Supporting Information

Effect of element-substitution on structural transformation and optical performances in $I_2BaM^{IV}Q_4$ (I = Li, Na, Cu and Ag; M^{IV} = Si, Ge and Sn; Q = S and Se)

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Table S1 (a) Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ag_2BaSiSe_4$. *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)	2b	5000	5000	10000	15(1)	2.03
Ag(1)	4d	5000	0	7500	48(1)	1.24
Se(1)	8i	1880(1)	1880(1)	11537(1)	14(1)	2.11
Si(1)	2a	0	0	10000	12(1)	3.94

Table S1 (b) Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ag_2BaGeSe_4$. *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)	2a	5000	5000	5000	20(1)	1.83
Ag(1)	4j	5000	0	2898(3)	48(1)	1.44
Ge(1)	2c	0	0	5000	15(1)	3.77
Se(1)	8k	1931(2)	1911(2)	6605(2)	19(1)	1.97

Table S1 (c) Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ag_2BaSnSe_4$. *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)	2a	0	10000	10000	19(1)	1.91
Ag(1)	4j	0	5000	8066(2)	41(1)	1.22
Se(1)	8k	2053(2)	11960(2)	6721(2)	17(1)	2.09
Sn(1)	2c	0	10000	5000	13(1)	3.98

Table S2 (a) Bond lengths (Å) and angles (°) for $Ag_2BaSiSe_4$.

Ba(1)-Se(1)#1	3.3647(16)	Se(1)-Ba(1)-Se(1)#5	71.69(2)
Ba(1)-Se(1)	3.3647(16)	Se(1)#3-Ba(1)-Se(1)#5	78.71(5)
Ba(1)-Se(1)#2	3.3647(16)	Se(1)#4-Ba(1)-Se(1)#5	134.20(4)
Ba(1)-Se(1)#3	3.3647(16)	Se(1)#1-Ba(1)-Se(1)#6	71.69(2)
Ba(1)-Se(1)#4	3.414(2)	Se(1)-Ba(1)-Se(1)#6	71.69(2)
Ba(1)-Se(1)#5	3.414(2)	Se(1)#2-Ba(1)-Se(1)#6	78.71(5)
Ba(1)-Se(1)#6	3.414(2)	Se(1)#3-Ba(1)-Se(1)#6	145.48(3)
Ba(1)-Se(1)#7	3.414(2)	Se(1)#4-Ba(1)-Se(1)#6	134.20(4)
Ag(11)-Se(1)#2	2.6932(12)	Se(1)#5-Ba(1)-Se(1)#6	66.78(6)
Ag(11)-Se(1)#11	2.6932(12)	Se(1)#1-Ba(1)-Se(1)#7	78.71(5)
Ag(11)-Se(1)#4	2.6932(12)	Se(1)-Ba(1)-Se(1)#7	145.48(3)
Ag(11)-Se(1)#12	2.6932(12)	Se(1)#2-Ba(1)-Se(1)#7	71.69(2)
Si(1)-Se(1)	2.2655(12)	Se(1)#3-Ba(1)-Se(1)#7	71.69(2)
Si(1)-Se(1)#11	2.2655(12)	Se(1)#4-Ba(1)-Se(1)#7	66.78(6)
Si(1)-Se(1)#15	2.2655(12)	Se(1)#5-Ba(1)-Se(1)#7	134.20(4)
Si(1)-Se(1)#16	2.2655(12)	Se(1)#6-Ba(1)-Se(1)#7	134.20(4)
Se(1)#1-Ba(1)-Se(1)	135.81(5)	Se(1)#2-Ag(11)-Se(1)#11	145.77(5)
Se(1)#1-Ba(1)-Se(1)#2	98.135(17)	Se(1)#2-Ag(11)-Se(1)#4	94.969(13)
Se(1)-Ba(1)-Se(1)#2	98.135(17)	Se(1)#11-Ag(11)-Se(1)#4	94.969(13)
Se(1)#1-Ba(1)-Se(1)#3	98.135(17)	Se(1)#2-Ag(11)-Se(1)#12	94.969(13)
Se(1)-Ba(1)-Se(1)#3	98.135(17)	Se(1)#11-Ag(11)-Se(1)#12	94.969(13)
Se(1)#2-Ba(1)-Se(1)#3	135.81(5)	Se(1)#4-Ag(11)-Se(1)#12	145.77(5)
Se(1)#1-Ba(1)-Se(1)#4	145.48(3)	Se(1)-Si(1)-Se(1)#11	108.19(3)
Se(1)-Ba(1)-Se(1)#4	78.71(5)	Se(1)-Si(1)-Se(1)#15	112.07(7)
Se(1)#2-Ba(1)-Se(1)#4	71.69(2)	Se(1)#11-Si(1)-Se(1)#15	108.19(3)
Se(1)#3-Ba(1)-Se(1)#4	71.69(2)	Se(1)-Si(1)-Se(1)#16	108.19(3)
Se(1)#2-Ba(1)-Se(1)#5	145.48(2)	Se(1)#11-Si(1)-Se(1)#16	112.07(7)
Se(1)#1-Ba(1)-Se(1)#5	71.69(2)	Se(1)#15-Si(1)-Se(1)#16	108.19(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z	#2 -y+1,x,-z+2	#3 y,-x+1,-z+2
#4 -x+1/2,-y+1/2,z-1/2	#5 -y+1/2,x+1/2,-z+5/2	#6 y+1/2,-x+1/2,-z+5/2
#7 x+1/2,y+1/2,z-1/2	#8 -x+1,y+1,-z+2	#9 x+1/2,y+1/2,z+1/2
#10 -x+1/2,y+1/2,-z+3/2	#11 y,-x,-z+2	#12 x+1/2,y-1/2,z-1/2
#13 x-1/2,y-1/2,z-1/2	#14 x,y-1,z	#15 -x,-y,z
#16 -y,x,-z+2	#17 -x+1,y,-z+2	#18 x-1/2,y+1/2,z+1/2
#19 x-1/2,y-1/2,z+1/2		

Table S2 (b) Bond lengths (Å) and angles (°) for $Ag_2BaGeSe_4$**.**

Ba(1)-Se(1)#1	3.415(5)	Se(1)#1-Ba(1)-Se(1)	133.98(12)
Ba(1)-Se(1)	3.415(5)	Se(1)#1-Ba(1)-Se(1)#2	97.12(17)
Ba(1)-Se(1)#2	3.415(5)	Se(1)-Ba(1)-Se(1)#2	100.47(17)
Ba(1)-Se(1)#3	3.415(5)	Se(1)#1-Ba(1)-Se(1)#3	100.47(17)
Ba(1)-Se(1)#4	3.437(6)	Se(1)-Ba(1)-Se(1)#3	97.12(17)
Ba(1)-Se(1)#5	3.437(6)	Se(1)#2-Ba(1)-Se(1)#3	133.98(12)
Ba(1)-Se(1)#6	3.437(6)	Se(1)#1-Ba(1)-Se(1)#4	147.79(5)
Ba(1)-Se(1)#7	3.437(6)	Se(1)-Ba(1)-Se(1)#4	78.23(13)
Ag(1)-Se(1)#3	2.626(5)	Se(1)#2-Ba(1)-Se(1)#4	72.08(12)
Ag(1)-Se(1)#10	2.626(5)	Se(1)#3-Ba(1)-Se(1)#4	70.46(12)
Ag(1)-Se(1)#11	2.855(5)	Se(1)#1-Ba(1)-Se(1)#5	78.23(13)
Ag(1)-Se(1)#4	2.855(5)	Se(1)-Ba(1)-Se(1)#5	147.79(5)
Ge(1)-Se(1)	2.372(3)	Se(1)#2-Ba(1)-Se(1)#5	70.46(12)
Ge(1)-Se(1)#10	2.372(3)	Se(1)#3-Ba(1)-Se(1)#5	72.08(12)
Ge(1)-Se(1)#13	2.372(3)	Se(1)#4-Ba(1)-Se(1)#5	69.56(15)
Ge(1)-Se(1)#14	2.372(3)	Se(1)#1-Ba(1)-Se(1)#6	72.08(12)
Se(1)#3-Ag(1)-Se(1)#10	161.91(15)	Se(1)-Ba(1)-Se(1)#6	70.46(12)
Se(1)#3-Ag(1)-Se(1)#11	94.60(15)	Se(1)#2-Ba(1)-Se(1)#6	147.79(5)
Se(1)#10-Ag(1)-Se(1)#11	92.19(15)	Se(1)#3-Ba(1)-Se(1)#6	78.23(13)
Se(1)#3-Ag(1)-Se(1)#4	92.19(15)	Se(1)#4-Ba(1)-Se(1)#6	131.99(13)
Se(1)#10-Ag(1)-Se(1)#4	94.60(15)	Se(1)#5-Ba(1)-Se(1)#6	132.85(13)
Se(1)#11-Ag(1)-Se(1)#4	135.75(16)	Se(1)#1-Ba(1)-Se(1)#7	70.46(12)
Se(1)-Ge(1)-Se(1)#10	109.17(16)	Se(1)-Ba(1)-Se(1)#7	72.08(12)
Se(1)-Ge(1)-Se(1)#13	107.76(17)	Se(1)#2-Ba(1)-Se(1)#7	78.23(13)
Se(1)#10-Ge(1)-Se(1)#13	111.51(16)	Se(1)#3-Ba(1)-Se(1)#7	147.79(5)
Se(1)-Ge(1)-Se(1)#14	111.51(16)	Se(1)#4-Ba(1)-Se(1)#7	132.85(13)
Se(1)#10-Ge(1)-Se(1)#14	107.76(17)	Se(1)#5-Ba(1)-Se(1)#7	131.99(13)
Se(1)#13-Ge(1)-Se(1)#14	109.17(16)	Se(1)#6-Ba(1)-Se(1)#7	69.56(15)

Symmetry transformations used to generate equivalent atoms:

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

Table S2 (c) Bond lengths (Å) and angles (°) for $Ag_2BaSnSe_4$**.**

Ba(1)-Se(1)#1	3.402(3)	Se(1)#4-Ba(1)-Se(1)#5	71.88(8)
Ba(1)-Se(1)#2	3.402(3)	Se(1)-Ba(1)-Se(1)#5	74.39(10)
Ba(1)-Se(1)#3	3.402(3)	Se(1)#1-Ba(1)-Se(1)#6	69.02(8)
Ba(1)-Se(1)#4	3.402(3)	Se(1)#2-Ba(1)-Se(1)#6	71.88(8)
Ba(1)-Se(1)	3.417(3)	Se(1)#3-Ba(1)-Se(1)#6	151.98(4)
Ba(1)-Se(1)#5	3.417(3)	Se(1)#4-Ba(1)-Se(1)#6	77.66(8)
Ba(1)-Se(1)#6	3.417(3)	Se(1)-Ba(1)-Se(1)#6	129.26(9)
Ba(1)-Se(1)#7	3.417(3)	Se(1)#5-Ba(1)-Se(1)#6	129.51(9)
Sn(1)-Se(1)#12	2.512(2)	Se(1)#1-Ba(1)-Se(1)#7	71.88(8)
Sn(1)-Se(1)#13	2.512(2)	Se(1)#2-Ba(1)-Se(1)#7	69.02(8)
Sn(1)-Se(1)#5	2.512(2)	Se(1)#3-Ba(1)-Se(1)#7	77.66(8)
Ag(1)-Se(1)#3	2.560(3)	Se(1)#4-Ba(1)-Se(1)#7	151.98(4)
Ag(1)-Se(1)#14	2.560(3)	Se(1)-Ba(1)-Se(1)#7	129.51(9)
Ag(1)-Se(1)#15	2.920(3)	Se(1)#5-Ba(1)-Se(1)#7	129.26(9)
Ag(1)-Se(1)#5	2.920(3)	Se(1)#6-Ba(1)-Se(1)#7	74.39(10)
Se(1)#1-Ba(1)-Se(1)#2	130.34(9)	Se(1)#12-Sn(1)-Se(1)#13	110.66(11)
Se(1)#1-Ba(1)-Se(1)#3	104.07(10)	Se(1)#12-Sn(1)-Se(1)#5	108.69(11)
Se(1)#2-Ba(1)-Se(1)#3	96.29(11)	Se(1)#13-Sn(1)-Se(1)#5	109.07(11)
Se(1)#1-Ba(1)-Se(1)#4	96.29(11)	Se(1)#12-Sn(1)-Se(1)	109.07(11)
Se(1)#2-Ba(1)-Se(1)#4	104.07(10)	Se(1)#13-Sn(1)-Se(1)	108.69(11)
Se(1)#3-Ba(1)-Se(1)#4	130.34(9)	Se(1)#5-Sn(1)-Se(1)	110.66(11)
Se(1)#1-Ba(1)-Se(1)	77.66(8)	Se(1)#3-Ag(1)-Se(1)#14	172.09(11)
Se(1)#2-Ba(1)-Se(1)	151.98(4)	Se(1)#3-Ag(1)-Se(1)#15	93.61(10)
Se(1)#3-Ba(1)-Se(1)	71.88(8)	Se(1)#14-Ag(1)-Se(1)#15	89.42(10)
Se(1)#4-Ba(1)-Se(1)	69.02(8)	Se(1)#3-Ag(1)-Se(1)#5	89.42(10)
Se(1)#1-Ba(1)-Se(1)#5	151.98(4)	Se(1)#14-Ag(1)-Se(1)#5	93.61(10)
Se(1)#2-Ba(1)-Se(1)#5	77.66(8)	Se(1)#15-Ag(1)-Se(1)#5	135.02(11)
Se(1)#3-Ba(1)-Se(1)#5	69.02(8)		

Symmetry transformations used to generate equivalent atoms:

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

Table S3 The *I* ionic radius and *I*-Se bond lengths in the I_2-Ba-Sn-Se_4 system (*I* = Li, Cu, Ag, and Na)

Compounds	Radius of *I* ionic (Å)	*I*-Se bond	Bond length (Å)	Average Bond length (Å)
$Li_2BaSnSe_4$	0.76	Li(1)-Se×4	2.642	2.64
$Cu_2BaSnSe_4$	0.73	Cu(1)-Se(1)	2.546(2)	2.48
		Cu(1)-Se(2)	2.453(19)	
		Cu(1)-Se(3)	2.431(3)	
		Cu(1)-Se(3)	2.492(2)	
$Ag_2BaSnSe_4$	1.26	Ag(1)-Se(1)	2.560(3)	2.74
		Ag(1)-Se(1)	2.560(3)	
		Ag(1)-Se(1)	2.920(3)	
		Ag(1)-Se(1)	2.920(3)	
$Na_2BaSnSe_4$	1.02	Na(1)-Se(1)	3.023(75)	3.08
		Na(1)-Se(1)	3.048(115)	
		Na(1)-Se(2)	3.085(103)	
		Na(1)-Se(3)	3.008(136)	
		Na(1)-Se(2)	2.917(76)	
		Na(1)-Se(3)	3.117(144)	
		Na(2)-Se(1)	3.137(91)	
		Na(2)-Se(1)	3.057(77)	
		Na(2)-Se(1)	3.445(91)	
		Na(2)-Se(2)	3.065(83)	
		Na(2)-Se(3)	2.961(105)	

Table S4 The crystal data and optical performances for all *I* – Ba – M^{IV} – Q compounds.

Compounds	Space group	Crystal system	Bandgap (eV)	SHG intensity ×$AgGaS_2$ (2.09μm)
$Cu_2BaSnSe_4$	*Ama*2	Orthorhombic	1.72	0.3
Cu_2BaGeS_4	$P3_12_1$	Trigonal	2.47	0.3
$Cu_2BaGeSe_4$	$P3_12_1$	Trigonal	1.88	0.3
Cu_2BaSnS_4	$P3_22_1$	Trigonal	1.96	1.6
$Cu_2BaSiSe_4$	$P3_22_1$	Trigonal	2.62	0.3
Ag_2BaGeS_4	$I\bar{4}2m$	Tetragonal	2.02	1.7
$Ag_2BaSiSe_4$	$I\bar{4}2m$	Tetragonal	1.83	0.1
$Ag_2BaGeSe_4$	*I*222	Orthorhombic	1.57	0.2
Ag_2BaSnS_4	*I*222	Orthorhombic	1.77	0.4
$Ag_2BaSnSe_4$	*I*222	Orthorhombic	1.42	0.2
Na_2BaSnS_4	$I\bar{4}2d$	Tetragonal	3.27	0.5
Na_2BaGeS_4	*R*3*c*	Trigonal	3.7	0.3
$Na_2BaGeSe_4$	*R*3*c*	Trigonal	2.46	1.3
$Na_2BaSnSe_4$	*R*3*c*	Trigonal	2.25	0.9
Li_2BaGeS_4	$I\bar{4}2m$	Tetragonal	3.66	0.5
$Li_2BaGeSe_4$	$I\bar{4}2m$	Tetragonal	2.40	1.1
Li_2BaSnS_4	$I\bar{4}2m$	Tetragonal	3.07	0.7
$Li_2BaSnSe_4$	$I\bar{4}2m$	Tetragonal	2.18	1.3

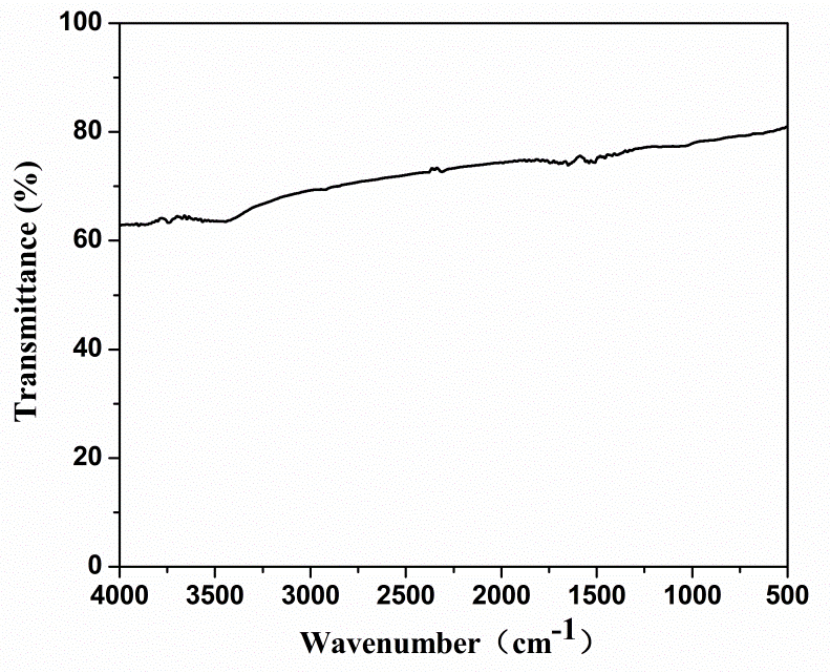

Fig. S1 (a) The IR spectrum of as-synthesized $Ag_2BaSiSe_4$.

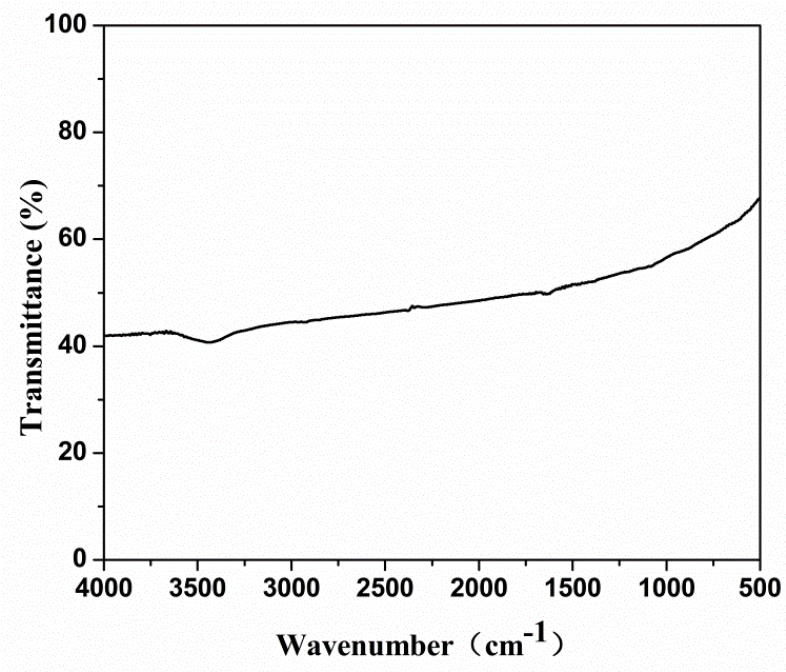

Fig. S1 (b) The IR spectrum of as-synthesized $Ag_2BaGeSe_4$.

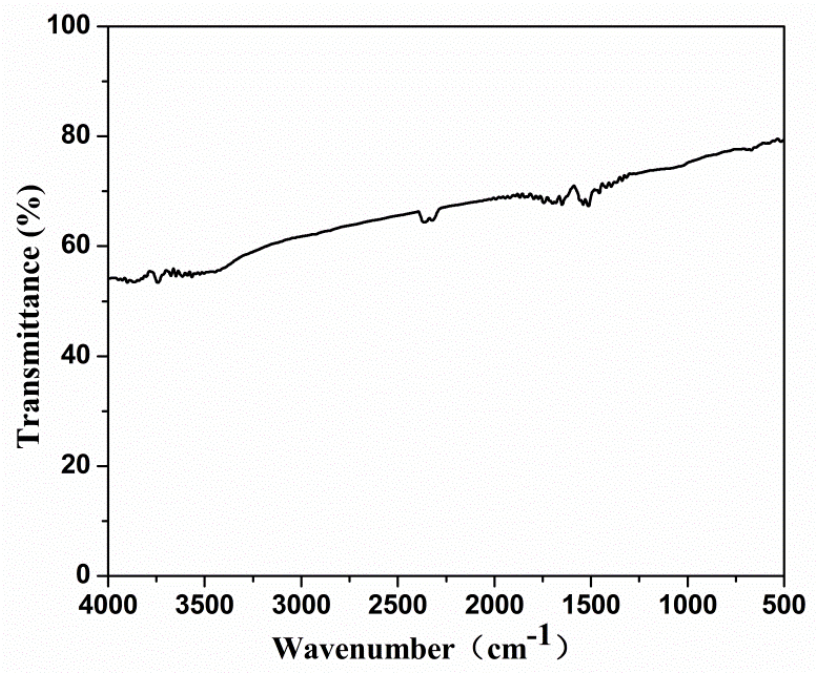

Fig. S1 (c) The IR spectrum of as-synthesized $Ag_2BaSnSe_4$.

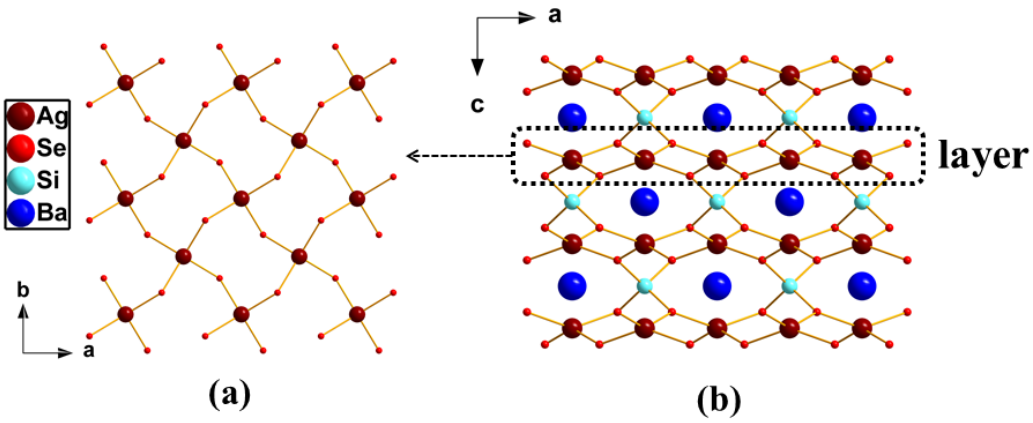

Fig. S2 (a) 2D $[AgSe_4]_\infty$ flat layers in $Ag_2BaSiSe_4$. **(b)** 3D framework of $Ag_2BaSiSe_4$.

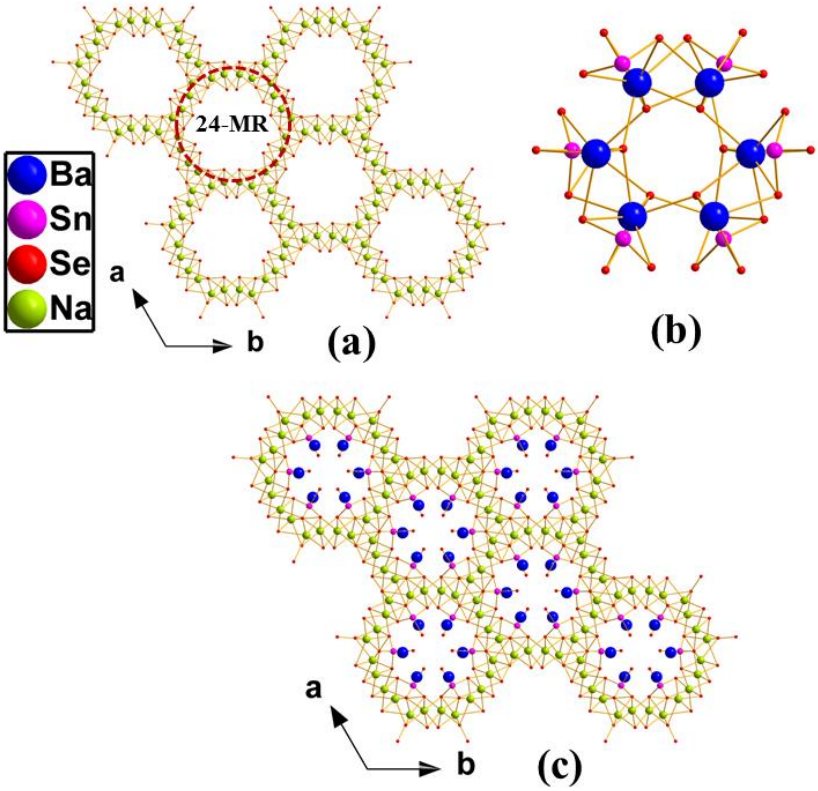

Fig. S3 (a) [$NaSe_6$] octahedra connect together to form a 24-MR tunnel in $Na_2BaSnSe_4$; **(b)** [$BaSe_7$] polyhedra connect with [$SnSe_4$] tetrahedra to form a tunnel structure; **(c)** The structure of $Na_2BaSnSe_4$.

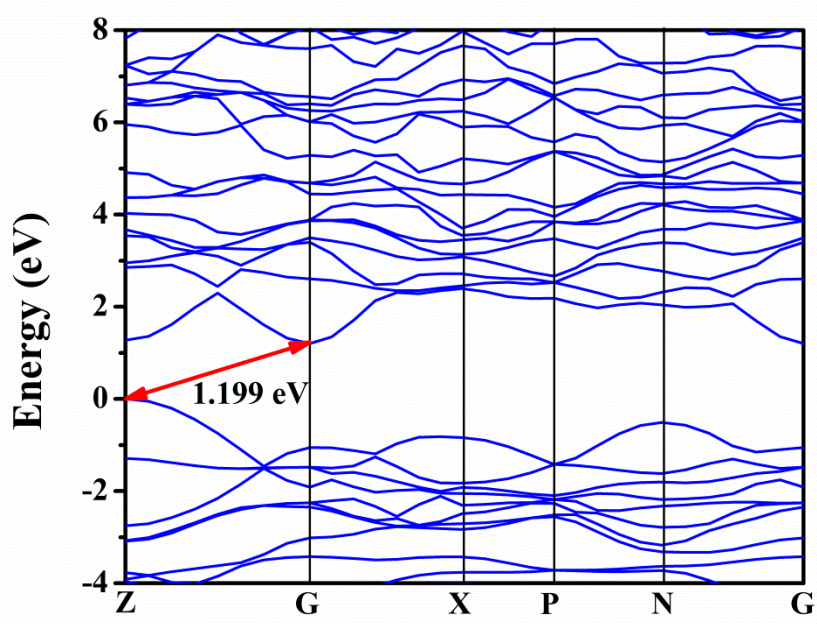

Fig. S4 (a) The electronic structure of $Ag_2BaSiSe_4$.

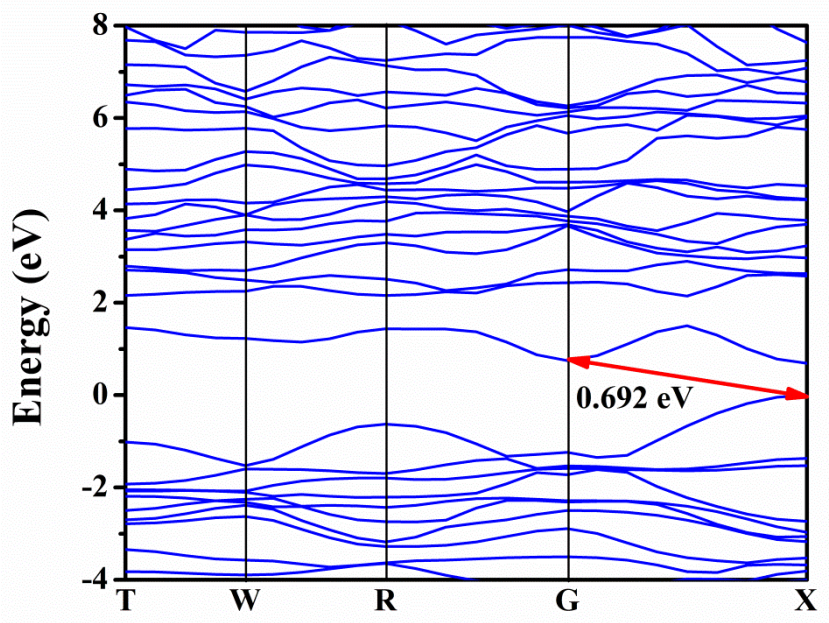

Fig. S4 (b) The electronic structure of $Ag_2BaGeSe_4$.

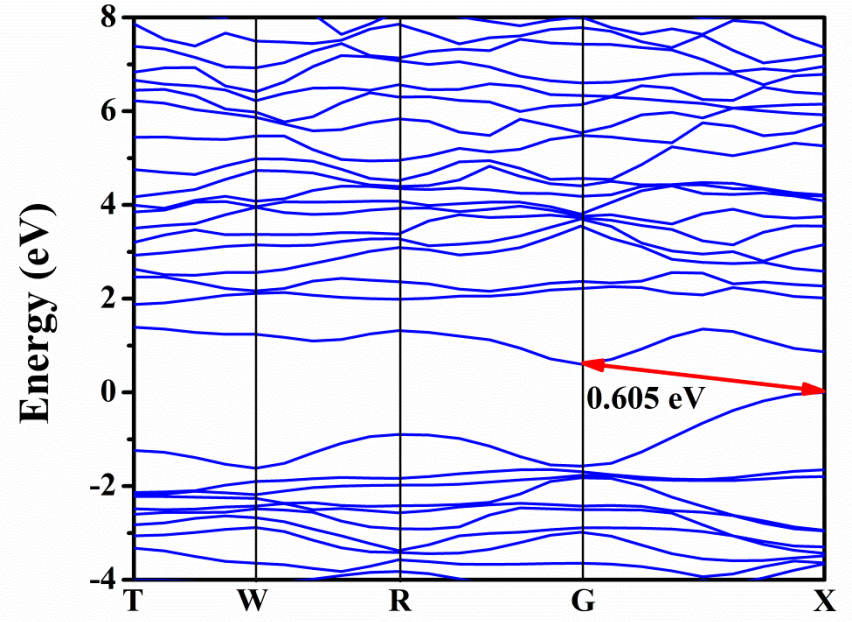

Fig. S4 (c) The electronic structure of $Ag_2BaSnSe_4$.

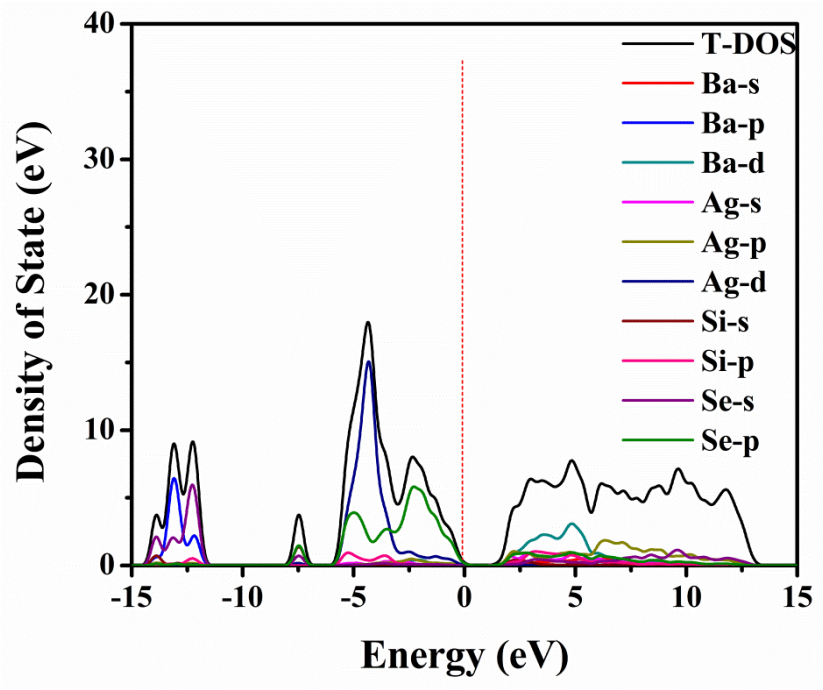

Fig. S5 (a) The PDOS of $Ag_2BaSiSe_4$.

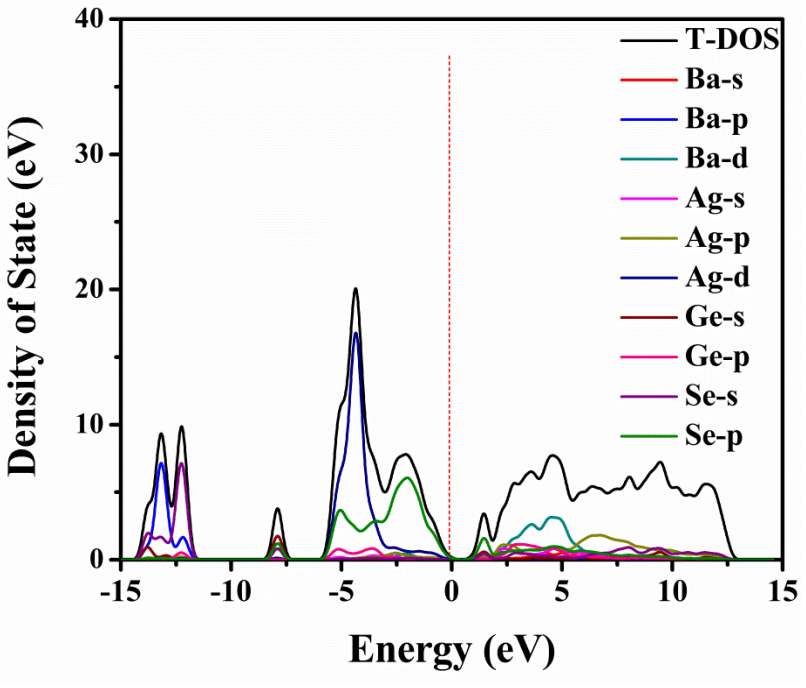

Fig. S5 (b) The PDOS of $Ag_2BaGeSe_4$.

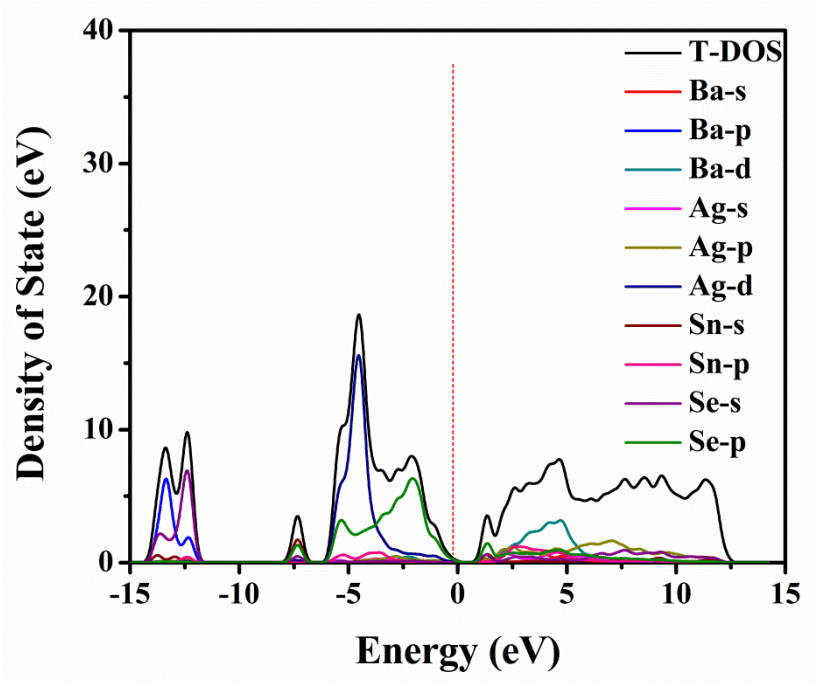

Fig. S5 (c) The PDOS of $Ag_2BaSnSe_4$.

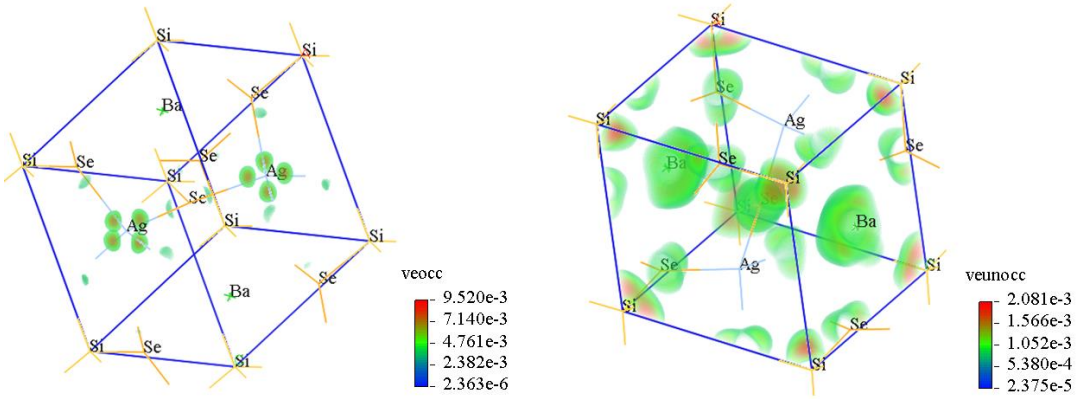

Fig. S6 (a) SHG density of $Ag_2BaSiSe_4$.

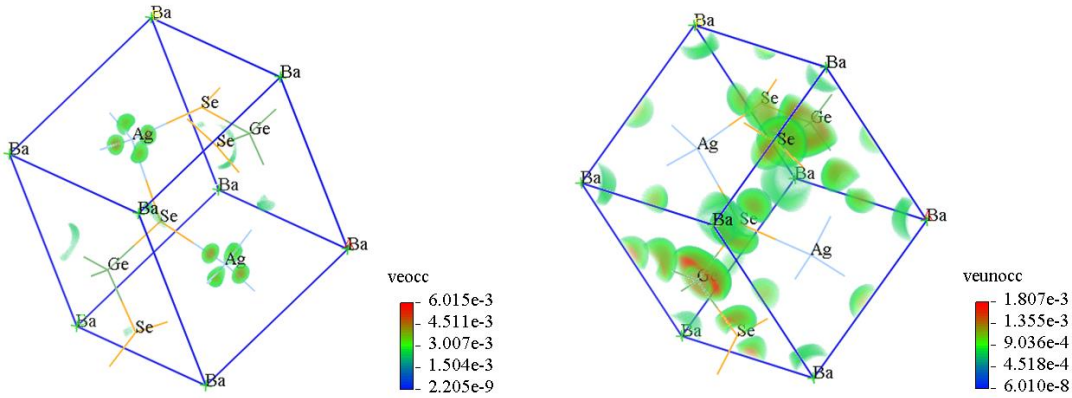

Fig. S6 (b) SHG density of $Ag_2BaGeSe_4$.

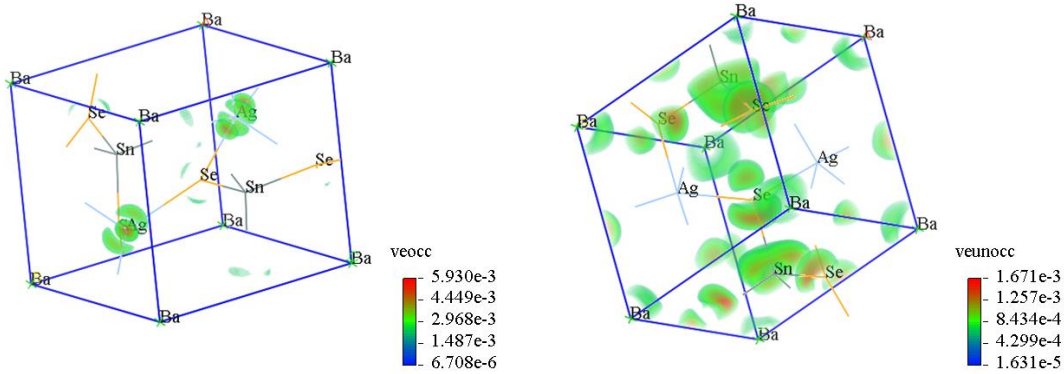

Fig. S6 (c) SHG density of $Ag_2BaSnSe_4$.