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Supporting Information

A New Infrared Nonlinear Optical Material $BaZnGeS_4$ with Wide Band Gap and Large Nonlinear Optical Response

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Table S1. Structure and optical properties of the $A^{II}B^{II}C^{IV}D_4^{VI}$ family compounds.

No.	Compound	Space group	Band gap (eV)	SHG(× AGS)	LIDT(×AGS)	Δ*n*		Ref.
1	**$BaZnGeS_4$**	***Fdd*2**	**3.36**	**0.8**	**5.4**	**0.135**	**PM**	**This work**
2	$SrZnGeS_4$	*Fdd*2	3.63	0.9	35	0.165	PM	[1]
3	$SrCdSiS_4$	*Ama*2	3.61	1.1	20.4	0.165	PM	[2]
4	$BaZnSnS_4$	*Fdd*2	3.25	0.6	9.8	0.17	PM	[3]
5	$SrZnSnS_4$	*Fdd*2	2.83	0.4a	N/A	0.2	PM	[4]
6	$BaHgSnS_4$	*Pnn*2	N/A	N/A	N/A	N/A	N/A	[5]
7	*β*-$BaHgSnS_4$	*Ama*2	2.77	2.8	N/A	~0.21	PM	[6]
8	$SrHgSnS_4$	*Ama*2	2.72	1.9	N/A	N/A	PM	[6]
9	$SrCdGeS_4$	*Ama*2	2.6	2	N/A	N/A	PM	[7]
10	$BaCdGeS_4$	*Fdd*2	2.58	0.3	13	0.149	PM	[8]
11	$BaMnSnS_4$	*Fdd*2	1.9	1.2	10.2	0.168	PM	[8]
12	$BaCdSnS_4$	*Fdd*2	2.3	0.7	N/A	N/A	NPM	[9]
13	$SrCdSnS_4$	*Fdd*2	2.05	1.3	10	0.22	PM	[10]
1	$BaZnSiSe_4$	*Ama*2	2.71	1/3	N/A	N/A	N/A	[11]
2	$BaZnGeSe_4$	*Ama*2	2.46	1	N/A	N/A	PM	[11]
3	$BaHgGeSe_4$	*Ama*2	2.49	4.7	N/A	N/A	PM	[12]
4	$SrHgGeSe_4$	*Ama*2	2.42	4.8	N/A	N/A	PM	[12]
5	$SrZnSnSe_4$	*Fdd*2	2.14	0.33	5	N/A	PM	[3]
6	$SrHgSnSe_4$	*Fdd*2	2.07	4.9	N/A	N/A	PM	[6]
7	$BaHgSnSe_4$	*Fdd*2	1.98	5.1	N/A	~0.29	PM	[6]

8	$SrCdGeSe_4$	*Ama*2	1.9	5	N/A	N/A	PM	[7]
9	$BaZnSnSe_4$	*Fdd*2	1.88	1	5.7	0.26	PM	[3]
10	$BaCdSnSe_4$	*Fdd*2	1.79	1.6	N/A	0.110 @1μm	NPM	[13]
11	$BaCdGeSe_4$	*Fdd*2	1.77	0.5	N/A	N/A	PM	[14]
12	$SrCdSnSe_4$	*Fdd*2	1.54	1.5	5	0.33	PM	[10]
13	$SrZnSiSe_4$	*Ama*2	1.95	2	10	0.1	PM	[15]
14	$SrMgSnSe_4$	*Fdd*2	2.0	/	/	/	/	[16]

Table S2. Crystal data and structure refinements of $Mg_{0.6}Cd_{1.4}GeS_4$, $CaCdGeS_4$, and $BaZnGeS_4$.

Empirical formula	$Mg_{0.6}Cd_{1.4}GeS_4$	$CaCdGeS_4$	$BaZnGeS_4$
Formula weight	372.78	353.31	403.08
Temperature (K)	298	298	298
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*	*Fdd*2
***a*(Å)**	13.0381(8)	13.4040(7)	21.0291(6)
***b*(Å)**	7.6057(5)	7.8948(4)	21.7992(6)
***c*(Å)**	6.1008(3)	6.2078(4)	12.3028(3)
V(Å)	604.98(6)	656.92(6)	5639.8(3)
Z	4	4	32
D_{calc} (g/cm^{-3})	4.093	3.572	3.798
Absorption coefficient (mm^{-1})	11.147	9.729	14.171
***F*(000)**	682	656	5817
Completeness to θ(%)	100	100	98.30
Max. and min. transmission	0.7456 and 0.5499	0.7456 and 0.5454	0.7456 and 0.4791
2θ range for data collection/°	6.250 to 55.002	6.078 to 55.006	4.266 to 54.958
Index ranges	$-16 \le h \le 16$, $-9 \le k \le 9$, $-7 \le l \le 7$	$-17 \le h \le 17$, $-10 \le k \le 10$, $-8 \le l \le 8$	$-27 \le h \le 27$, $-28 \le k \le 28$, $-14 \le l \le 15$
Reflections collected	12804	13541	14300
Independent reflections	746 [R(int) = 0.0685]	807 [R(int) = 0.0707]	3022 [R(int) = 0.0409]
Observed reflections [$I>2\sigma(I)$]	680	677	2291
Data / restraints / parameters	746 / 0 / 40	807 / 0 / 41	3022 / 1 / 132
Absorpt correction type	multi-scan	multi-scan	multi-scan
GooF on F^2	1.211	1.136	1.022
R_1, wR_2 ($I>2\sigma$ (I))[a]	0.0207, 0.0666	0.0239, 0.0769	0.0176, 0.0382
R_1, wR_2 (all data)[a]	0.0219, 0.0677	0.0244, 0.0776	0.0225, 0.0408
diff peak, hole (e/Å^3)	0.947, -0.901	1.496, -1.065	0.463, -1.195
Flack parameter	/	/	0.027(14)

[a] $R_1=\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S3. Fractional atomic coordinates, equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and bond valence sum (BVS) for $BaZnGeS_4$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atoms	Wyck.	x	y	z	U_{eq}	BVS[a]
Ba(1)	8a	0.25	0.75	0.68 (1)	14(1)	2.31
Ba(2)	8a	0.50	0.50	0.43 (1)	14(1)	2.32
Ba(3)	16b	0.50 (1)	0.75 (1)	0.43 (1)	15(1)	2.32
Zn(1)	16b	0.39(1)	0.62 (1)	0.69 (1)	17(1)	1.90
Zn(2)	16b	0.67 (1)	0.62 (1)	0.47 (1)	17(1)	1.89
Ge(1)	16b	0.57 (1)	0.62 (1)	0.64 (1)	11(1)	4.05
Ge(2)	16b	0.61 (1)	0.62 (1)	0.18 (1)	11(1)	4.02
S(1)	16b	0.37 (1)	0.70 (1)	0.82 (1)	15(1)	2.03
S(2)	16b	0.37(1)	0.55 (1)	0.82 (1)	14(1)	2.01
S(3)	16b	0.47 (1)	0.62 (1)	0.57 (1)	14(1)	2.14
S(4)	16b	0.53 (1)	0.62 (1)	0.30 (1)	15(1)	2.04
S(5)	16b	0.55 (1)	0.63 (1)	0.82 (1)	14(1)	2.07
S(6)	16b	0.62 (1)	0.70 (1)	0.57 (1)	14(1)	2.05
S(7)	16b	0.62 (1)	0.55 (1)	0.57 (1)	14(1)	2.02
S(8)	16b	0.70 (1)	0.62 (1)	0.29 (1)	13(1)	2.14

[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 S4. Fractional atomic coordinates, equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and bond valence sum (BVS) for $Mg_{0.6}Cd_{1.4}GeS_4$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atoms	Occupancy	Wyck.	x	y	z	U_{eq}	BVS[a]
Mg/Cd(1)	0.1/0.9	4c	0.27 (1)	-0.25	0.49 (1)	19(1)	2.08
Mg/Cd(2)	0.5/0.5	4b	0.50	0	0	24(1)	2.11
Ge(1)	1	4c	0.41 (1)	0.25	0.41 (1)	10(1)	4.02
S(1)	1	4c	0.43 (1)	-0.25	0.74 (2)	13(1)	2.11
S(2)	1	8d	0.33 (1)	0.022 (1)	0.25 (1)	13(1)	1.92
S(3)	1	4c	0.41 (1)	0.25	0.77 (2)	13(1)	2.04

[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 S5. Fractional atomic coordinates, equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and bond valence sum (BVS) for $CaCdGeS_4$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Atoms	Occupancy	Wyck.	x	y	z	U_{eq}	BVS[a]
Ca/Cd(1)	0.8/0.2	4c	0.27 (1)	0.75	0.51 (1)	16(1)	2.20
Ca/Cd(2)	0.2/0.8	4b	0.50	0.50	0	26(1)	2.20
Ge(1)	1	4c	0.59 (1)	0.75	0.41 (1)	17(1)	4.03
S(1)	1	4c	0.44 (1)	0.75	0.25 (2)	20(1)	2.30
S(2)	1	8d	0.66 (1)	0.97 (1)	0.25 (1)	21(1)	2.06
S(3)	1	4c	0.59 (1)	0.75	0.76 (2)	21(1)	2.11

[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 S6. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $BaZnGeS_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba(1)	11(1)	14(1)	18(1)	0	0	0(1)
Ba(2)	12(1)	14(1)	17(1)	0	0	0(1)
Ba(3)	12(1)	14(1)	18(1)	0(1)	-1(1)	0(1)
Zn(1)	14(1)	23(1)	13(1)	0(1)	2(1)	0(1)
Zn(2)	15(1)	22(1)	13(1)	0(1)	3(1)	0(1)
Ge(1)	10(1)	13(1)	10(1)	0(1)	0(1)	0(1)
Ge(2)	10(1)	13(1)	10(1)	0(1)	0(1)	0(1)
S(1)	16(1)	14(1)	14(1)	1(1)	-2(1)	1(1)
S(2)	15(1)	14(1)	13(1)	-2(1)	-2(1)	0(1)
S(3)	10(1)	21(1)	12(1)	0(1)	0(1)	-1(1)
S(4)	11(1)	20(1)	13(1)	0(1)	3(1)	-1(1)
S(5)	14(1)	19(1)	10(1)	0(1)	1(1)	0(1)
S(6)	12(1)	14(1)	16(1)	1(1)	0(1)	-1(1)
S(7)	12(1)	14(1)	16(1)	-1(1)	0(1)	1(1)
S(8)	11(1)	17(1)	10(1)	0(1)	0(1)	-1(1)

Table S7. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Mg_{0.6}Cd_{1.4}GeS_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mg/Cd(1)	17(1)	22(1)	18(1)	0	1(1)	0
Mg/Cd(2)	28(1)	22(1)	22(1)	-5(1)	2(1)	4(1)
Ge(1)	11(1)	12(1)	7(1)	0	0(1)	0
S(1)	10(1)	16(1)	13(1)	0	0(1)	0
S(2)	14(1)	12(1)	12(1)	1(1)	-1(1)	-3(1)
S(3)	14(1)	16(1)	7(1)	0	0(1)	0

Table S8. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $CaCdGeS_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca/Cd(1)	16(1)	18(1)	15(1)	0	-2(1)	0
Ca/Cd(2)	30(1)	23(1)	25(1)	-10(1)	-7(1)	-1(1)
Ge(1)	18(1)	19(1)	13(1)	0	-1(1)	0
S(1)	17(1)	24(1)	19(1)	0	0(1)	0
S(2)	24(1)	20(1)	18(1)	-1(1)	0(1)	-4(1)
S(3)	26(1)	24(1)	12(1)	0	-1(1)	0

Table S9. Selected bond lengths (Å) of $BaZnGeS_4$.

Atoms	Distance (Å)	Atoms	Distance (Å)
Ba(1)-S(1)#1	3.2125(15)	Ba(3)-S(5)#8	3.2515(15)
Ba(1)-S(1)	3.2126(15)	Ba(3)-S(6)	3.1880(15)
Ba(1)-S(2)#2	3.2188(14)	Ba(3)-S(7)#2	3.2257(14)
Ba(1)-S(2)#3	3.2188(14)	Ba(3)-S(8)#9	3.2285(14)
Ba(1)-S(5)#3	3.2475(15)	Zn(1)-S(1)	2.3901(17)
Ba(1)-S(5)#2	3.2475(15)	Zn(1)-S(2)	2.3995(17)
Ba(1)-S(8)#4	3.2374(15)	Zn(1)-S(3)	2.2913(16)
Ba(1)-S(8)#5	3.2374(15)	Zn(1)-S(5)#2	2.3896(14)
Ba(2)-S(3)#6	3.2240(15)	Zn(2)-S(4)#11	2.4015(13)
Ba(2)-S(3)	3.2240(15)	Zn(2)-S(6)	2.3904(16)
Ba(2)-S(4)	3.2561(15)	Zn(2)-S(7)	2.4034(16)
Ba(2)-S(4)#6	3.2561(15)	Zn(2)-S(8)	2.2885(17)
Ba(2)-S(6)#2	3.2244(14)	Ge(1)-S(3)	2.2253(12)
Ba(2)-S(6)#7	3.2244(14)	Ge(1)-S(5)	2.1867(16)
Ba(2)-S(7)#6	3.2051(15)	Ge(1)-S(6)	2.2189(15)
Ba(2)-S(7)	3.2051(15)	Ge(1)-S(7)	2.2188(15)
Ba(3)-S(1)#8	3.2184(15)	Ge(2)-S(1)#10	2.2218(16)
Ba(3)-S(2)#3	3.2287(15)	Ge(2)-S(2)#10	2.2214(16)
Ba(3)-S(3)	3.2345(16)	Ge(2)-S(4)	2.1954(15)
Ba(3)-S(4)	3.2466(15)	Ge(2)-S(8)	2.2240(13)

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

Table S10. Selected bond angles (°) of $BaZnGeS_4$.

Atoms	Angle (°)	Atoms	Angle (°)
S(1)#1-Ba(1)-S(1)	115.90(7)	S(7)-Ba(2)-S(6)#2	142.81(3)
S(1)-Ba(1)-S(2)#2	142.41(3)	S(7)#6-Ba(2)-S(7)	116.38(6)
S(1)-Ba(1)-S(2)#3	69.65(4)	S(1)#8-Ba(3)-S(2)#3	141.88(3)
S(1)#1-Ba(1)-S(2)#2	69.65(4)	S(1)#8-Ba(3)-S(3)	130.71(4)
S(1)#1-Ba(1)-S(2)#3	142.41(3)	S(1)#8-Ba(3)-S(4)	83.86(4)
S(1)#1-Ba(1)-S(5)#3	72.61(4)	S(1)#8-Ba(3)-S(5)#8	79.60(4)
S(1)-Ba(1)-S(5)#2	72.61(4)	S(1)#8-Ba(3)-S(7)#2	129.32(5)
S(1)#1-Ba(1)-S(5)#2	138.49(3)	S(1)#8-Ba(3)-S(8)#9	67.61(3)
S(1)-Ba(1)-S(5)#3	138.49(3)	S(2)#3-Ba(3)-S(3)	81.32(4)
S(1)-Ba(1)-S(8)#4	77.34(4)	S(2)#3-Ba(3)-S(4)	133.21(4)
S(1)-Ba(1)-S(8)#5	77.28(4)	S(2)#3-Ba(3)-S(5)#8	72.42(4)
S(1)#1-Ba(1)-S(8)#5	77.34(4)	S(3)-Ba(3)-S(4)	66.28(3)
S(1)#1-Ba(1)-S(8)#4	77.28(4)	S(3)-Ba(3)-S(5)#8	149.52(3)
S(2)#2-Ba(1)-S(2)#3	130.47(7)	S(4)-Ba(3)-S(5)#8	122.87(4)
S(2)#2-Ba(1)-S(5)#2	80.46(4)	S(6)-Ba(3)-S(1)#8	70.78(5)
S(2)#2-Ba(1)-S(5)#3	79.08(4)	S(6)-Ba(3)-S(2)#3	116.05(5)
S(2)#3-Ba(1)-S(5)#3	80.46(4)	S(6)-Ba(3)-S(3)	67.18(3)
S(2)#3-Ba(1)-S(5)#2	79.08(4)	S(6)-Ba(3)-S(4)	82.26(4)
S(2)#2-Ba(1)-S(8)#5	136.81(3)	S(6)-Ba(3)-S(5)#8	138.84(4)
S(2)#3-Ba(1)-S(8)#5	67.52(3)	S(6)-Ba(3)-S(7)#2	143.33(3)
S(2)#3-Ba(1)-S(8)#4	136.81(3)	S(6)-Ba(3)-S(8)#9	77.60(4)
S(2)#2-Ba(1)-S(8)#4	67.52(3)	S(7)#2-Ba(3)-S(2)#3	69.29(5)
S(5)#2-Ba(1)-S(5)#3	129.83(6)	S(7)#2-Ba(3)-S(3)	78.65(3)
S(8)#5-Ba(1)-S(5)#2	141.05(2)	S(7)#2-Ba(3)-S(4)	71.83(3)
S(8)#4-Ba(1)-S(5)#2	64.74(3)	S(7)#2-Ba(3)-S(5)#8	77.80(4)
S(8)#5-Ba(1)-S(5)#3	64.74(3)	S(7)#2-Ba(3)-S(8)#9	135.70(3)
S(8)#4-Ba(1)-S(5)#3	141.05(2)	S(8)#9-Ba(3)-S(2)#3	77.16(3)

S(8)#5-Ba(1)-S(8)#4	131.09(6)	S(8)#9-Ba(3)-S(3)	124.37(4)
S(3)#6-Ba(2)-S(3)	118.97(6)	S(8)#9-Ba(3)-S(4)	149.16(3)
S(3)-Ba(2)-S(4)#6	158.49(2)	S(8)#9-Ba(3)-S(5)#8	64.79(3)
S(3)#6-Ba(2)-S(4)#6	66.29(3)	S(1)-Zn(1)-S(2)	91.15(6)
S(3)-Ba(2)-S(4)	66.29(3)	S(3)-Zn(1)-S(1)	124.42(6)
S(3)#6-Ba(2)-S(4)	158.49(2)	S(3)-Zn(1)-S(2)	125.25(6)
S(3)#6-Ba(2)-S(6)#2	129.60(3)	S(3)-Zn(1)-S(5)#2	101.79(6)
S(3)#6-Ba(2)-S(6)#7	78.78(3)	S(5)#2-Zn(1)-S(1)	106.31(5)
S(3)-Ba(2)-S(6)#2	78.78(3)	S(5)#2-Zn(1)-S(2)	106.13(5)
S(3)-Ba(2)-S(6)#7	129.60(3)	S(4)#11-Zn(2)-S(7)	104.40(5)
S(4)-Ba(2)-S(4)#6	117.31(6)	S(6)-Zn(2)-S(4)#11	103.57(5)
S(6)#2-Ba(2)-S(4)#6	82.61(4)	S(6)-Zn(2)-S(7)	91.29(5)
S(6)#2-Ba(2)-S(4)	71.04(3)	S(8)-Zn(2)-S(4)#11	100.91(5)
S(6)#7-Ba(2)-S(4)#6	71.04(3)	S(8)-Zn(2)-S(6)	126.49(6)
S(6)#7-Ba(2)-S(4)	82.61(4)	S(8)-Zn(2)-S(7)	127.01(6)
S(6)#2-Ba(2)-S(6)#7	128.30(6)	S(5)-Ge(1)-S(3)	104.48(6)
S(7)-Ba(2)-S(3)#6	81.72(4)	S(5)-Ge(1)-S(6)	118.80(6)
S(7)-Ba(2)-S(3)	66.96(3)	S(5)-Ge(1)-S(7)	119.18(6)
S(7)#6-Ba(2)-S(3)	81.72(4)	S(6)-Ge(1)-S(3)	106.19(6)
S(7)#6-Ba(2)-S(3)#6	66.96(3)	S(7)-Ge(1)-S(3)	105.90(6)
S(7)#6-Ba(2)-S(4)	133.54(3)	S(7)-Ge(1)-S(6)	101.14(5)
S(7)#6-Ba(2)-S(4)#6	81.93(4)	S(1)#10-Ge(2)-S(8)	107.56(5)
S(7)-Ba(2)-S(4)	81.93(4)	S(2)#10-Ge(2)-S(1)#10	100.69(6)
S(7)-Ba(2)-S(4)#6	133.54(3)	S(2)#10-Ge(2)-S(8)	107.63(5)
S(7)#6-Ba(2)-S(6)#2	70.31(4)	S(4)-Ge(2)-S(1)#10	117.47(6)
S(7)-Ba(2)-S(6)#7	70.31(4)	S(4)-Ge(2)-S(2)#10	117.62(6)
S(7)#6-Ba(2)-S(6)#7	142.81(3)	S(4)-Ge(2)-S(8)	105.29(6)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+3/2,z; #2 x-1/4,-y+5/4,z-1/4; #3 -x+3/4,y+1/4,z-1/4; #4 x-1/2,y,z+1/2;
#5 -x+1,-y+3/2,z+1/2; #6 -x+1,-y+1,z; #7 -x+5/4,y-1/4,z-1/4; #8 -x+1,-y+3/2,z-1/2;

#9 -x+5/4,y+1/4,z+1/4; #10 x+1/4,-y+5/4,z-3/4; #11 x+1/4,-y+5/4,z+1/4

Table S11. Selected bond lengths (Å) of $Mg_{0.6}Cd_{1.4}GeS_4$.

Atoms	Distance (Å)	Atoms	Distance (Å)
Mg/Cd(1)-S(1)	2.6078(12)	Mg/Cd(2)-S(2)	2.6465(8)
Mg/Cd(1)-S(2)	2.6528(8)	Mg/Cd(2)-S(2)#7	2.6465(8)
Mg/Cd(1)-S(2)#1	2.6528(8)	Mg/Cd(2)-S(3)#6	2.6581(7)
Mg/Cd(1)-S(2)#2	2.7450(9)	Mg/Cd(2)-S(3)#8	2.6581(7)
Mg/Cd(1)-S(2)#3	2.7450(9)	Ge(1)-S(1)#6	2.2334(12)
Mg/Cd(1)-S(3)#4	2.7290(12)	Ge(1)-S(2)	2.2265(9)
Mg/Cd(2)-S(1)#6	2.6002(7)	Ge(1)-S(2)#5	2.2265(8)
Mg/Cd(2)-S(1)#8	2.6002(7)	Ge(1)-S(3)	2.1793(11)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+3/2,z; #2 x-1/4,-y+5/4,z-1/4; #3 -x+3/4,y+1/4,z-1/4; #4 x-1/2,y,z+1/2; #5 -x+1,-y+3/2,z+1/2; #6 -x+1,-y+1,z; #7 -x+5/4,y-1/4,z-1/4; #8 -x+1,-y+3/2,z-1/2

Table S12. Selected bond angles (°) of $Mg_{0.6}Cd_{1.4}GeS_4$.

Atoms	Angle (°)	Atoms	Angle (°)
S(1)-Mg/Cd(1)-S(2)	95.49(2)	S(1)#6-Mg/Cd(2)-S(3)#6	93.24(2)
S(1)-Mg/CdCd(1)-S(2)#1	95.50(2)	S(1)#6-Mg/Cd(2)-S(3)#8	86.76(2)
S(1)-Mg/Cd(1)-S(2)#2	93.88(3)	S(1)#8-Mg/Cd(2)-S(2)	97.11(3)
S(1)-Mg/Cd(1)-S(2)#3	93.88(3)	S(1)#8-Mg/Cd(2)-S(2)#7	82.89(3)
S(1)-Mg/Cd(1)-S(3)#4	172.68(4)	S(1)#8-Mg/Cd(2)-S(3)#6	86.76(2)
S(2)-Mg/Cd(1)-S(2)#2	88.746(14)	S(1)#8-Mg/Cd(2)-S(3)#8	93.24(2)
S(2)-Mg/Cd(1)-S(2)#3	164.39(3)	S(2)-Mg/Cd(2)-S(2)#7	180.0
S(2)-Mg/Cd(1)-S(3)#4	89.06(2)	S(2)-Mg/Cd(2)-S(3)#6	96.40(3)
S(2)#1-Mg/Cd(1)-S(2)	102.72(4)	S(2)-Mg/Cd(2)-S(3)#8	83.60(3)
S(2)#1-Mg/Cd(1)-S(2)#2	164.39(3)	S(2)#7-Mg/Cd(2)-S(3)#6	83.60(3)
S(2)#1-Mg/Cd(1)-S(2)#3	88.745(14)	S(2)#7-Mg/Cd(2)-S(3)#8	96.40(3)
S(2)#1-Mg/Cd(1)-S(3)#4	89.06(2)	S(3)#6-Mg/Cd(2)-S(3)#8	180.00(4)
S(2)#2-Mg/Cd(1)-S(2)#3	78.18(4)	S(2)-Ge(1)-S(1)#6	102.29(3)
S(3)#4-Mg/Cd(1)-S(2)#2	80.47(3)	S(2)-Ge(1)-S(2)#5	102.03(4)
S(3)#4-Mg/Cd(1)-S(2)#3	80.47(3)	S(2)#5-Ge(1)-S(1)#6	102.29(3)
S(1)#6-Mg/Cd(2)-S(1)#8	180.00(4)	S(3)-Ge(1)-S(1)#6	116.20(5)
S(1)#6-Mg/Cd(2)-S(2)	82.89(3)	S(3)-Ge(1)-S(2)	115.93(3)
S(1)#6-Mg/Cd(2)-S(2)#7	97.11(3)	S(3)-Ge(1)-S(2)#5	115.93(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+3/2,z; #2 x-1/4,-y+5/4,z-1/4; #3 -x+3/4,y+1/4,z-1/4; #4 x-1/2,y,z+1/2; #5 -x+1,-y+3/2,z+1/2; #6 -x+1,-y+1,z; #7 -x+5/4,y-1/4,z-1/4; #8 -x+1,-y+3/2,z-1/2

Table S13. Selected bond lengths (Å) of $CaCdGeS_4$.

Atoms	Distance (Å)	Atoms	Distance (Å)
Ca/Cd(1)-S(1)	2.7396(12)	Ca/Cd(2)-S(2)#6	2.7035(7)
Ca/Cd(1)-S(2)#1	2.7686(8)	Ca/Cd(2)-S(2)#9	2.7035(7)
Ca/Cd(1)-S(2)#2	2.8187(9)	Ca/Cd(2)-S(3)#10	2.7674(8)
Ca/Cd(1)-S(2)#3	2.7686(8)	Ca/Cd(2)-S(3)#11	2.7674(8)
Ca/Cd(1)-S(2)#4	2.8187(9)	Ge(1)-S(1)	2.2344(11)
Ca/Cd(1)-S(3)#5	2.8403(12)	Ge(1)-S(2)	2.2252(8)
Ca/Cd(2)-S(1)	2.6516(7)	Ge(1)-S(2)#6	2.2252(8)
Ca/Cd(2)-S(1)#8	2.6516(7)	Ge(1)-S(3)	2.1772(12)

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

Table S14. Selected bond angles (°) of $CaCdGeS_4$.

Atoms	Angle (°)	Atoms	Angle (°)
S(1)-Ca/Cd(1)-S(2)#1	93.99(2)	S(1)#12-Ca/Cd(2)-S(2)#6	98.79(3)
S(1)-Ca/Cd(1)-S(2)#2	94.31(3)	S(1)#12-Ca/Cd(2)-S(2)#9	81.21(3)
S(1)-Ca/Cd(1)-S(2)#3	93.99(2)	S(1)-Ca/Cd(2)-S(3)#10	85.90(2)
S(1)-Ca/Cd(1)-S(2)#4	94.31(3)	S(1)-Ca/Cd(2)-S(3)#11	94.10(2)
S(1)-Ca/Cd(1)-S(3)#5	173.68(4)	S(1)#12-Ca/Cd(2)-S(3)#10	94.10(2)
S(2)#1-Ca/Cd(1)-S(2)#2	88.433(14)	S(1)#12-Ca/Cd(2)-S(3)#11	85.90(2)
S(2)#1-Ca/Cd(1)-S(2)#4	163.22(3)	S(2)#6-Ca/Cd(2)-S(2)#9	180.0
S(2)#2-Ca/Cd(1)-S(2)#4	76.42(3)	S(2)#6-Ca/Cd(2)-S(3)#10	84.13(3)
S(2)#3-Ca/Cd(1)-S(2)#1	105.50(4)	S(2)#6-Ca/Cd(2)-S(3)#11	95.87(3)
S(2)#3-Ca/Cd(1)-S(2)#2	163.22(3)	S(2)#9-Ca/Cd(2)-S(3)#10	95.87(3)
S(2)#3-Ca/Cd(1)-S(2)#4	88.433(14)	S(2)#9-Ca/Cd(2)-S(3)#11	84.13(3)
S(2)#1-Ca/Cd(1)-S(3)#5	89.83(2)	S(3)#11-Ca/Cd(2)-S(3)#10	180.0
S(2)#2-Ca/Cd(1)-S(3)#5	80.74(3)	S(2)-Ge(1)-S(1)	102.81(3)
S(2)#3-Ca/Cd(1)-S(3)#5	89.83(2)	S(2)#6-Ge(1)-S(1)	102.81(3)
S(2)#4-Ca/Cd(1)-S(3)#5	80.74(3)	S(2)#6-Ge(1)-S(2)	103.18(4)
S(1)-Ca/Cd(2)-S(1)#12	180.0	S(3)-Ge(1)-S(1)	115.59(4)
S(1)-Ca/Cd(2)-S(2)#6	81.21(3)	S(3)-Ge(1)-S(2)	115.32(3)
S(1)-Ca/Cd(2)-S(2)#9	98.79(3)	S(3)-Ge(1)-S(2)#6	115.32(3)

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

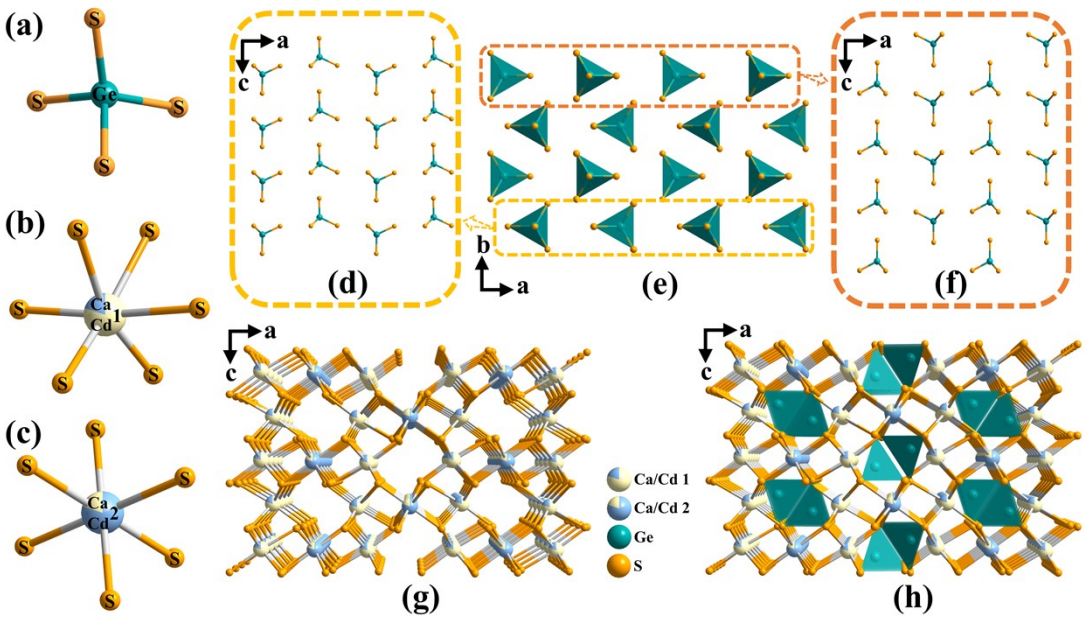

Figure S1. Crystal structure of $CaCdGeS_4$. (a-c) The coordination environments of Ge and M (Ca/Cd) atoms; (d-f) The formed $[GeS_4]_\infty$ pseudo-layers viewed along *b* and *c* directions, respectively; (g) The formed $[MS_6]_\infty$ framework; (h) The 3D crystal structure of $CaCdGeS_4$ along *c* direction.

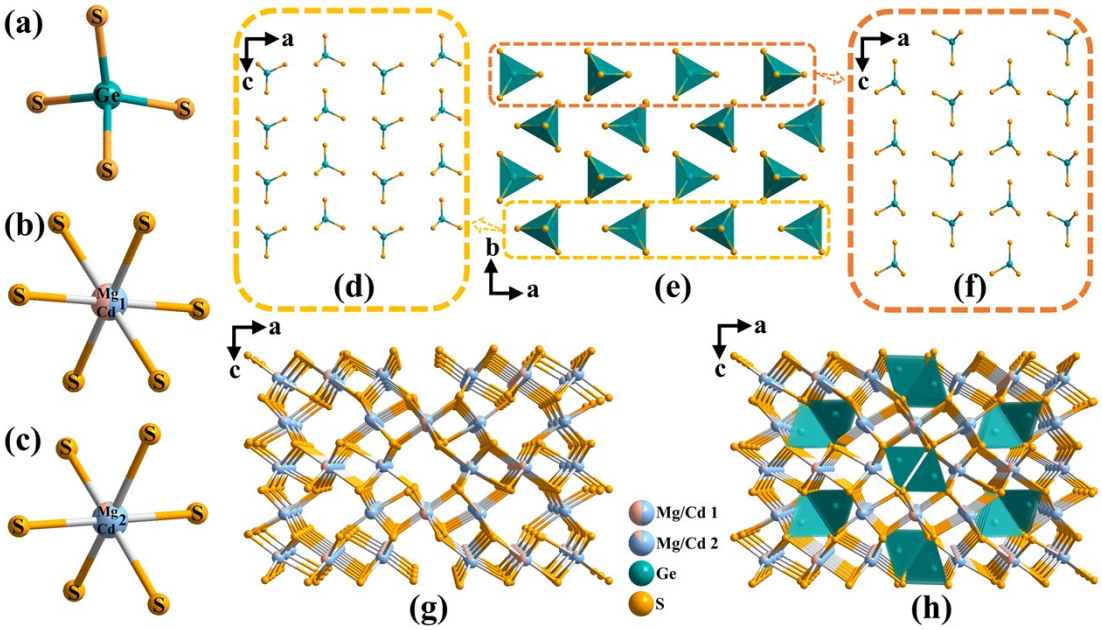

Figure S2. Crystal structure of $Mg_{0.6}Cd_{1.4}GeS_4$. (a-c) The coordination environments of Ge and N (Mg/Cd) atoms; (d-f) The formed $[GeS_4]_\infty$ pseudo-layers viewed along *b* and *c* directions, respectively; (g) The formed $[NS_6]_\infty$ framework; (h) The 3D crystal structure of $Mg_{0.6}Cd_{1.4}GeS_4$ along *c* direction.

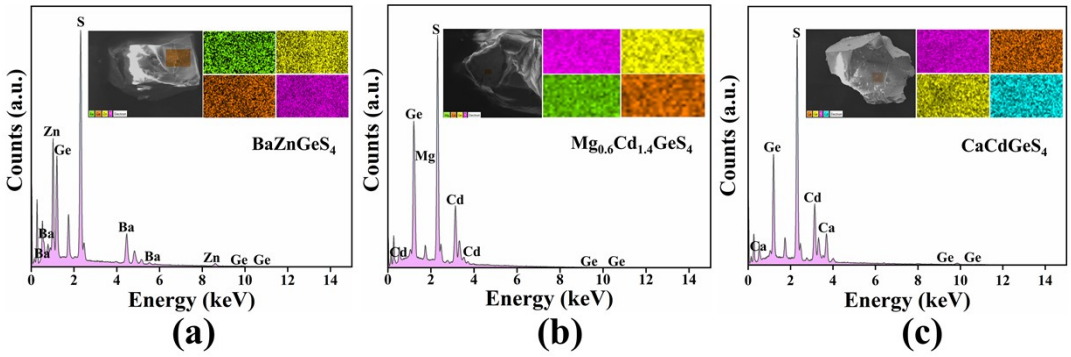

Figure S3. X-ray energy dispersive spectra of (a) $BaZnGeS_4$, (b) $Mg_{0.6}Cd_{1.4}GeS_4$, and (c) $CaCdGeS_4$.

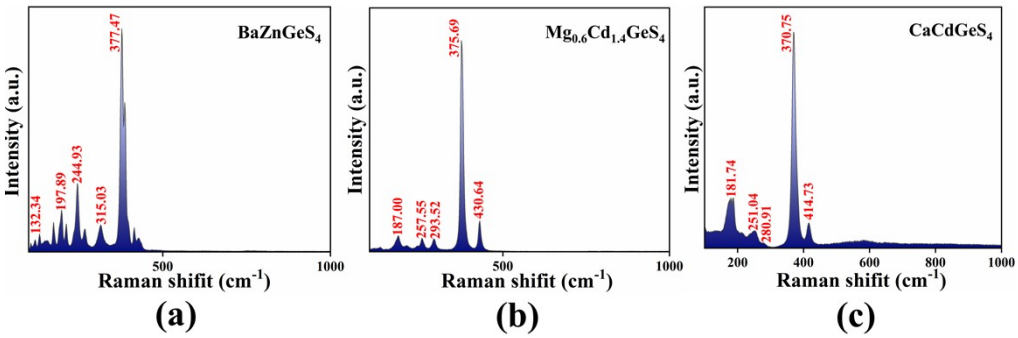

Figure S4. Raman spectra of (a) $BaZnGeS_4$, (b) $Mg_{0.6}Cd_{1.4}GeS_4$, and (c) $CaCdGeS_4$.

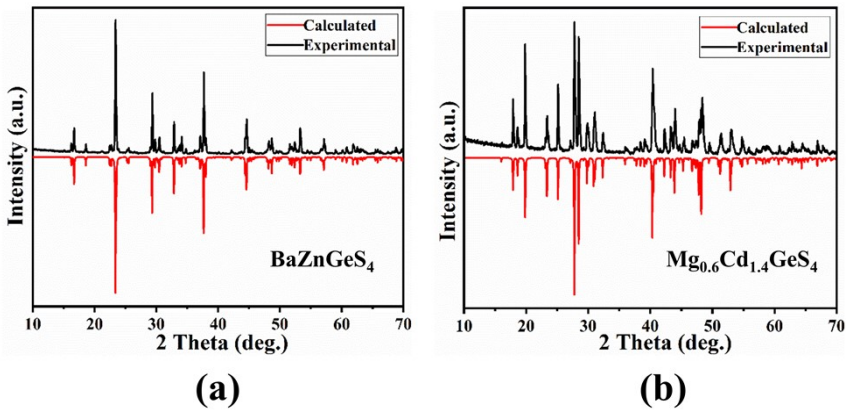

Figure S5. Experimental and calculated XRD patterns for (a) $BaZnGeS_4$ and (b) $Mg_{0.6}Cd_{1.4}GeS_4$.

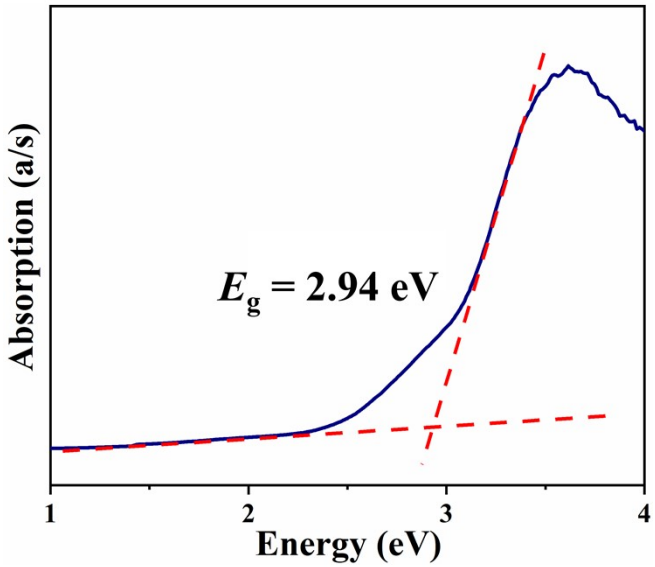

Figure S6. The experimental band gap of $Mg_{0.6}Cd_{1.4}GeS_4$.

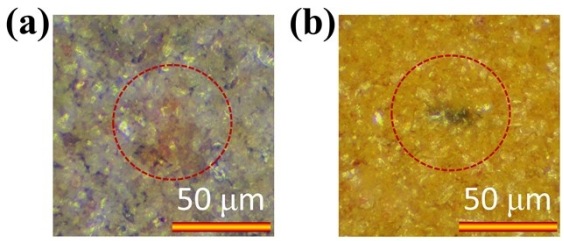

Figure S7. The optical images showing the laser-induced damages in $BaZnGeS_4$ (a) and $AgGaS_2$ (b) under a pulsed YAG laser (1.06 μm, 10 ns, 1 Hz).

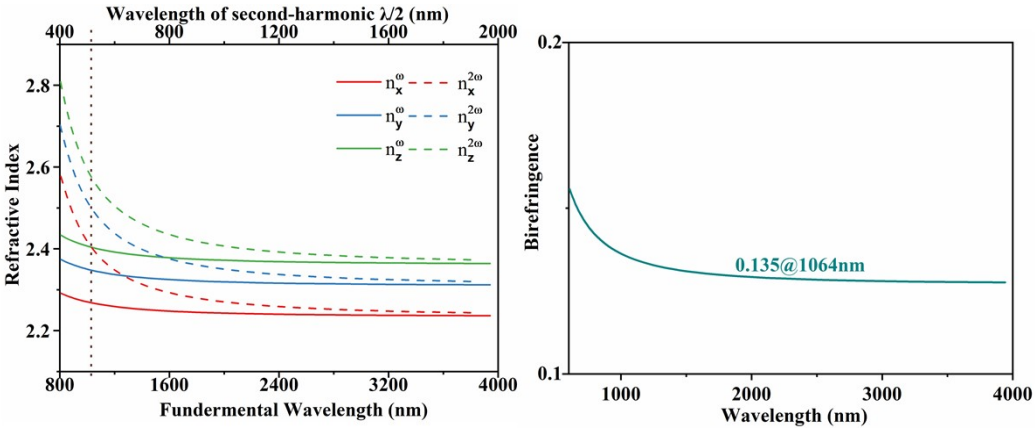

Figure S8. Calculated refractive index dispersion curves (a) and birefringence curve (b) of $BaZnGeS_4$.

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