	98.23(6)
Sn(1)- Se(3)	2.5266(18)	Se(2)#3-Cu(1)-Se(3)#2	115.30(7)
Se(3)#1-Ba(1)-Se(3)	121.00(7)	Se(3)#6-Cu(1)-Se(1)	110.83(6)
Se(3)#1-Ba(1)-Se(2)#2	83.49(4)	Se(2)#3-Cu(1)-Se(1)	96.01(8)
Se(3)-Ba(1)-Se(2)#2	128.24(3)	Se(3)#2-Cu(1)-Se(1)	101.21(7)
Se(3)#1-Ba(1)-Se(2)#3	128.24(3)	Se(3)#6-Cu(1)-Cu(1)#7	105.04(4)
Se(3)-Ba(1)-Se(2)#3	83.49(4)	Se(2)#3-Cu(1)-Cu(1)#7	56.64(4)
Se(2)#2-Ba(1)-Se(2)#3	118.23(8)	Se(3)#2-Cu(1)-Cu(1)#7	153.10(4)
Se(3)#1-Ba(1)-Se(1)#4	71.23(5)	Se(1)-Cu(1)-Cu(1)#7	58.01(4)
Se(3)-Ba(1)-Se(1)#4	83.71(5)	Se(1)-Sn(1)-Se(3)#7	119.06(4)
Se(2)#2-Ba(1)-Se(1)#4	147.11(4)	Se(1)-Sn(1)-Se(3)	119.06(4)
Se(2)#3-Ba(1)-Se(1)#4	67.04(6)	Se(3)#7-Sn(1)-Se(3)	103.15(8)
Se(3)#1-Ba(1)-Se(1)#5	83.71(5)	Se(1)-Sn(1)-Se(2)	105.11(6)
Se(3)-Ba(1)-Se(1)#5	71.23(5)	Se(3)#7-Sn(1)-Se(2)	104.34(5)
Se(2)#2-Ba(1)-Se(1)#5	67.04(6)	Se(3)-Sn(1)-Se(2)	104.34(5)

Symmetry transformations used to generate equivalent atoms:

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

Table S3 Calculated NLO SHG coefficients and percentage of VH (Virtual-Hole) and VE (Virtual-Electron) in $BaCu_2M^{IV}Q_4$ (M^{IV} = Si, Ge, and Sn; Q = S, Se).

Compounds	**SHG coefficients (pm/V)**		
	Total	VH	VE
$BaCu_2SiSe_4$	d_{12}= 4.18	36.53%	63.47%
$BaCu_2GeS_4$	d_{12}= 0.28	48.46%	51.54%
$BaCu_2GeSe_4$	d_{12}= 5.62	43.37%	56.63%
$BaCu_2SnS_4$	d_{12}= 12.09	90.01%	9.99%
$BaCu_2SnSe_4$	d_{12}= 1.45	47.72%	52.28%

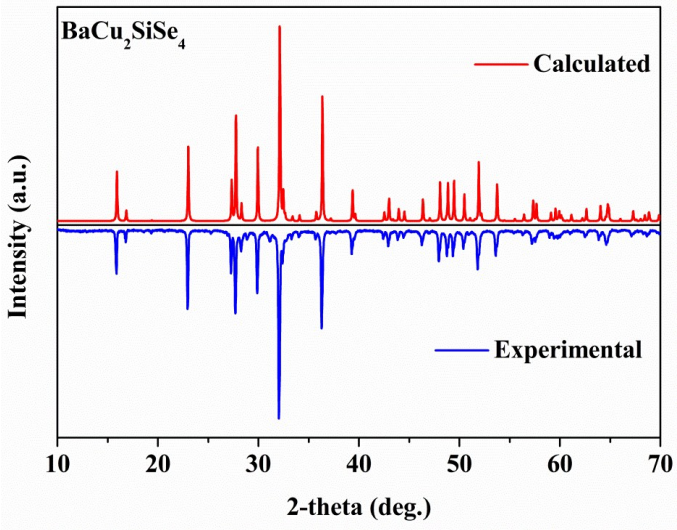


Fig. S1(a) Powder XRD patterns of $BaCu_2SiSe_4$.

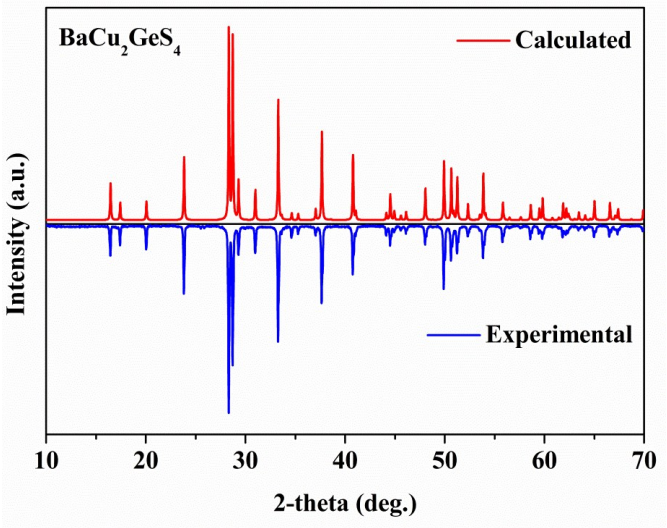


Fig. S1(b) Powder XRD patterns of $BaCu_2GeS_4$.

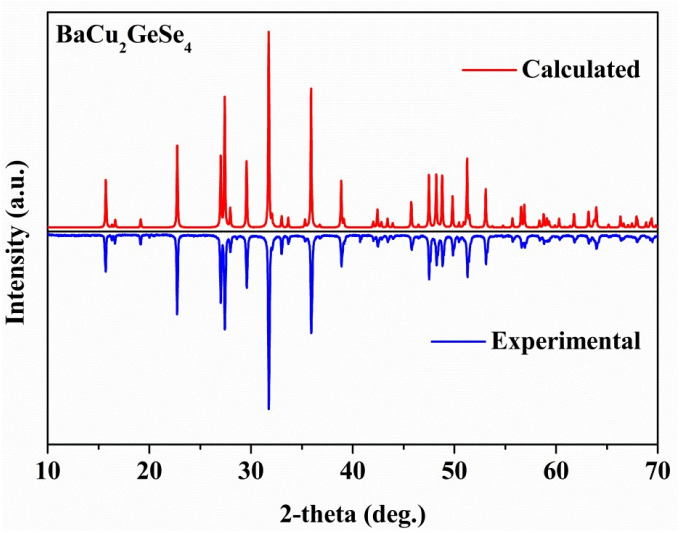


Fig. S1(c) Powder XRD patterns of $BaCu_2GeSe_4$.

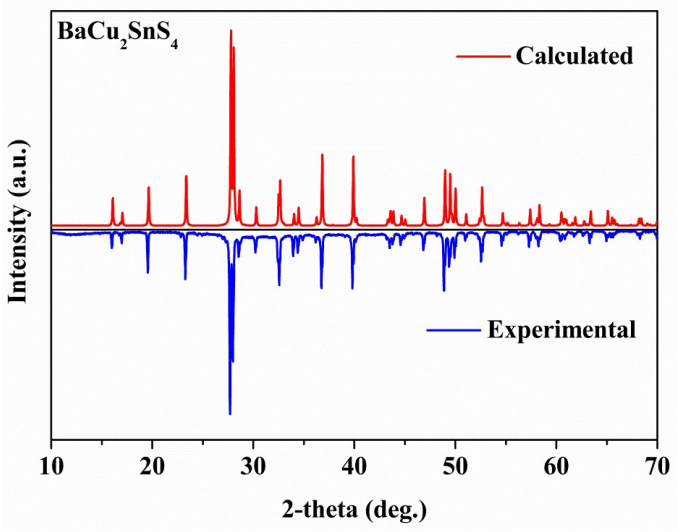


Fig. S1(d) Powder XRD patterns of $BaCu_2SnS_4$.

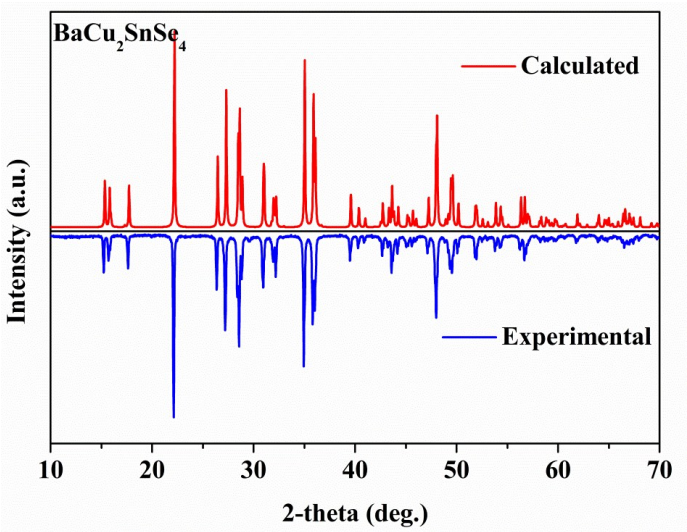


Fig. S1(e) Powder XRD patterns of $BaCu_2SnSe_4$.

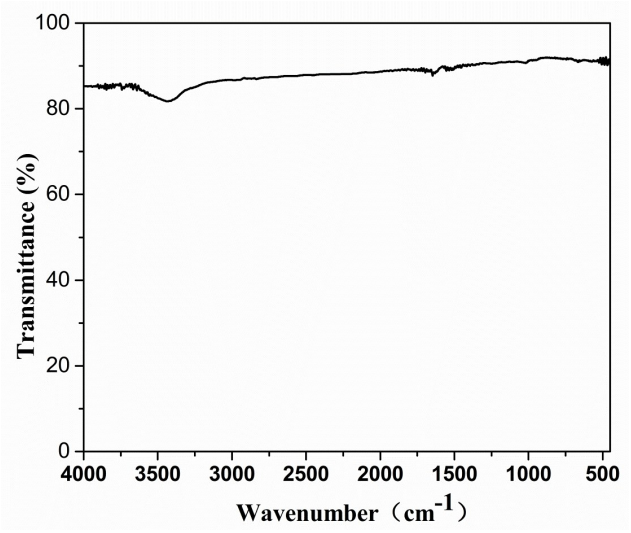


Fig. S2(a) The IR spectrum of as-synthesized $BaCu_2SiSe_4$.

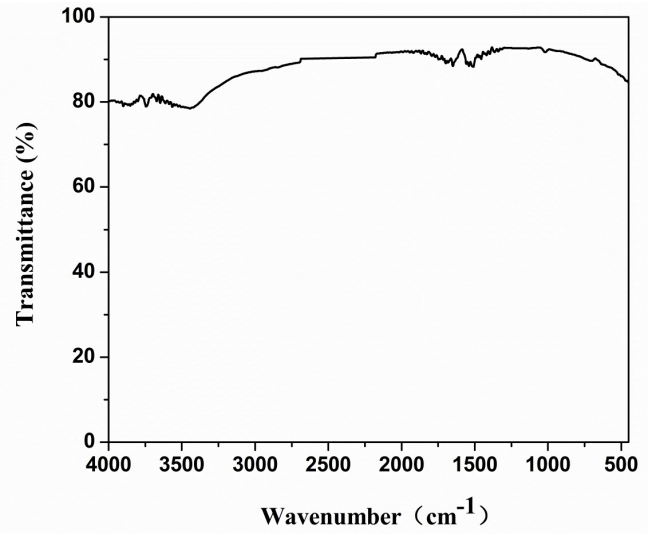


Fig. S2(b) The IR spectrum of as-synthesized $BaCu_2GeS_4$.

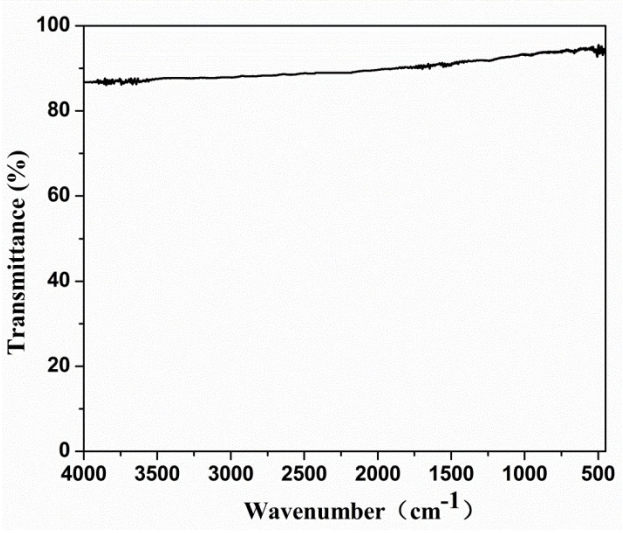


Fig. S2(c) The IR spectrum of as-synthesized $BaCu_2GeSe_4$.

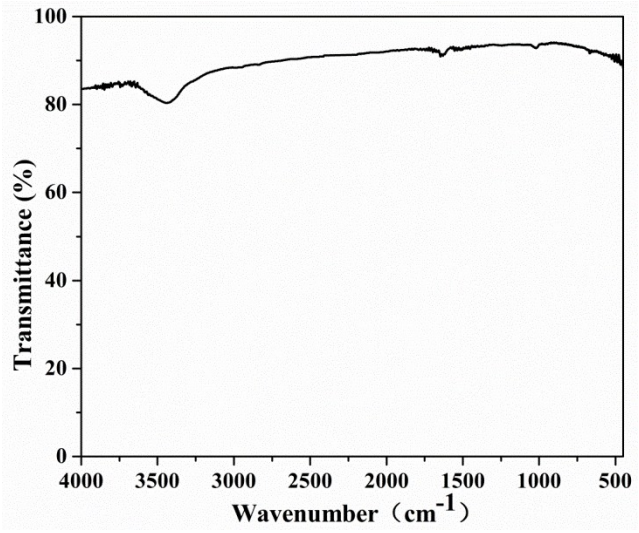


Fig. S2(d) The IR spectrum of as-synthesized $BaCu_2SnS_4$.

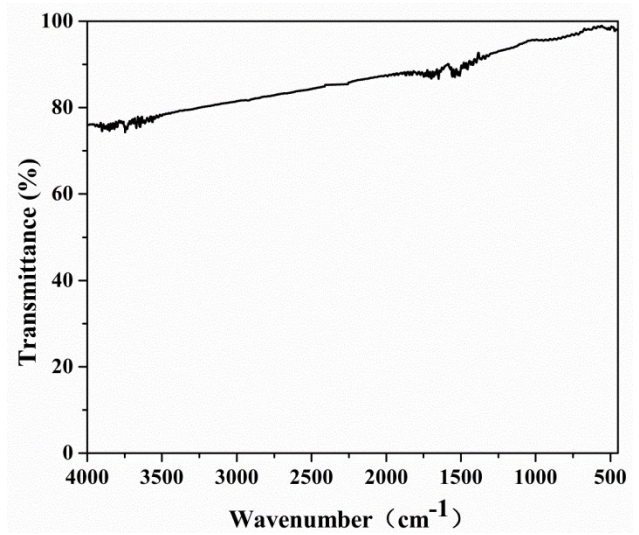


Fig. S2(e) The IR spectrum of as-synthesized $BaCu_2SnSe_4$.

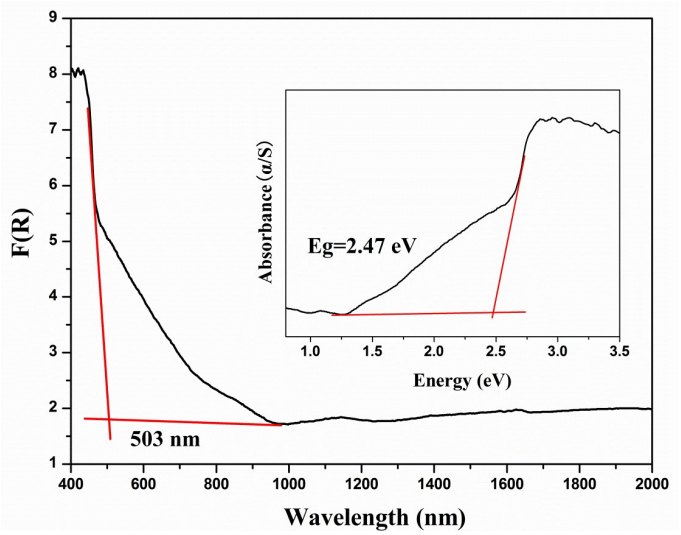


Fig. S3(a) Absorption spectrum of $BaCu_2SiSe_4$. The inset diagram is the experimental band gap.

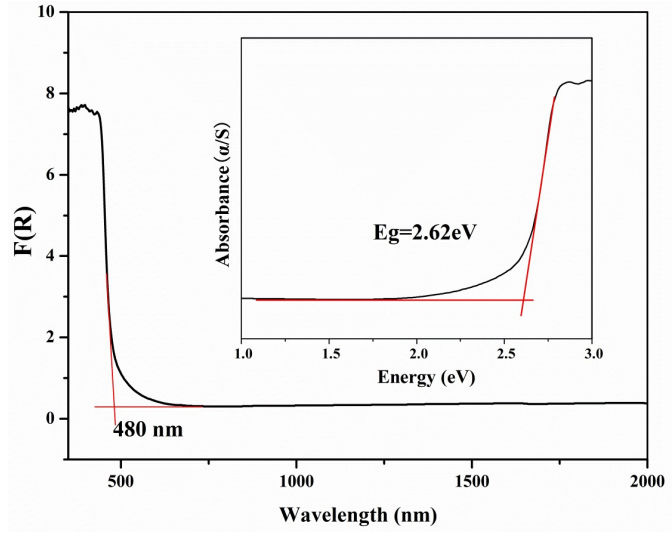


Fig. S3(b) Absorption spectrum of $BaCu_2GeS_4$. The inset diagram is the experimental band gap.

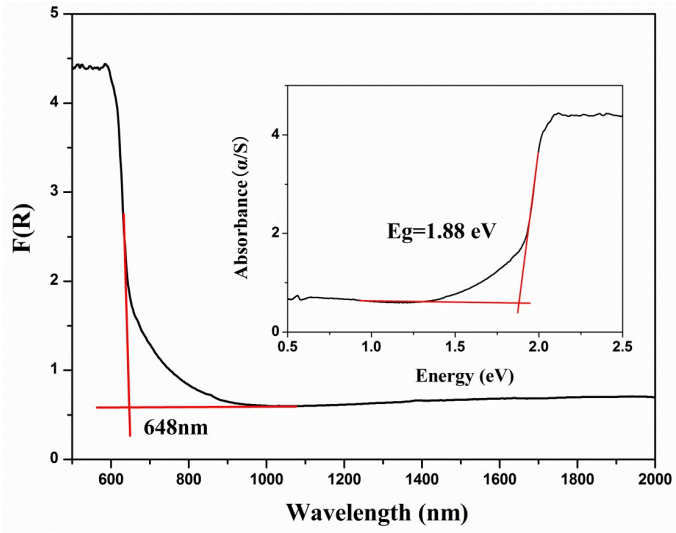


Fig. S3(c) Absorption spectrum of $BaCu_2GeSe_4$. The inset diagram is the experimental band gap.

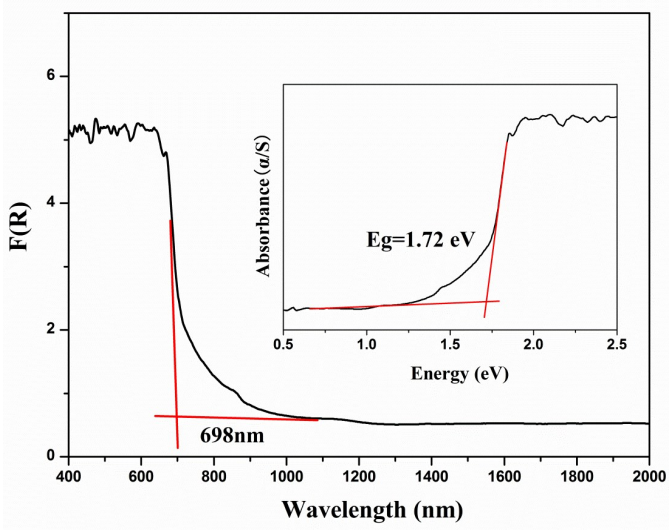


Fig. S3(d) Absorption spectrum of $BaCu_2SnSe_4$. The inset diagram is the experimental band gap.

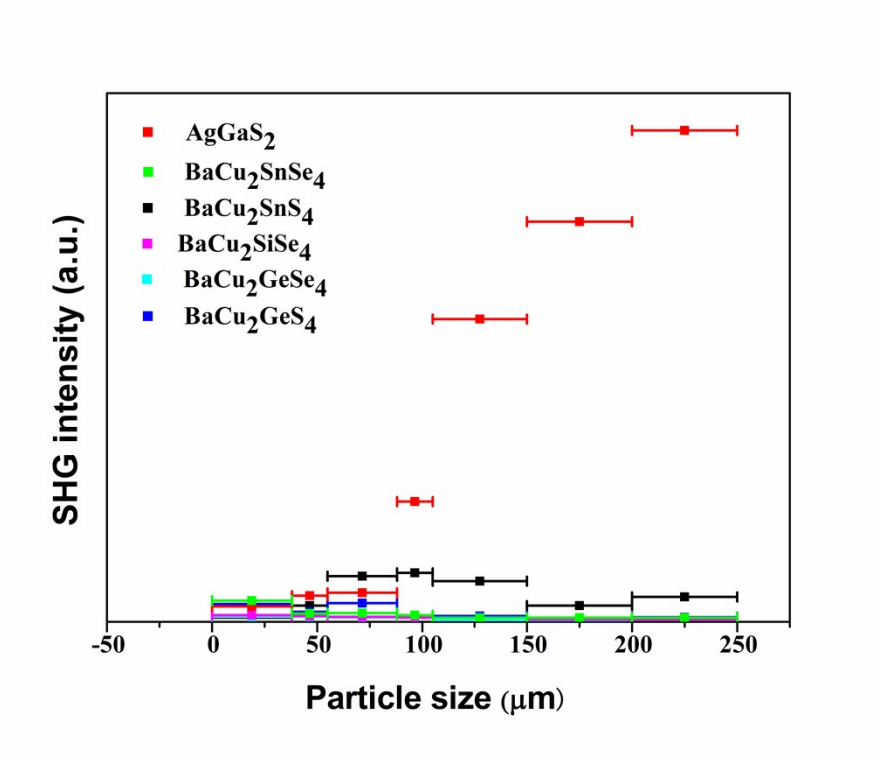


Fig. S4 SHG response for title compounds in different particle sizes ($AgGaS_2$ as the reference).

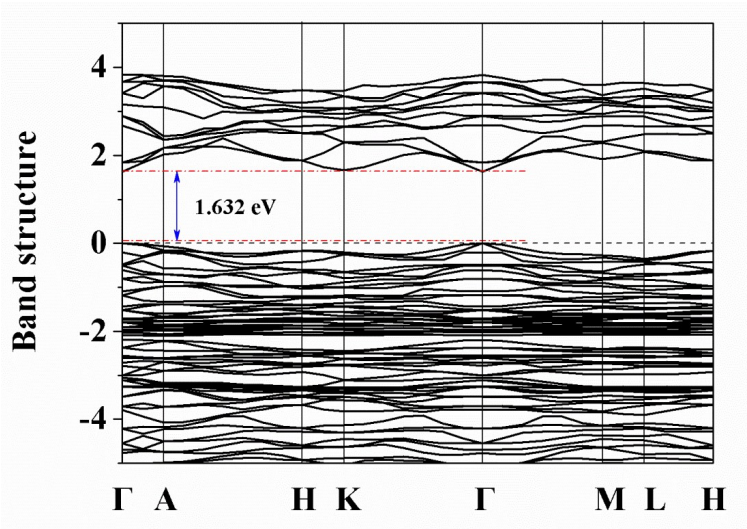


Fig. S5(a) The electronic structure of $BaCu_2SiSe_4$.

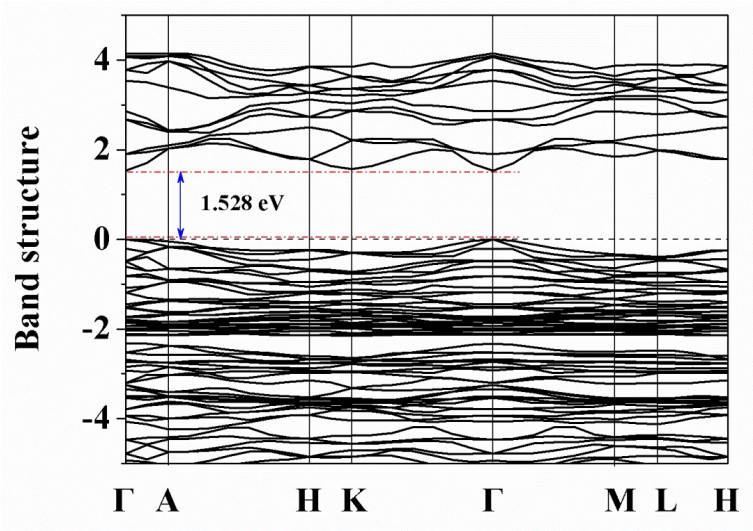


Fig. S5(b) The electronic structure of $BaCu_2GeS_4$.

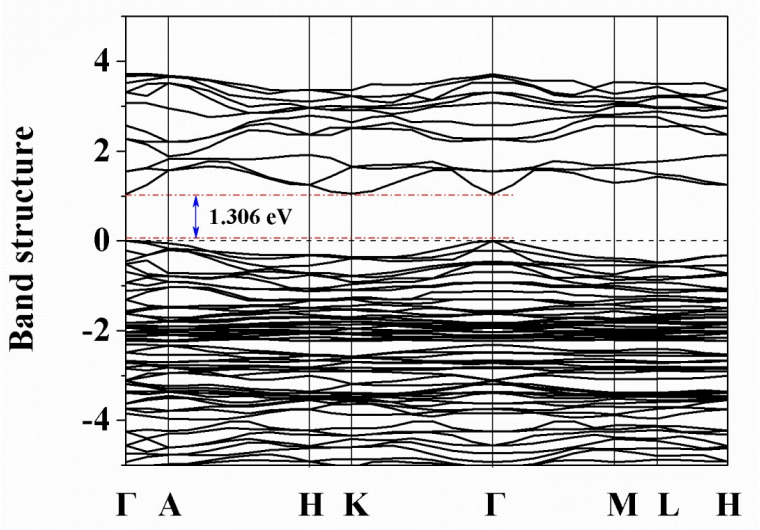


Fig. S5(c) The electronic structure of $BaCu_2GeSe_4$.

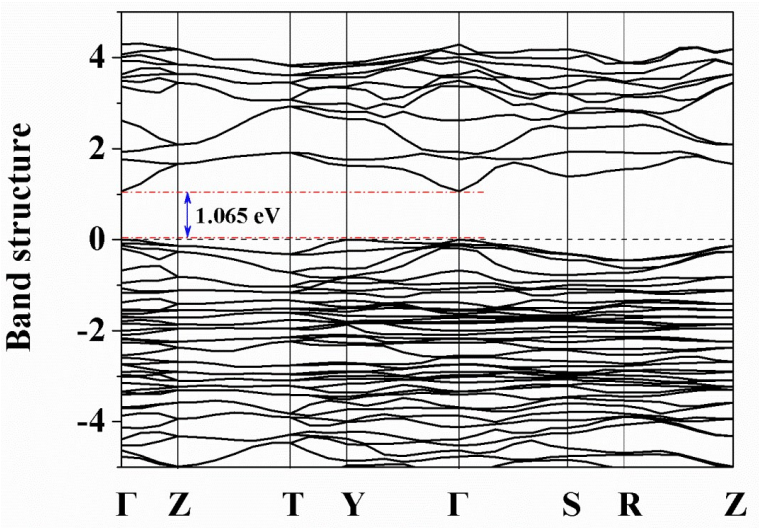


Fig. S5(d) The electronic structure of $BaCu_2SnSe_4$.

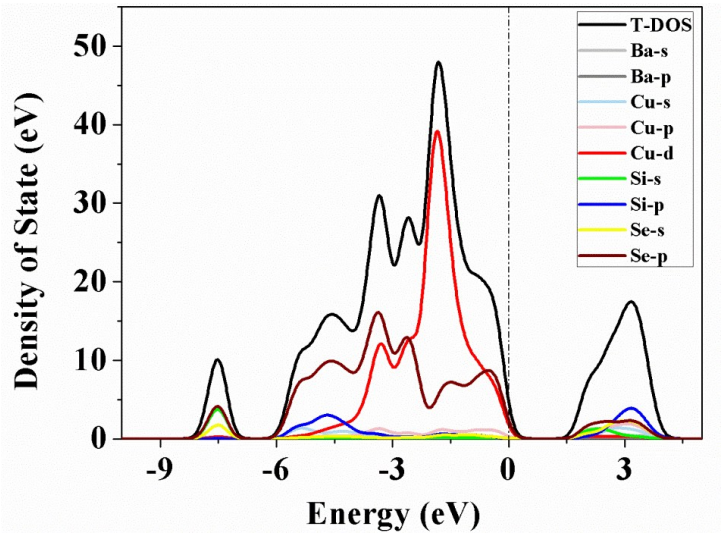


Fig. S6(a) The PDOS of $BaCu_2SiSe_4$.

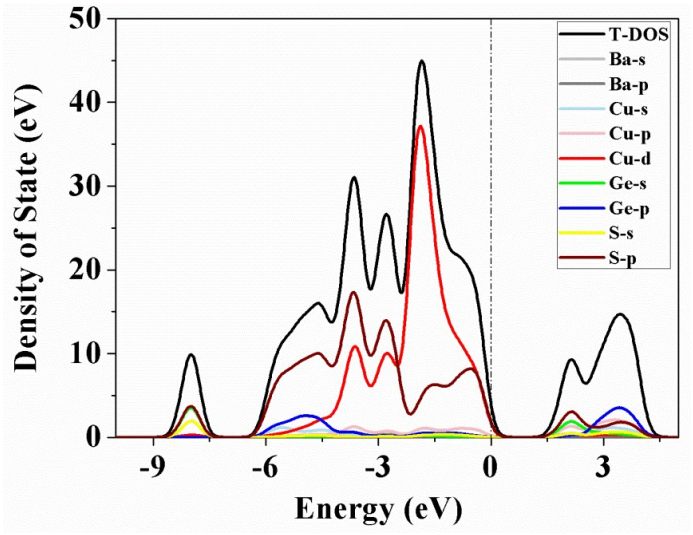


Fig. S6(b) The PDOS of $BaCu_2GeS_4$.

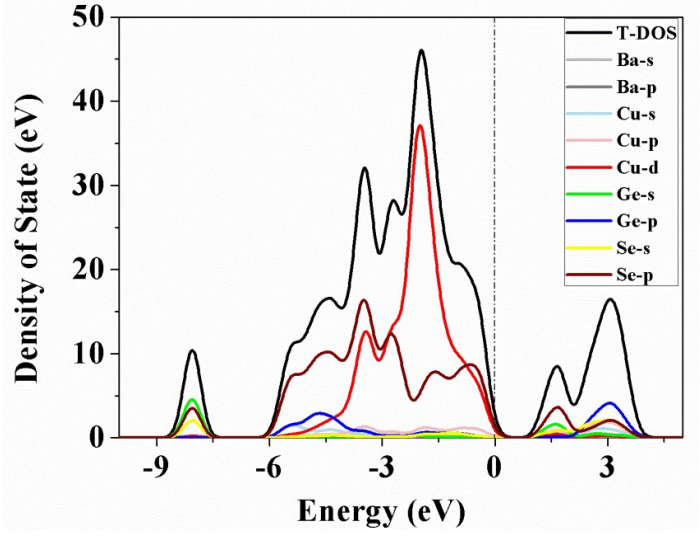


Fig. S6(c) The PDOS of $BaCu_2GeSe_4$.

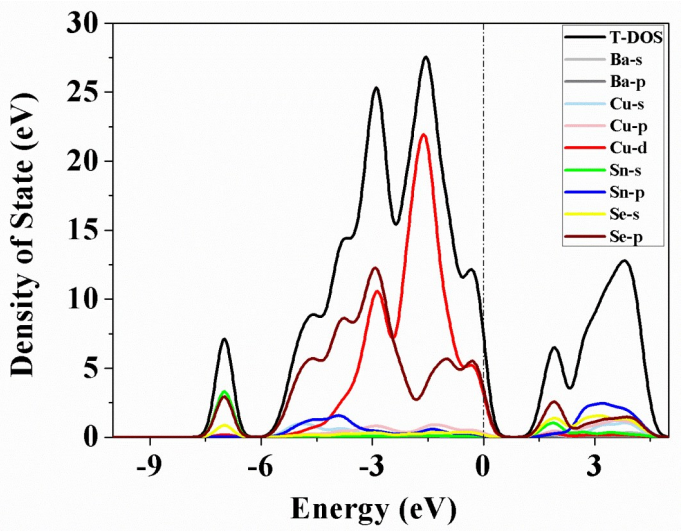


Fig. S6(d) The PDOS of $BaCu_2SnSe_4$.

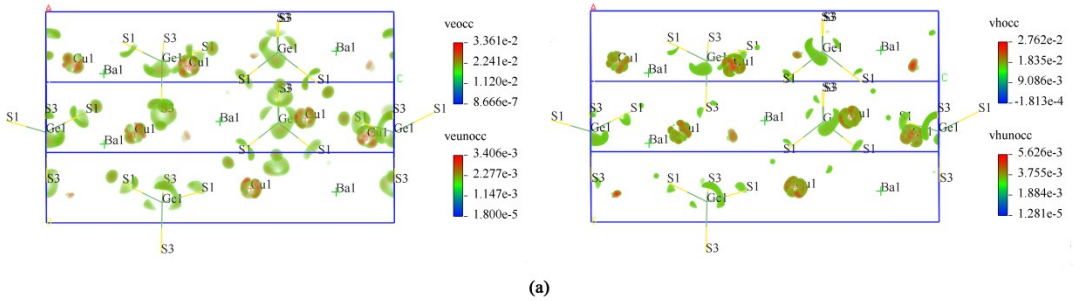


Fig. S7(a) SHG density of $BaCu_2GeS_4$.

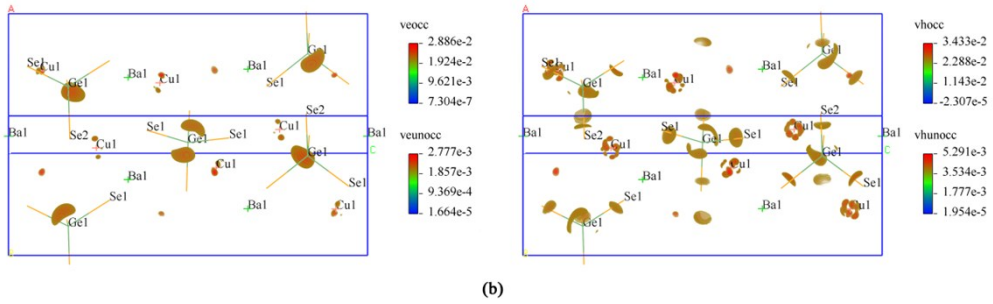


Fig. S7(b) SHG density of $BaCu_2GeSe_4$.

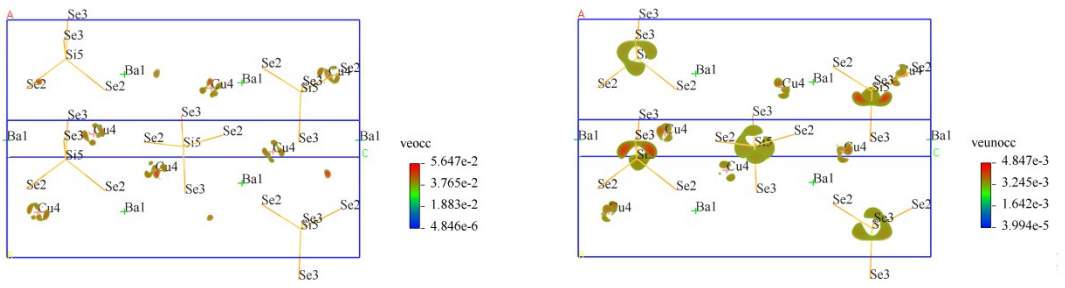
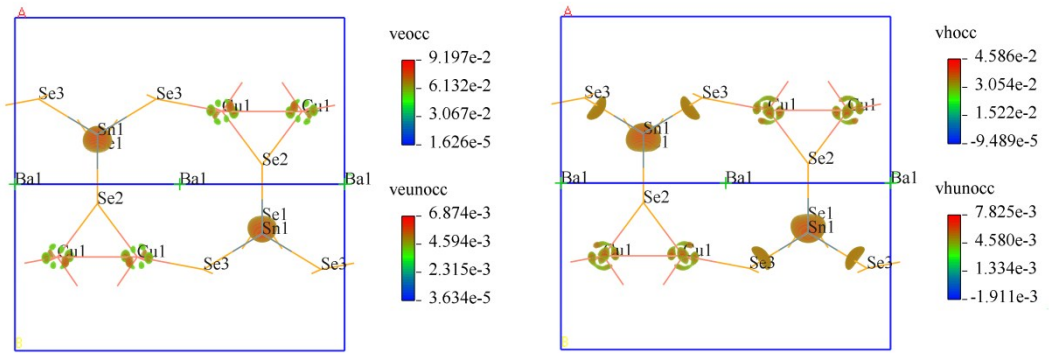


Fig. S7(c) SHG density of $BaCu_2SiSe_4$.



(d)

Fig. S7(d) SHG density of $BaCu_2SnSe_4$.