Electronic Supplementary Information

Syntheses and characterization of three new sulfides with large band gaps: acentric $Ba_4Ga_4SnS_{12}$, centric $Ba_{12}Sn_4S_{23}$ and $Ba_7Sn_3S_{13}$

Rui-Huan Duan,[a,b] Peng-Fei Liu,[c,d] Hua Lin,[b,*] Shang-Xiong Huangfu[e] and Li-Ming Wu [b,f,*]

[a]*Henan Province Key Laboratory of Utilization of Non-metallic Mineral in the South of Henan, College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, China*

[b]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China*

[c]*Institute of High Energy Physics, Chinese Academy of Sciences (CAS), Beijing 100049, China*

[d]*Dongguan Neutron Science Center, Dongguan 523803, China*

[e]*Physics Institute of the University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland*

[f]*Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, Beijing Normal University, Beijing 100875, P. R. China*

E-mail: linhua@fjirsm.ac.cn and liming_wu@fjirsm.ac.cn.

Table S1. Atomic coordinates, equivalent isotropic displacement parameters and occupancies of $Ba_4Ga_4SnS_{12}$ (**1**), $Ba_{12}Sn_4S_{23}$ (**2**) and $Ba_7Sn_3S_{13}$ (**3**).

1

Atom	Wyckoff	*x*	*Y*	*z*	U_{eq}	*Occu.*
Ba1	8*e*	0.02346(2)	0.30237(2)	0.04514(6)	0.0172(2)	1
Ga1	8*e*	-0.26034(4)	0.35857(4)	0.0492(2)	0.0114(2)	0.17
Sn1	4*e*	-0.26034(4)	0.35857(4)	0.0492(2)	0.0114(2)	0.83
Ga2	2*b*	0	0	1/2	0.0118(4)	0.31
Sn2	2*b*	0	0	1/2	0.0118(4)	0.69
S1	8*e*	-0.14247(9)	0.48432(9)	0.0428(2)	0.0133(2)	1
S2	8*e*	-0.1994(2)	0.2091(2)	0.2096(2)	0.0149(3)	1
S3	8*e*	0.0999(2)	0.0902(2)	0.2615(2)	0.0155(3)	1

2

Atom	Wyckoff	*x*	*Y*	*z*	U_{eq}	*Occu.*
Ba1	4*e*	0.44212(5)	0.44106(6)	0.09213(3)	0.0142(2)	1
Ba2	4*e*	0.58219(5)	-0.47636(6)	0.41276(3)	0.0181(2)	1
Ba3	4*e*	0.43316(5)	0.04582(6)	0.34135(3)	0.0179(2)	1
Ba4	4*e*	0.69096(5)	-0.17378(6)	0.34043(3)	0.0185 (2)	1
Ba5	4*e*	0.25056(6)	0.18198(7)	0.15254(3)	0.208(2)	1
Ba6	4*e*	0.56826(5)	1.00086(6)	0.16007(3)	0.0133(2)	1
Ba7	4*e*	0.42692(6)	-0.32679(6)	0.21241(3)	0.0174(2)	1
Ba8	4*e*	0.7308(4)	0.6777(3)	0.09904(9)	0.0199(7)	0.87
Ba8'	4*e*	0.696(5)	0.657(3)	0.092(2)	0.037(8)	0.13
Ba9	4*e*	-0.06304(5)	-0.16836(6)	0.22577(3)	0.0192(2)	1
Ba10	4*e*	0.18927(7)	-0.15751(7)	0.09825(3)	0.0280(2)	1
Ba11	4*e*	0.44493(7)	0.82042(7)	0.00066(3)	0.0277(2)	1
Ba12	4*e*	-0.04792(7)	0.6707(3)	-0.0058(2)	0.0191(7)	0.91
Ba'	4*e*	-0.0532(2)	0.638(2)	-0.0229(2)	0.013(4)	0.09
Sn1	4*e*	0.21914(6)	-0.09320(6)	0.23993(3)	0.0121(2)	1
Sn2	4*e*	0.22755(6)	0.60198(6)	-0.01414(3)	0.0118(2)	1
Sn3	4*e*	0.71900(6)	-0.39427(6)	0.23556(3)	0.0110(2)	1
Sn4	4*e*	0.77531(6)	-0.60241(6)	0.51462(3)	0.0135(2)	1
S1	4*e*	0.4822(2)	0.2374(2)	0.1667(2)	0.0182(6)	1
S2	4*e*	0.5896(2)	0.2356(3)	0.1147 (2)	0.0178(6)	1
S3	4*e*	0.6128(2)	0.6128(2)	0.1806(2)	0.0218(7)	1
S4	4*e*	0.3690(2)	0.6847(3)	0.0974(2)	0.0199(6)	1

S5	4*e*	0.6979(2)	-0.2066(2)	0.2199(2)	0.0196(6)	1
S6	4*e*	0.6930(2)	-0.4368(3)	0.3190(2)	0.0179(6)	1
S7	4*e*	0.6150(2)	0.0642(3)	0.2793(2)	0.0212(6)	1
S8	4*e*	0.2891(2)	0.4571(3)	0.1758(2)	0.0184(6)	1
S9	4*e*	0.6089(2)	0.4585(3)	0.0195(2)	0.0233(7)	1
S10	4*e*	0.4551(2)	-0.1911(3)	0.3107(2)	0.0207(6)	1
S11	4*e*	0.6213(2)	-0.0085(3)	0.4230(2)	0.0188(6)	1
S12	4*e*	0.3898(3)	-0.4426(3)	0.4705(2)	0.0286(8)	1
S13	4*e*	0.4723(3)	-0.2544(3)	0.38305(2)	0.0267(7)	1
S14	4*e*	0.3514(3)	0.0592(3)	0.4422(2)	0.0300(8)	1
S15	4*e*	0.4063(2)	-0.4918(2)	0.3099(2)	0.0182(6)	1
S16	4*e*	0.8137(3)	-0.5631(3)	0.4333(2)	0.0387(2)	1
S17	4*e*	0.3176(2)	0.2196(3)	0.27113(2)	0.0210(6)	1
S18	4*e*	0.5097(2)	0.7568(3)	0.1115(2)	0.0247(7)	1
S19	4*e*	0.2923(3)	0.2913(3)	0.0251(2)	0.0289(8)	1
S20	4*e*	0.5403(3)	-0.7257(3)	0.3923(2)	0.0331(8)	1
S21	4*e*	0.7053(3)	-0.2903(3)	0.4762(2)	0.0285(8)	1
S22	4*e*	0.3649(3)	-0.0632(3)	0.2015(2)	0.0425(2)	1
S23	4*e*	0.8831(4)	-0.5067(3)	0.5727(2)	0.0460(2)	1

			3			
Atom	Wyckoff	*x*	*Y*	*z*	U_{eq}	*Occu.*
Ba1	8*d*	1.31172(7)	0.53498(3)	0.1191(2)	0.0189(2)	1
Ba2	8*d*	1.0230(3)	0.65943(2)	0.0814(2)	0.0208(8)	0.89
Ba2’	8*d*	1.016(4)	0.650(4)	0.124(2)	0.028(2)	0.11
Ba3	4*c*	0.8615(2)	0.7500	0.6036(2)	0.0236(3)	1
Ba4	8*d*	0.6608(2)	0.65341(2)	-0.1025(7)	0.0262(8)	0.93
Ba4’	8*d*	0.6550(2)	0.637(2)	-0.048(6)	0.012(9)	0.07
Sn1	4*c*	0.7428(2)	0.7500	0.1957(2)	0.0152(3)	1
Sn2	8*d*	1.04898(7)	0.44948(4)	0.2012(2)	0.0170(2)	1
S1	4*c*	0.8435(4)	0.7500	-0.0342(6)	0.0187(2)	1
S2	4*c*	1.1092(5)	0.7500	-0.1696(7)	0.0320(2)	1
S3	8*d*	1.5786(3)	0.5375(2)	0.1855(4)	0.0191(7)	1
S4	4*c*	0.5520(4)	0.7500	0.1427(6)	0.0221(2)	1
S5	8*d*	1.1367(3)	0.5690(2)	-0.1416(4)	0.0194(7)	1
S6	8*d*	0.7799(3)	0.6675(2)	0.3230(5)	0.0277(8)	1
S7	8*d*	1.1613(3)	0.4304(2)	-0.0104(4)	0.0214(7)	1

S8	*8d*	1.4097(3)	0.6215(2)	-0.1216(5)	0.0273(8)	1

Table S2. Selected Bond Lengths (Å) of compound **1**, **2** and **3**.

1			
Ba1–S1	3.192(2)	Sn1–S1	2.252(2)
Ba1–S2	3.205(2)	Sn1–S3	2.282(2)
Ba1–S1	3.218(2)	Sn1–S2	2.306(2)
Ba1–S3	3.247(2)	Sn1–S2	2.339(2)
Ba1–S1	3.259(2)	Sn2–S3×4	2.314(2)
Ba1–S1	3.288(2)		
Ba1–S2	3.323(2)		
Ba1–S3	3.598(2)		

2					
Ba1–S9	3.120(3)	Ba6–S16	3.197(4)	Ba10–S21	3.368(4)
Ba1–S19	3.163(3)	Ba6–S23	3.239(4)	Ba10–S23	3.428(5)
Ba1–S4	3.189(4)	Ba6–S6	3.285(3)	Ba10–S15	3.549(4)
Ba1–S8	3.197(3)	Ba6–S7	3.295(4)	Ba10–S22	3.644(6)
Ba1–S3	3.203(3)	Ba6–S18	3.362(4)	Ba11–S18	3.115(4)
Ba1–S1	3.237(3)	Ba6–S22	3.149(4)	Ba11–S2	3.163(3)
Ba1–S2	3.248(3)	Ba6–S1	3.169(3)	Ba11–S23	3.179(5)
Ba1–S9	3.254(3)	Ba6–S5	3.417(3)	Ba11–S21	3.235(4)
Ba2–S6	3.089(3)	Ba7–S4	3.111(3)	Ba11–S4	3.340(4)
Ba2–S12	3.169(3)	Ba7–S10	3.122(3)	Ba11–S9	3.569(4)
Ba2–S20	3.186(4)	Ba7–S18	3.204(4)	Ba12–S13	3.199(4)
Ba2–S13	3.189(4)	Ba7–S8	3.350(4)	Ba12–S14	3.296(4)

Ba2–S21	3.225(3)	Ba7–S15	3.359(3)	Ba12–S19	3.298(4)
Ba2–S12	3.277(4)	Ba7–S22	3.384(5)	Ba12–S20	3.300(6)
Ba2–S16	3.279(5)	Ba7–S17	3.401(4)	Ba12–S11	3.362(3)
Ba2–S15	3.449(3)	Ba7–S3	3.487(4)	Ba12–S14	3.399(6)
Ba3–S14	3.026(4)	Ba8–S11	3.141(4)	Ba12–S12	3.523(5)
Ba3–S10	3.078(4)	Ba8–S18	3.173(5)	Ba'–S14	2.88(3)
Ba3–S7	3.097(3)	Ba8–S20	3.280(7)	Ba'–S13	2.96(2)
Ba3–17	3.166(3)	Ba8–S19	3.338(5)	Ba'–S11	3.30(2)
Ba3–S8	3.167(3)	Ba8–S16	3.372(5)	Ba'–S19	3.32(2)
Ba3–S11	3.241(3)	Ba8–S3	3.610(5)	Ba'–S14	3.43(2)
Ba3–S20	3.404(4)	Ba8–S5	3.616(4)	Ba'–S11	3.44(2)
Ba4–S10	3.189(3)	Ba8'–S19	3.22(2)	Sn1–S22	2.331(4)
Ba4–S11	3.229(3)	Ba8'–S11	3.25(3)	Sn1–S8	2.362(3)
Ba4–S2	3.264(3)	Ba8'–S16	3.54(3)	Sn1–S17	2.389(3)
Ba4–S5	3.274(4)	Ba8'–S18	2.89(4)	Sn1–S15	2.398(3)
Ba4–S6	3.318(4)	Ba8'–S9	3.27(6)	Sn2–S9	2.336(3)
Ba4–S13	3.404(4)	Ba8'–S3	3.38(3)	Sn2–S14	2.356(4)
Ba4–S3	3.471(4)	Ba9–S1	3.201(3)	Sn2–S21	2.369(4)
Ba4–S7	3.483(4)	Ba9–S5	3.228(3)	Sn2–S11	2.395(3)
Ba5–S13	3.144(4)	Ba9 S15	3.249(3)	Sn3–S7	2.357(3)
Ba5–S1	3.166(3)	Ba9–S20	3.292(4)	Sn3–S6	2.363(3)
Ba5–S15	3.245(3)	Ba9–S3	3.367(4)	Sn3–S3	2.367(3)
Ba5–S17	3.253(4)	Ba9–S7	3.394(4)	Sn3–S5	2.381(3)
Ba5–S10	3.408(3)	Ba9–S6	3.512(3)	Sn4–S23	2.340(4)
Ba5–S8	3.503(4)	Ba9–S17	3.566(4)	Sn4–S16	2.345(4)
Ba5–S22	3.598(4)	Ba10–S4	3.108(3)	Sn4–S12	2.356(3)
Ba5–S23	3.643(5)	Ba10–S20	3.228(4)	Sn4–S19	2.371(4)
Ba6–S2	3.184(4)	Ba10–S12	3.355(4)		

3			
Ba1–S8	3.227(4)	Ba3–S4	3.216(5)
Ba1–S6	3.268(4)	Ba3–S1	3.221(5)
Ba1–S5	3.275(4)	Ba3–S6×2	3.346(5)
Ba1–S7	3.344(4)	Ba3–S2	3.669(7)
Ba1–S5	3.352(4)	Ba4–S5	3.067(4)
Ba1–S3	3.359(4)	Ba4–S2	3.155(8)
Ba1–S3	3.368(4)	Ba4–S7	3.156(5)
Ba1–S7	3.409(4)	Ba4–S8	3.208(5)
Ba1–S3	3.494(4)	Ba4–S1	3.308(5)
Ba2–S7	3.212(5)	Ba4–S4	3.463(4)
Ba2–S5	3.267(7)	Ba4'–S7	2.85(4)
Ba2–S1	3.284(7)	Ba4'–S8	3.13(2)
Ba2–S6	3.299(6)	Ba4'–S5	3.22(3)
Ba2–S2	3.30(2)	Ba4'– S3	3.32(7)
Ba2–S4	3.304(9)	Ba4'–S4	3.45(2)
Ba2–S3	3.667(9)	Ba4'–S1	3.59(4)
Ba2'–S7	3.10(6)	Sn1–S6×2	2.338(4)
Ba2'–S4	3.21(3)	Sn1–S1	2.391(5)
Ba2'–S3	3.30(2)	Sn1–S4	2.410(5)
Ba2'–S6	3.33(5)	Sn2–S3	2.381(3)
Ba2'–S5	3.41(4)	Sn2–S7	2.381(4)
Ba2'–S6	3.44(8)	Sn2–S8	2.383(4)
Ba2'–S1	3.52(7)	Sn2–S5	2.402(4)
Ba3–S8×2	3.167(4)		
Ba3–S2	3.179(7)		

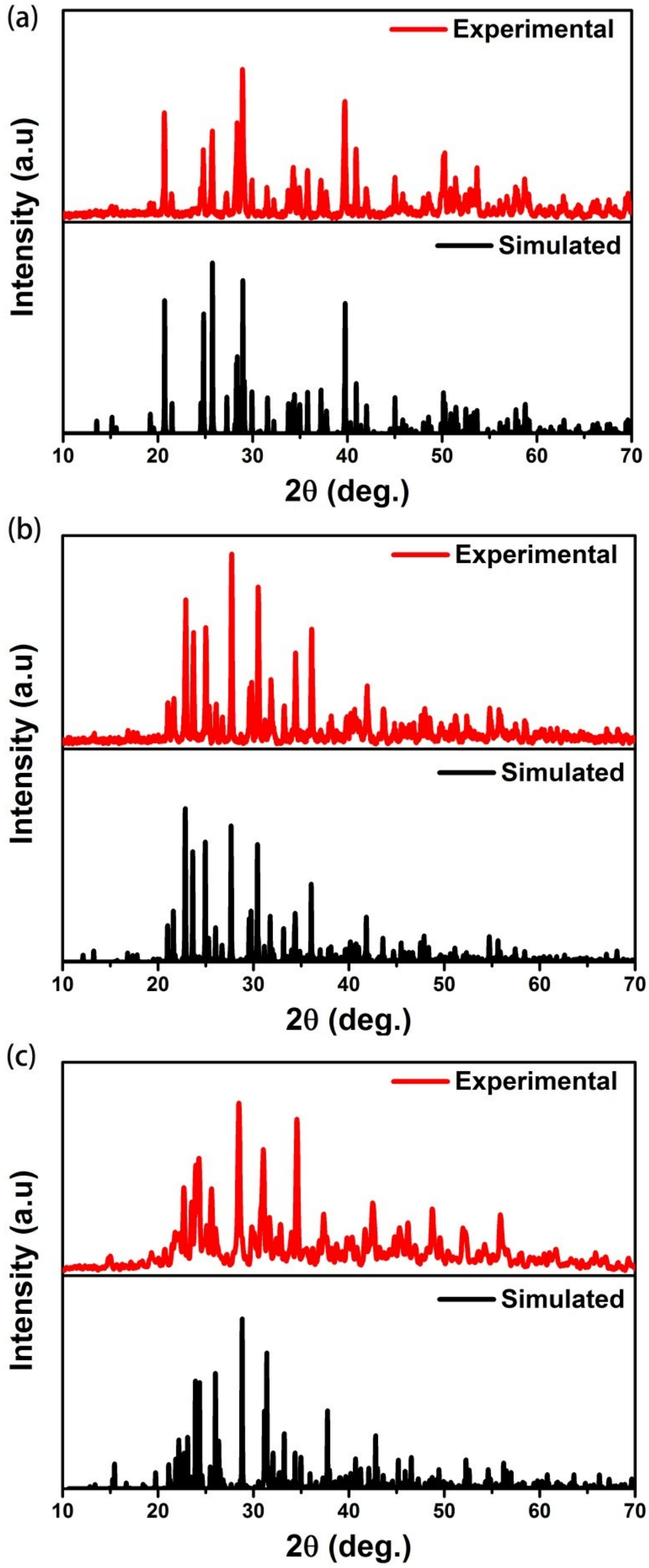

Figure S1. Experimental and simulated powder X-ray diffraction (XRD) data for compound **1** (a), **2** (b) and **3** (c).

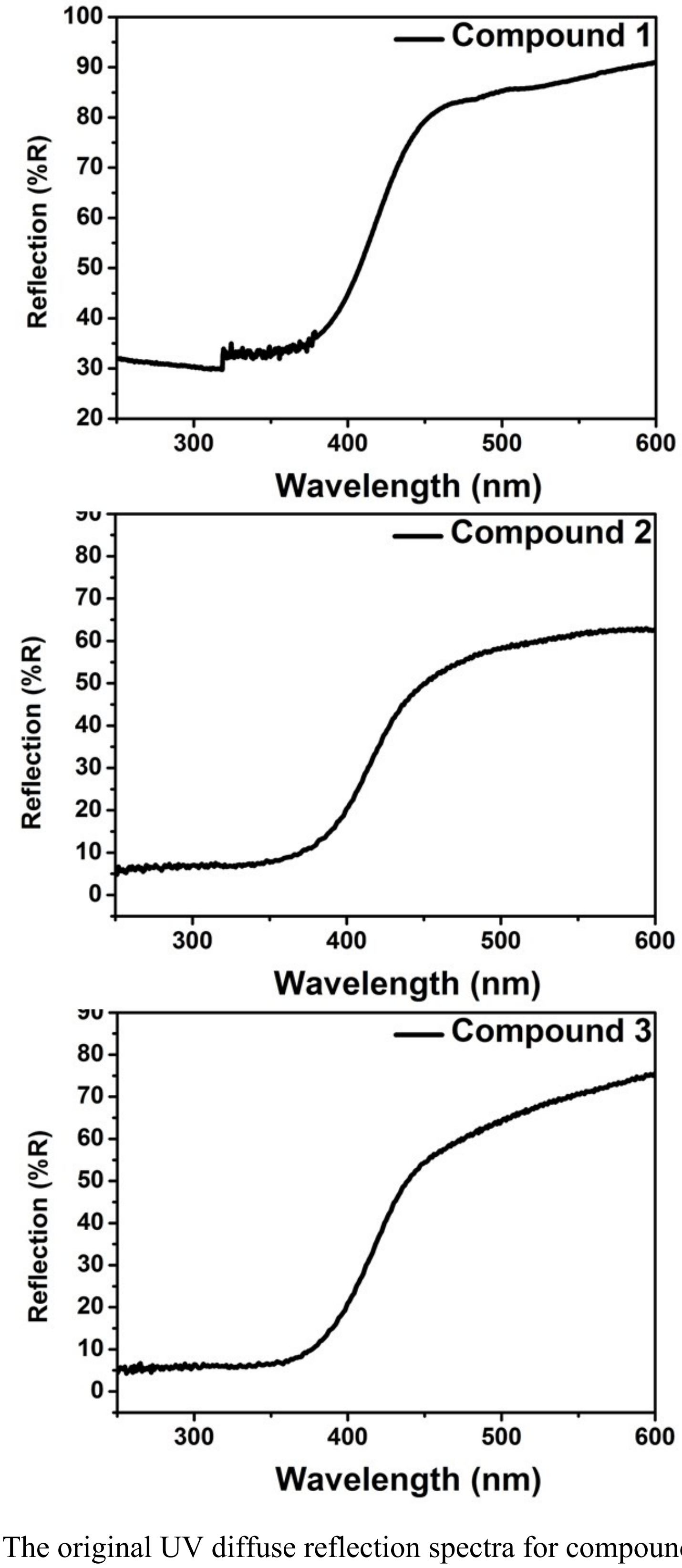

Figure S2. The original UV diffuse reflection spectra for compound **1**, **2** and **3**.

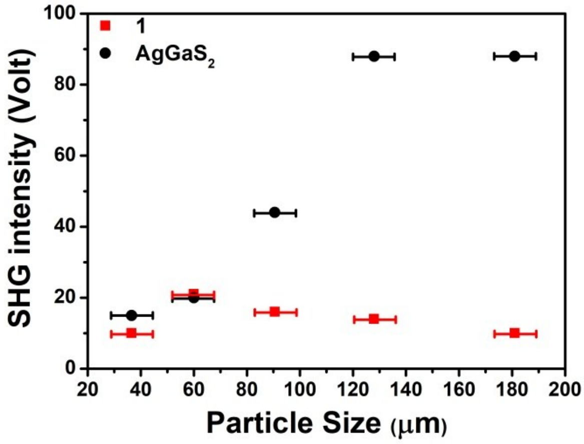

Figure S3. The SHG vs particle size patterns of compounds **1** and $AgGaS_2$ (reference) at 2.05μm.

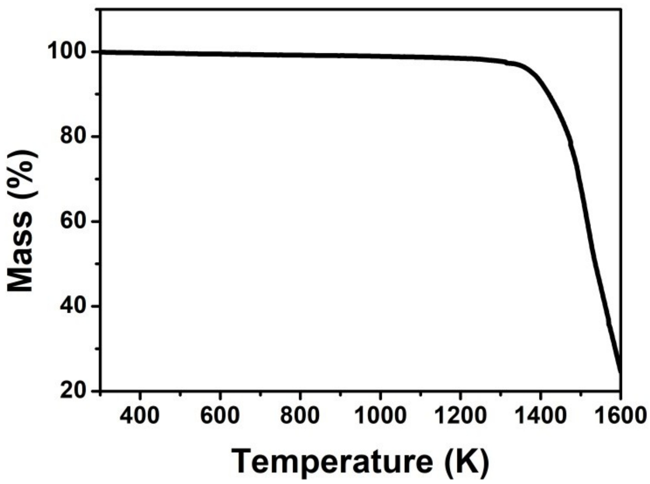

Figure S4. The TGA patterns of compounds **1** under N_2 flow.

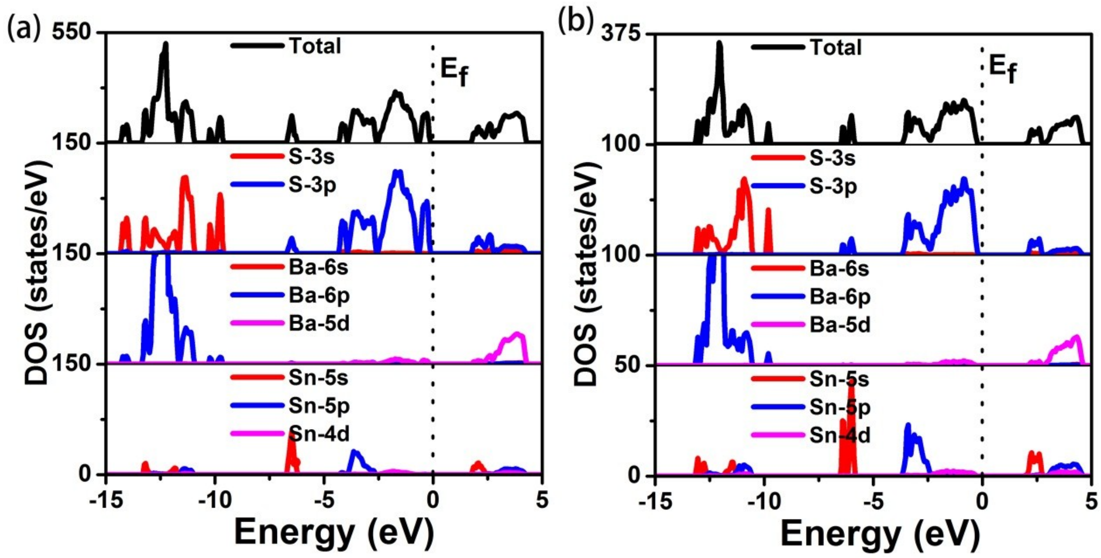

Figure S5. Calculated band structures of compound **2** (a) and **3** (b).

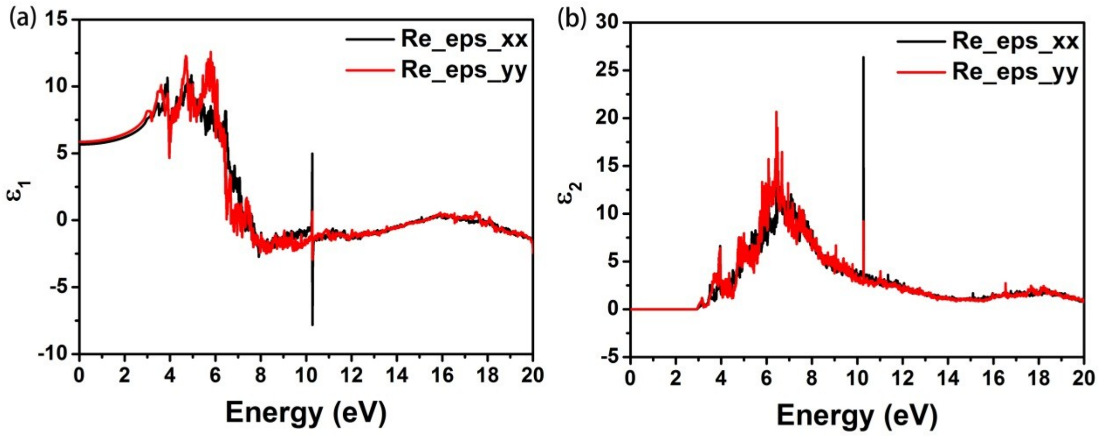

Figure S6. Energy dependences of the real part (ε_1) and imaginary part (ε_2) of compound **1**.

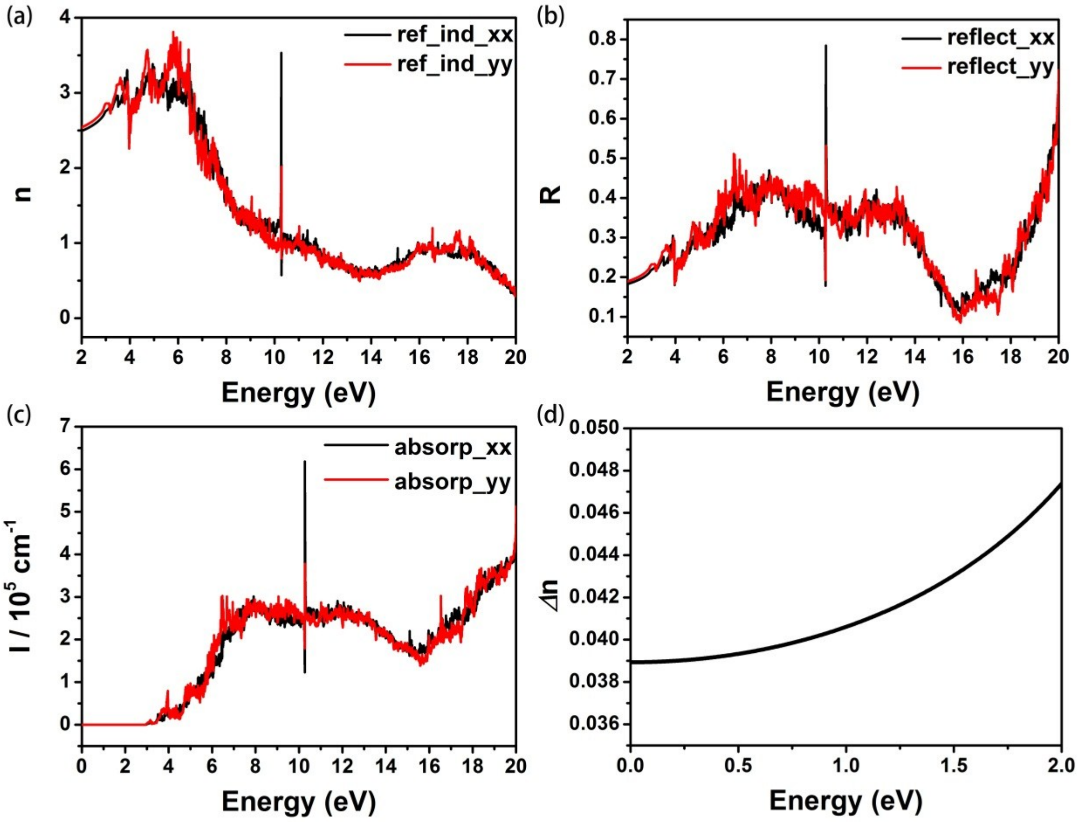

Figure S7. the calculated (a) refractive index $n(\omega)$, (b) reflectivity $R(\omega)$ and (c) absorption coefficient $I(\omega)$ and (d) birefringence (Δn) of compound **1**.