Syntheses and Characterizations of New Mid-Infrared Transparency Compounds: Centric Ba_2BiGaS_5 and Acentric Ba_2BiInS_5

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Supporting Information

Table S1. Atomic Coordinates and Equivalent Isotropic Displacement Parameters $U_{eq}{}^{a}$ (Å^2 × 10^3) for Ba_2BiMS_5 (M = Ga, In)

Atom	*x*	*y*	*z*	U_{eq}
Ba_2BiGaS_5				
Ba(1)	0.3228(1)	0.0084(1)	0.3839(1)	11(1)
Bi(1)	0.0184(1)	0.2500	0.5375(1)	11(1)
Ga(1)	0.0951(1)	0.2500	0.1724(1)	9 (1)
S(1)	0.0554(1)	0.0493(2)	0.3246(1)	12(1)

S(2)	0.2150(2)	0.2500	0.6275(2)	12(1)
S(3)	0.2760(2)	0.2500	0.1196(2)	11(1)
S(4)	0.4934(2)	0.2500	0.5339(2)	12(1)
Ba_2BiInS_5				
Ba(1)	0	0.1117(1)	0.6861(1)	12(1)
Ba(2)	0	0.1294(1)	0.3093(1)	13(1)
Bi(1)	0	0.2178(1)	0.2200(1)	17(1)
In(1)	0	0.4450(1)	0.4486(1)	16(1)
S(1)	0	0.4300(4)	0.5090(5)	34(2)
S(2)	0	0.2843(3)	0.6648(5)	14(1)
S(3)	0	0.3156(3)	0.3670(4)	16(1)
S(4)	0	0.3585(3)	0.0000(4)	12(1)
S(5)	0	0.5039(3)	0.2753(5)	13(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Selected bond lengths, angles and bond valence sums (BVS) for Ba_2BiMS_5 (M = Ga, In)

Ba_2BiGaS_5					
atom	distance	BVS	atom	distance	BVS
Ba(1)–S(3)	3.2463(18)	0.2760	Bi(1)–S(1)	2.6504(16)	0.7623
Ba(1)–S(4)	3.2809(18)	0.2514	Bi(1)–S(1) #5	2.6504(16)	0.7623
Ba(1)–S(2) #1	3.2820(18)	0.2506	Bi(1)–S(1) #6	3.0756(19)	0.2416
Ba(1)–S(4) #2	3.2970(18)	0.2407	Bi(1)–S(1) #7	3.0756(19)	0.2416
Ba(1)–S(1)	3.319(2)	0.2268		∑=	3.0748
Ba(1)–S(2)	3.3317(18)	0.2191	Ga(1)–S(4) #8	2.219(2)	0.8760
Ba(1)–S(3) #3	3.3460(18)	0.2108	Ga(1)–S(3)	2.253(2)	0.7991
Ba(1)–S(1) #4	3.4098(19)	0.1774	Ga(1)–S(1)	2.2999(16)	0.7039
	∑=	1.8528	Ga(1)–S(1) #5	2.2999(16)	0.7039
Bi(1)–S(2)	2.526(2)	1.067		∑=	3.0829

S(2)–Bi(1)–S(1)	93.82(5)	S(1)#5–Bi(1)–S(1)#7	157.47(3)
S(2)–Bi(1)–S(1)#5	93.82(5)	S(1)#6–Bi(1)–S(1)#7	120.60(6)
S(1)–Bi(1)–S(1)#5	85.04(7)	S(4)#8–Ga(1)–S(3)	111.85(8)
S(2)–Bi(1)–S(1)#6	98.62(4)	S(4)#8–Ga(1)–S(1)	111.92(5)
S(1)–Bi(1)–S(1)#6	157.47(3)	S(3)–Ga(1)–S(1)	109.20(5)
S(1)#5–Bi(1)–S(1)#6	75.50(5)	S(4)#8–Ga(1)–S(1)#5	111.92(5)
S(2)–Bi(1)–S(1)#7	98.62(4)	S(3)–Ga(1)–S(1)#5	109.20(5)
S(1)–Bi(1)–S(1)#7	75.50(5)	S(1)–Ga(1)–S(1)#5	102.31(8)

Ba_2BiInS_5

atom	distance		BVS	atoms	distance		BVS
Ba(1)–S(2)	3.160(6)		0.3485	Ba(2)–S(3)	3.476(6)		0.1484
Ba(1)–S(5)#1	3.203(4)		0.3103	Ba(2)–S(1)	3.638(7)		0.0958
Ba(1)–S(5)#2	3.203(4)		0.3103			∑=	2.109
Ba(1)–S(4)#1	3.223(4)		0.2940	Bi(1)–S(4)	2.582(5)		0.9171
Ba(1)–S(4)#2	3.223(4)		0.2940	Bi(1)–S(2)#7	2.794(4)		0.5171
Ba(1)–S(1)#3	3.304(7)		0.2362	Bi(1)–S(2)#6	2.794(4)		0.5171
Ba(1)–S(3)#2	3.399(4)		0.1827	Bi(1)–S(3)#6	2.959(4)		0.3311
Ba(1)–S(3)#1	3.399(4)		0.1827	Bi(1)–S(3)#7	2.959(4)		0.3311
		∑=	2.1587	Bi(1)-S(1)	3.212(4)		0.1764
Ba(2)–S(5)#4	3.156(4)		0.3523			∑=	2.7899
Ba(2)–S(5)#5	3.156(4)		0.3523	In(1)–S(5)	2.447(6)		0.7905
Ba(2)–S(2)#6	3.219(4)		0.2972	In(1)–S(1)#2	2.501(4)		0.6831
Ba(2)–S(2)#7	3.219(5)		0.2972	In(1)–S(1)#1	2.501(4)		0.6831
Ba(2)–S(4)#2	3.229(4)		0.2829	In(1)–S(3)	2.578(6)		0.5548
Ba(2)–S(4)#1	3.229(4)		0.2829			∑=	2.7115

S(4)–Bi(1)–S(2)#7	94.79(14)	S(2)#6–Bi(1)–S(3)#7	167.12(16)
S(4)–Bi(1)–S(2)#6	94.79(14)	S(3)#6–Bi(1)–S(3)#7	91.89(16)
S(2)#7–Bi(1)–S(2)#6	99.12(19)	S(5)–In(1)–S(1)#2	115.30(16)
S(4)–Bi(1)–S(3)#6	97.65(14)	S(5)–In(1)–S(1)#1	115.30(15)
S(2)#7–Bi(1)–S(3)#6	167.12(16)	S(1)#2–In(1)–S(1)#1	116.5(3)
S(2)#6–Bi(1)–S(3)#6	83.16(12)	S(5)–In(1)–S(3)	92.39(19)
S(4)–Bi(1)–S(3)#7	97.65(14)	S(1)#2–In(1)–S(3)	106.77(17)
S(2)#7–Bi(1)–S(3)#7	83.16(12)	S(1)#1–In(1)–S(3)	106.77(17)

Symmetry transformations used to generate equivalent atoms:

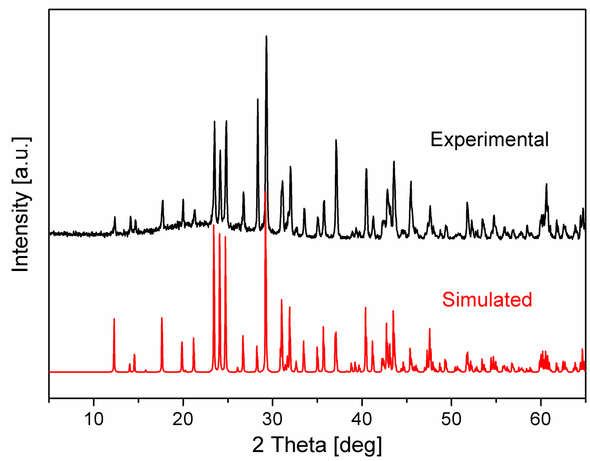
For Ba_2BiGaS_5: #1 −x+1/2,−y,z−1/2; #2 −x+1,−y,−z+1; #3 −x+1/2,−y,z+1/2; #4 x+1/2,y,−z+1/2; #5 x,−y+1/2,z; #6 −x,y+1/2,−z+1; #7 −x,−y,−z+1; #8 x−1/2,y,−z+1/2.

For Ba_2BiInS_5: #1 −x−1/2,−y+1/2,z+1/2; #2 −x+1/2,−y+1/2,z+1/2; #3 −x,−y,z+1/2; #4 x−1/2,y−1/2,z; #5 x+1/2,y−1/2,z; #6 −x−1/2,−y+1/2,z−1/2; #7 −x+1/2,−y+1/2,z−1/2.

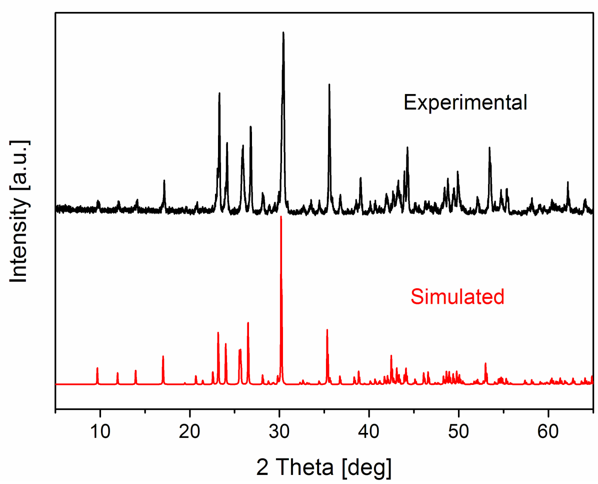
Table S3. The special *k*-point definitions in the first BZ and the corresponding state energies (eV) of the valence band maximum (VBM) and conduction band minimum (CBM) for Ba_2BiMS_5 (M = Ga, In)

k-point	VBM	CBM
Ba_2BiGaS_5		
Γ(0.0, 0.0, 0.0)	0	2.5762
Z(0.0, 0.0, 0.5)	-0.03827	2.5447
T(-0.5, 0.0, 0.5)	-0.1112	2.5117
Y(-0.5, 0.0, 0.0)	-0.1355	2.6946
S(-0.5, 0.5, 0.0)	-0.0556	2.4096
X(0.0, 0.5, 0.0)	-0.0519	2.5353
U(0.0, 0.5, 0.5)	-0.0134	2.6921
R(-0.5, 0.5, 0.5)	-0.1208	2.8048
Ba_2BiInS_5		
Γ(0.0, 0.0, 0.0)	-0.2381	1.6137

Z(0.0, 0.0, 0.5)	-0.3012	2.0031
T(0.5, 0.5, 0.5)	-0.3401	1.8868
Y(0.5, 0.5, 0.0)	-0.3008	1.9138
S(0.0, 0.5, 0.0)	-0.2655	3.0876
R(0.0, 0.5, 0.5)	-0.1776	3.0444
Z(0.0, 0.0, 0.5)	-0.3012	2.0031



(a)



(b)

Figure S1. Experimented (upper) and simulated (lower) powder X-ray (λ = 1.5418 Å) diffraction patterns for (a) Ba_2BiGaS_5 and (b) Ba_2BiInS_5.

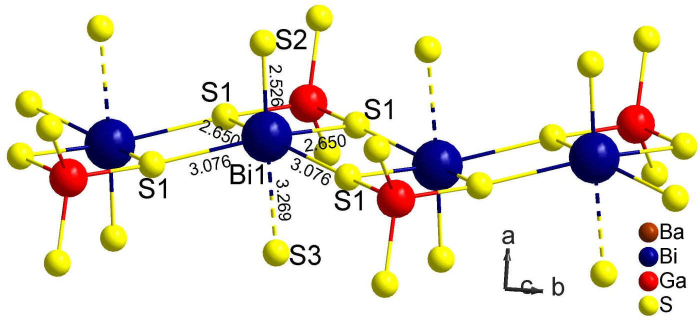
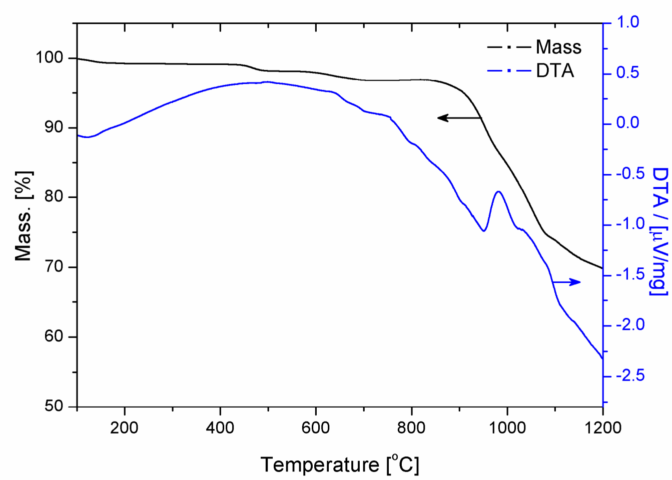
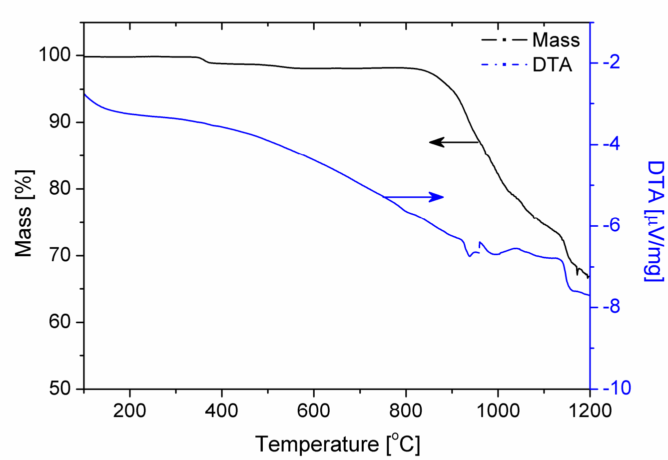


Figure S2. The farther S3 atoms are considered as complement of a distorted BiS_6 octahedral coordination. The Bi^{3+} cations move considerably away from the center of the BiS_6 octahedra.

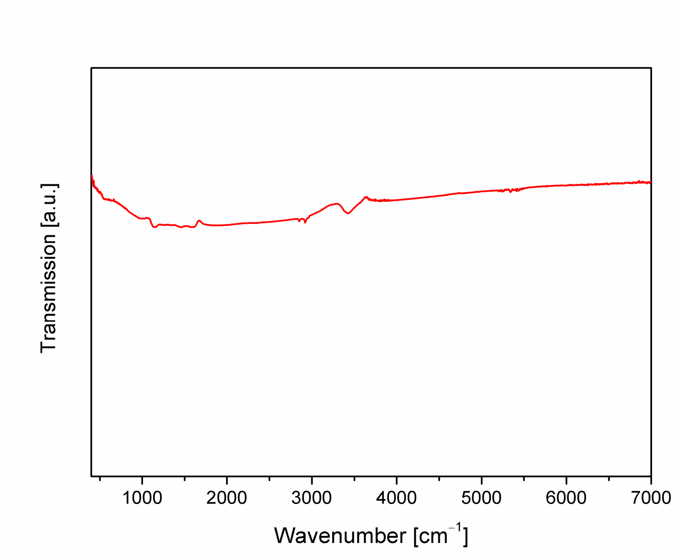


(a)

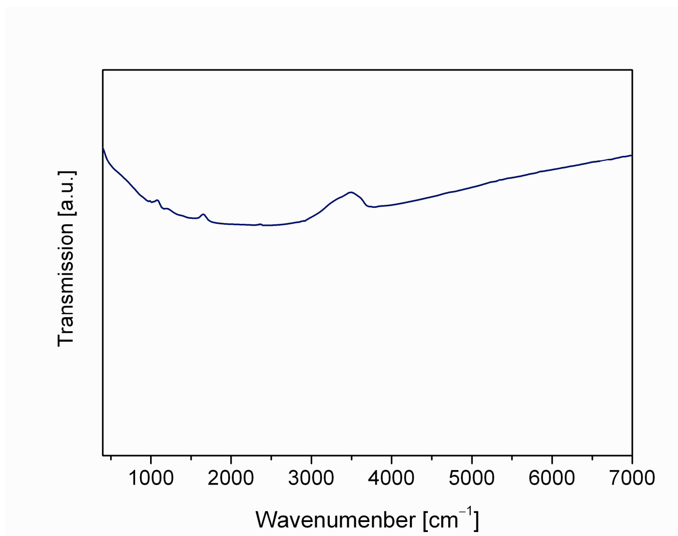


(b)

Figure S3. TGA and DTA diagrams of (a) Ba_2BiGaS_5 and (b) Ba_2BiInS_5, indicating the thermal stability up to 800 °C under N_2 atmosphere for both compounds.



(a)



(b)

Figure S4. IR spectra of polycrystalline samples of (a) Ba_2BiGaS_5 and (b) Ba_2BiInS_5. (The peaks at ~1100, 1600 and 3500 cm-1 are the remains that are not fully subtracted from the background.)