Electronic Supplementary Information

Ba_2GeS_4 and Mg_2SnS_4: synthesis, structures, optical properties and electronic structures

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Figure S1. (a) EDX spectrum of Ba_2GeS_4.

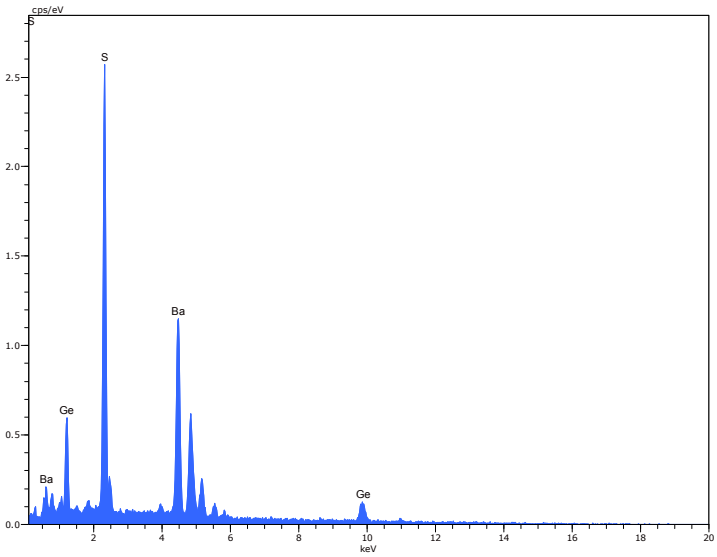

Table S1 (a) Average EDX data for Ba_2GeS_4.

Element	Weight %	Atomic %	Formula
S	25.72	55.76	3.96
Ge	14.70	14.08	1
Ba	59.57	30.16	2.14

Formula: $Ba_{2.14}GeS_{3.96}$

Figure S1. (b) EDX spectrum of Mg_2SnS_4.

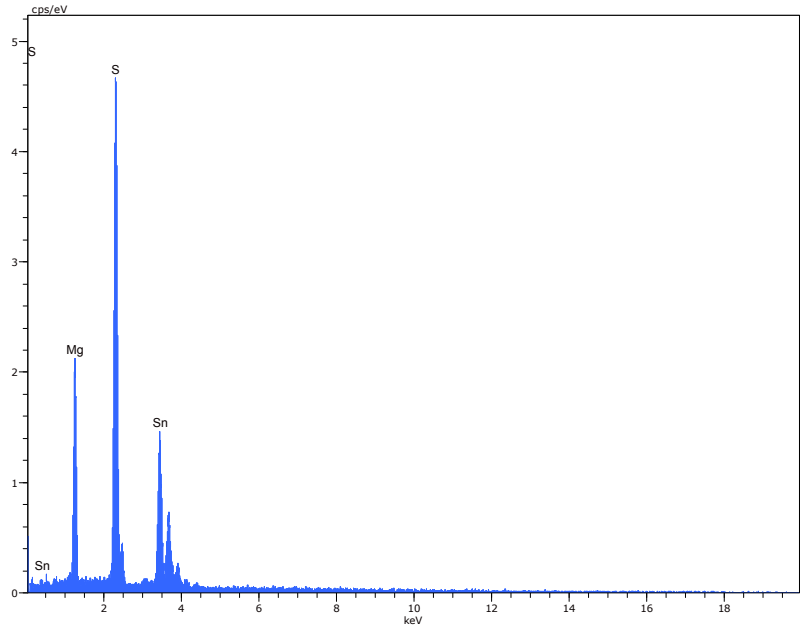

Table S1 (b) Average EDX data for Mg_2SnS_4.

Element	Weight %	Atomic %	Formula
S	39.94	55.22	3.81
Sn	44.64	16.67	1.15
Mg	15.41	28.11	1.9

Formula: $Mg_{1.94}Sn_{1.15}S_{3.81}$

Table S2. (a) Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for Ba_2GeS_4 U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Ba1	4811(1)	2500	6715(1)	20(1)
Ba2	1291(1)	2500	4113(1)	32(1)
Ge1	7285(1)	2500	4247(1)	14(1)
S1	4862(2)	2500	4051(2)	28(1)
S2	1756(1)	106(2)	6482(1)	33(1)
S3	8119(2)	2500	5937(1)	32(1)

Table S2. (b) Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for Mg_2SnS_4 U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Sn1	901(1)	2500	4245(1)	10(1)
Mg1	2698(1)	2500	9988(2)	13(1)
Mg2	0	0	0	14(1)
S1	1682(1)	42(1)	2428(1)	12(1)
S2	-750(1)	2500	2492(2)	11(1)
S3	923(1)	2500	8020(2)	10(1)

Table S3. (a) Selected bond distances (Å) and angles (deg) for Ba_2GeS_4.

Ba1-S3	3.120(4)	S3-Ba1-S2	141.87(6)
Ba1-S2	3.213(3)	S3-Ba1-S2#1	141.87(6)
Ba1-S2#1	3.213(3)	S2-Ba1-S2#1	61.63(10)
Ba1-S3#2	3.247(4)	S3-Ba1-S3#2	135.65(4)
Ba1-S1	3.255(5)	S2-Ba1-S3#2	71.25(6)
Ba1-S2#3	3.258(3)	S2#1-Ba1-S3#2	71.25(6)
Ba1-S2#4	3.258(3)	S3-Ba1-S1	71.46(5)
Ba1-S1#5	3.575(4)	S2-Ba1-S1	85.60(4)
Ba1-S1#6	3.575(4)	S2#1-Ba1-S1	85.60(4)
Ba2-S1	3.209(4)	S3#2-Ba1-S1	152.89(6)
Ba2-S2#9	3.350(3)	S3-Ba1-S2#3	72.27(8)
Ba2-S2#10	3.350(3)	S2-Ba1-S2#3	140.96(4)
Ba2-S2#1	3.356(4)	S2#1-Ba1-S2#3	105.02(8)
Ba2-S2	3.356(4)	S3#2-Ba1-S2#3	69.71(9)
Ba2-S3#6	3.479(4)	S1-Ba1-S2#3	131.97(6)
Ba2-S3#5	3.479(4)	S3-Ba1-S2#4	72.27(8)
Ba2-S3#11	3.617(4)	S2-Ba1-S2#4	105.02(8)
Ge1-S2#5	2.178(3)	S2#1-Ba1-S2#4	140.96(4)
Ge1-S2#14	2.178(2)	S3#2-Ba1-S2#4	69.71(9)
Ge1-S1	2.190(3)	S1-Ba1-S2#4	131.97(6)
Ge1-S3	2.198(3)	S2#3-Ba1-S2#4	60.68(9)
S1-Ba1#5	3.575(4)	S3-Ba1-S1#5	80.90(3)
S1-Ba1#6	3.575(4)	S2-Ba1-S1#5	63.54(6)
S2-Ge1#5	2.178(2)	S2#1-Ba1-S1#5	122.66(5)
S2-Ba1#2	3.258(3)	S3#2-Ba1-S1#5	105.67(4)
S2-Ba2#9	3.350(3)	S1-Ba1-S1#5	74.75(4)
S3-Ba1#4	3.247(4)	S2#3-Ba1-S1#5	128.23(5)
S3-Ba2#6	3.479(4)	S2#4-Ba1-S1#5	69.35(7)
S3-Ba2#5	3.479(4)	S3-Ba1-S1#6	80.90(3)
S3-Ba2#15	3.617(4)	S2-Ba1-S1#6	122.66(5)
S1-Ba2-S2#9	144.23(5)	S2#1-Ba1-S1#6	63.54(6)
S1-Ba2-S2#10	144.23(5)	S3#2-Ba1-S1#6	105.67(4)
S2#9-Ba2-S2#10	64.65(10)	S1-Ba1-S1#6	74.75(4)
S1-Ba2-S2#1	84.02(4)	S2#3-Ba1-S1#6	69.35(7)
S2#9-Ba2-S2#1	123.44(4)	S2#4-Ba1-S1#6	128.23(5)
S2#10-Ba2-S2#1	91.52(6)	S1#5-Ba1-S1#6	148.12(8)
S1-Ba2-S2	84.02(4)	S1-Ba2-S3#11	143.31(6)
S2#9-Ba2-S2	91.52(6)	S2#9-Ba2-S3#11	59.37(7)
S2#10-Ba2-S2	123.44(4)	S2#10-Ba2-S3#11	59.37(7)
S2#1-Ba2-S2	58.74(10)	S2#1-Ba2-S3#11	64.32(7)
S1-Ba2-S3#6	81.20(3)	S2-Ba2-S3#11	64.32(7)
S2#9-Ba2-S3#6	130.48(5)	S3#6-Ba2-S3#11	97.53(3)
S2#10-Ba2-S3#6	65.94(7)	S3#5-Ba2-S3#11	97.53(3)

S2#1-Ba2-S3#6	60.76(6)	S3#6-Ba2-S3#5	162.33(7)
S2-Ba2-S3#6	118.74(6)	S2#5-Ge1-S2#14	110.67(11)
S1-Ba2-S3#5	81.20(3)	S2#5-Ge1-S1	110.42(6)
S2#9-Ba2-S3#5	65.94(7)	S2#14-Ge1-S1	110.42(6)
S2#10-Ba2-S3#5	130.48(5)	S2#5-Ge1-S3	104.43(7)
S2#1-Ba2-S3#5	118.74(6)	S2#14-Ge1-S3	104.43(7)
S2-Ba2-S3#5	60.76(6)	S1-Ge1-S3	116.18(8)

Note. Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z #2 x-1/2,y,-z+3/2 #3 x+1/2,-y+1/2,-z+3/2
#4 x+1/2,y,-z+3/2 #5 -x+1,-y,-z+1
#6 -x+1,-y+1,-z+1 #7 -x+1/2,-y+1,z+1/2
#8 -x+1/2,-y,z+1/2 #9 -x,-y,-z+1
#10 -x,y+1/2,-z+1 #11 x-1,y,z #12 -x+1/2,-y,z-1/2
#13 -x+1/2,-y+1,z-1/2 #14 -x+1,y+1/2,-z+1
#15 x+1,y,z

Table S3. (b) Selected bond distances (Å) and angles (deg) for Mg_2SnS_4.

Sn1-S3	2.3506(19)	S2#8-Mg1-S3	170.08(7)
Sn1-S1	2.3905(13)	S2#8-Mg1-S1#9	97.61(5)
Sn1-S1#1	2.3905(13)	S3-Mg1-S1#9	89.14(5)
Sn1-S2	2.4023(16)	S2#8-Mg1-S1#10	97.61(5)
Sn1-Mg2#2	3.4459(16)	S3-Mg1-S1#10	89.14(5)
S1-Mg1#3	2.6135(17)	S1#9-Mg1-S1#10	93.87(7)
S1-Mg2	2.6542(15)	S2#8-Mg1-S1#11	92.19(6)
S1-Mg1#4	2.7299(17)	S3-Mg1-S1#11	80.53(5)
S2-Mg1#5	2.552(2)	S1#9-Mg1-S1#11	169.05(6)
S2-Mg2	2.6228(13)	S1#10-Mg1-S1#11	89.64(5)
S2-Mg2#2	2.6228(13)	S2#8-Mg1-S1#7	92.19(6)
S3-Mg2#6	2.5450(13)	S3-Mg1-S1#7	80.53(5)
S3-Mg2#7	2.5450(13)	S1#9-Mg1-S1#7	89.64(5)
S3-Mg1	2.608(2)	S1#10-Mg1-S1#7	169.05(6)
Mg1-S2#8	2.552(2)	S1#11-Mg1-S1#7	85.10(7)
Mg1-S1#9	2.6135(17)	S3#4-Mg2-S3#12	180.00(5)
Mg1-S1#10	2.6135(17)	S3#4-Mg2-S2	86.14(5)
Mg1-S1#11	2.7299(17)	S3#12-Mg2-S2	93.86(5)
Mg1-S1#7	2.7299(17)	S3#4-Mg2-S2#13	93.86(5)
Mg2-S3#4	2.5450(13)	S3#12-Mg2-S2#13	86.14(5)
Mg2-S3#12	2.5450(13)	S2-Mg2-S2#13	180.003
Mg2-S2#13	2.6228(13)	S3#4-Mg2-S1	83.16(4)
Mg2-S1#13	2.6542(15)	S3#12-Mg2-S1	96.84(4)
S3-Sn1-S1	117.90(3)	S2-Mg2-S1	87.66(4)
S3-Sn1-S1#1	117.90(3)	S2#13-Mg2-S1	92.34(4)
S1-Sn1-S1#1	101.11(6)	S3#4-Mg2-S1#13	96.84(4)
S3-Sn1-S2	117.71(4)	S3#12-Mg2-S1#13	83.16(4)
S1-Sn1-S2	99.37(4)	S2-Mg2-S1#13	92.34(4)
S1#1-Sn1-S2	99.37(4)	S2#13-Mg2-S1#13	87.66(4)
S1-Mg2-S1#13	180.00(3)		

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

Figure S2. IR spectra of Ba_2GeS_4 and Mg_2SnS_4.