Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Band Gap Tuning from Indirect $EuGa_2S_4$ to Direct $EuZnGeS_4$ Semiconductor: Syntheses, Crystal and Electronic Structures, and Optical Properties

Yang Chi, Sheng-Ping Guo* and Huai-Guo Xue

College of Chemistry & Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, P. R. China

Corresponding authors: spguo@yzu.edu.cn

Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (U_{eq}[a], Å^2 × 10^3) for **1**–**4**.

atom	*x*	*y*	*z*	U_{eq}/Å^2
		1		
Eu(1)	6250	3732(1)	1250	9(1)
Eu(2)	6250	6250	1250	9(1)
Eu(3)	6250	6250	6250	10(1)
Zn(1)	5541(1)	4998(1)	4138(1)	6(1)
Ge(1)	7375(1)	5005(1)	3741(1)	11(1)
S(1)	6550(2)	5009(2)	4956(3)	7(1)
S(2)	5794(2)	4988(2)	2351(3)	7(1)
S(3)	7503(2)	5830(2)	2487(4)	14(1)
S(4)	5000(2)	4167(2)	5007(4)	14(1)
		2		
Eu(1)	1250	1250	3768(1)	9(1)
Eu(2)	1250	1250	6250	10(1)
Eu(3)	1250	1250	1250	10(1)
Ga(1)	1263(1)	-122(1)	2506(1)	8(1)
Ga(2)	-1642(1)	539(1)	2502(1)	8(1)
S(1)	150(1)	789(1)	2513(1)	8(1)
S(2)	2547(1)	944(1)	5008(1)	9(1)
S(3)	11(2)	1(1)	4168(1)	8(1)
S(4)	2511(2)	4(1)	3328(1)	9(1)
		3		
Eu(1)	6250	1250	1250	13(1)
Eu(2)	8750	1282(1)	3750	14(1)
Eu(3)	8750	3750	3750	13(1)
In(1)	6260(1)	2507(1)	2619(1)	13(1)
In(2)	9092(1)	2501(1)	1962(1)	13(1)
S(1)	7320(1)	2515(1)	1626(1)	12(1)
S(2)	9992(2)	1605(1)	2503(1)	13(1)
S(3)	5019(2)	1614(1)	2502(1)	14(1)
		4		
Eu(1)	6250	1250	1250	13(1)
Eu(2)	8750	1276(1)	3750	13(1)
Eu(3)	8750	3750	3750	14(1)
In(1)	6253(1)	2505(1)	2611(1)	11(1)
In(2)	9118(1)	2501(1)	1957(1)	12(1)
Se(1)	7324(1)	2514(1)	1610(1)	9(1)
Se(2)	9987(1)	1590(1)	2501(1)	11(1)
Se(3)	5013(1)	1598(1)	2499(1)	11(1)

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

Table S2. Selected bond distances (Å) of **1–4**.[a]

Bond	Dist.	Bond	Dist.	Bond	Dist.
		1			
Eu(1)–S(2)	3.070(4)	Eu(3)–S(1)	3.077(4)	Ge(1)–S(1)	2.246(4)
Eu(1)–S(4)#2	3.082(5)	Eu(3)–S(4)#10	3.100(5)	Ge(1)–S(3)#5	2.301(5)
Eu(1)–S(3)#4	3.112(5)	Zn(1)–S(2)	2.247(4)	Ge(1)–S(3)	2.309(5)
Eu(2)–S(2)	3.080(4)	Zn(1)–S(1)	2.288(4)	Ge(1)–S(2)#12	2.315(4)
Eu(2)–S(3)#1	3.095(5)	Zn(1)–S(4)#10	2.302(5)		
Eu(2)–S(3)	3.095(5)	Zn(1)–S(4)	2.303(5)		
		2			
Eu(1)–S(1)	3.071(3)	Eu(3)–S(1)	3.085(3)	Ga(2)–S(1)	2.246(3)
Eu(1)–S(2)	3.076(3)	Eu(3)–S(4)#10	3.102(3)	Ga(2)–S(3)#10	2.294(2)
Eu(1)–S(3)	3.081(3)	Ga(1)–S(2)#10	2.243(2)	Ga(2)–S(3)#14	2.298(2)
Eu(1)–S(4)	3.113(3)	Ga(1)–S(4)#11	2.296(3)	Ga(2)–S(2)#15	2.303(2)
Eu(2)–S(2)	3.082(3)	Ga(1)–S(4)	2.299(3)		
Eu(2)–S(3)#4	3.108(3)	Ga(1)–S(1)	2.305(2)		
		3			
Eu(1)–S(1)	3.078(2)	Eu(3)–S(4)	3.069(3)	In(2)–S(1)	2.413(2)
Eu(1)–S(3)	3.178(3)	Eu(3)–S(2)#10	3.194(2)	In(2)–S(2)	2.477(2)
Eu(2)–S(4)	3.063(3)	In(1) –S(4)	2.414(2)	In(2)–S(2)#11	2.479(2)
Eu(2)–S(1)#5	3.080(2)	In(1)–S(3)	2.472(2)	In(2)–S(4)#15	2.508(2)
Eu(2)–S(2)	3.158(2)	In(1)–S(3)#14	2.484(2)		
Eu(2)–S(3)#2	3.213(2)	In(1)–S(1)	2.506(2)		
		4			
Eu(1)–Se(1)	3.206(2)	Eu(3)–Se(4)	3.190(2)	In(2)–Se(1)	2.536(8)
Eu(1)–Se(3)	3.288(2)	Eu(3)–Se(2)#10	3.306(2)	In(2)–Se(2)	2.591(2)
Eu(2)–Se(4)	3.194(2)	In(1)–Se(4)	2.530(8)	In(2)–Se(2)#12	2.601(2)
Eu(2)–Se(1)#5	3.202(2)	In(1)–Se(3)	2.599(1)	Se(4)–In(2)#13	2.621(8)
Eu(2)–Se(2)	3.272(2)	In(1)–Se(3)#14	2.603(1)		
Eu(2)–Se(3)#1	3.323(2)	In(1)–Se(1)	2.621(8)		

[a]Symmetry transformations used to generate equivalent atoms: Compound **1**: #1 -*x*+5/4, *y*, -*z*+1/4; 2 -*x*+5/4, -*y*+3/4, *z*-1/2; #3 *x*, -*y*+3/4, -*z*+3/4; #4 *x*-1/4, -*y*+1, *z*-1/4; #5 -*x*+3/2, -*y*+1, -*z*+1/2; #6 -*x*+5/4, -*y*+5/4, *z*; #7 *x*, -*y*+5/4, -*z*+1/4; #8 *x*, -*y*+5/4, -*z*+5/4; #9 -*x*+5/4, *y*, -*z*+5/4; #10 -*x*+1, -*y*+1, -*z*+1; #11 -*x*+1, *y*+1/4, *z*+1/4 ; #12 *x*+1/4, -*y*+1, *z*+1/4; Compound **2**: #1 -*x*+1/4, -*y*+1/4, *z*; #2 *x*, -*y*+1/4, -*z*+5/4; #3 -*x*+1/4, *y*, -*z*+5/4; #4 -*x*, -*y*, -*z*+1; #5 -*x*, *y*+1/4, *z*+1/4; #6 *x*+1/4, *y*+1/4, -*z*+1; #7 *x*+1/4, -*y*, *z*+1/4; #8 *x*, -*y*+1/4, -*z*+1/4; #9 -*x*+1/4, *y*, -*z*+1/4; #10 *x*-1/4, -*y*, *z*-1/4; #11 -*x*+1/2, -*y*, -*z*+1/2; #12 *x*-1/4, *y*+1/4, -*z*+1/2; #13 -*x*+1/2, *y*+1/4, *z*-1/4; #14 -*x*-1/4, *y*, -*z*+3/4; #15 *x*-1/2, -*y*+1/4, -*z*+3/4; Compound **3**: #1 *x*, -*y*+1/4, -*z*+1/4; #2 -*x*+5/4, -*y*+1/4, *z*; #3 -

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

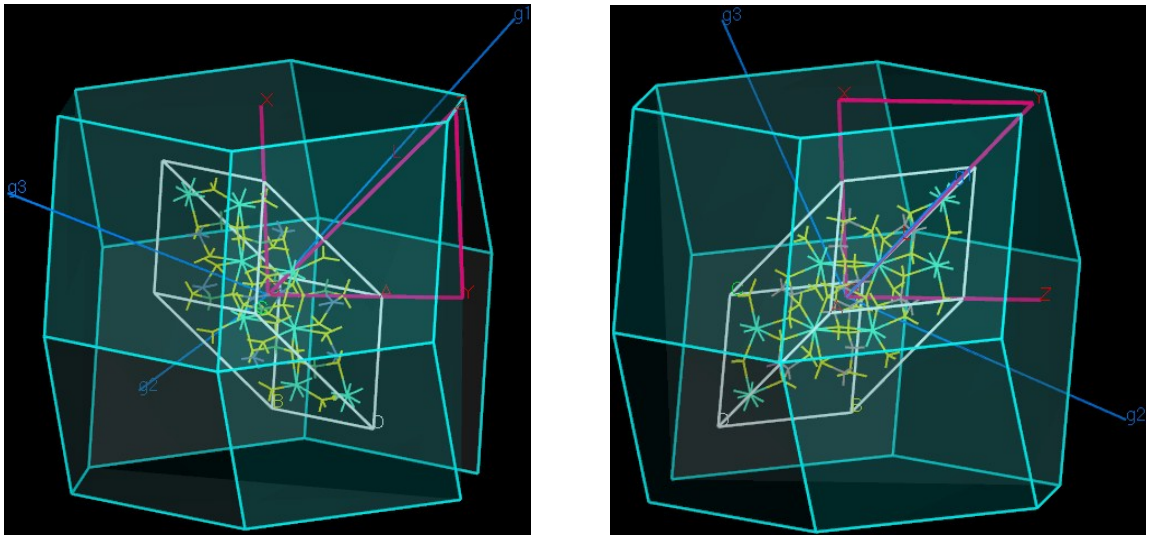

Fig. S1 The Brillouin zones of **1** (left) and **2** (right), respectively.