Centrosymmetric to Noncentrosymmetric Structural Transformation of New Quaternary Selenides Induced by Isolated Dimeric [Sn_2Se_4] Units: From $Ba_8Ga_2Sn_7Se_{18}$ to $Ba_{10}Ga_2Sn_9Se_{22}$

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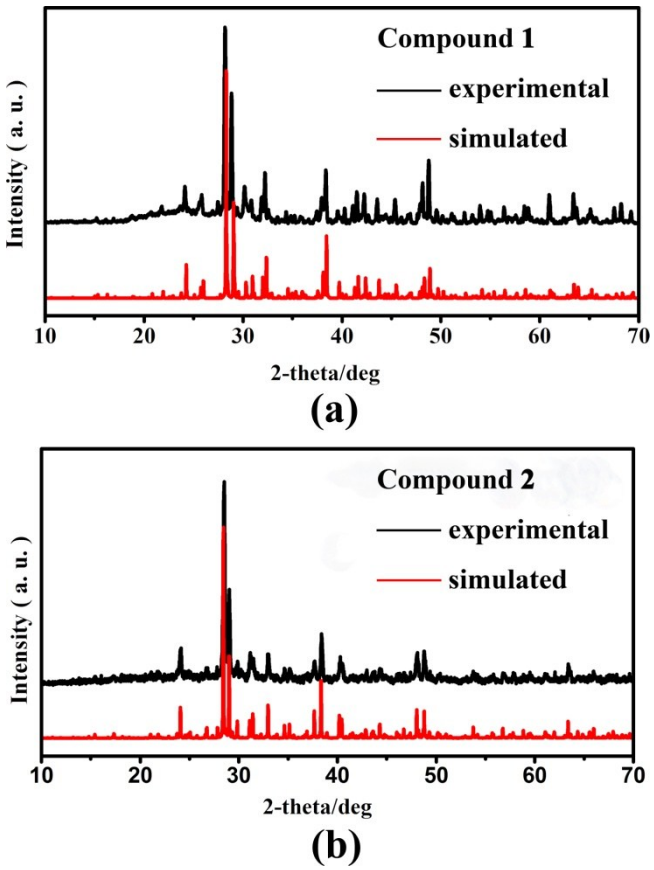

Figure S1. Experimental and simulated X-ray diffraction patterns of $Ba_8Ga_2Sn_7Se_{18}$, **1** (a) and $Ba_{10}Ga_2Sn_9Se_{22}$, **2** (b).

Table S1a. Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $Ba_8Ga_2Sn_7Se_{18}$, **1**.

Atom	Oxidation	Wyckoff	SOF	*x*	*y*	*z*	U_{eq}(Å)[a]
Ba1	+2	8d	1	0.33913(4)	0.00401(6)	0.19235(3)	0.0207(2)
Ba2	+2	8d	1	0.32052(4)	0.00064(6)	0.44933(3)	0.0222(2)
Ga1	+3	4c	1	0.0991(2)	0.25	0.11216(8)	0.0197(3)
Sn1	+2	4c	0.5	0.4320(2)	0.25	0.6445(2)	0.0309(4)
Sn2	+2	4c	1	0.07474(7)	0.25	0.30432(6)	0.0328(3)
Sn3	+2	4c	1	0.02118(7)	0.25	0.50443(5)	0.0232(2)
Sn4	+2	4c	1	0.39702(8)	0.25	0.80707(6)	0.0282(2)
Se1	-2	4c	1	0.1865(2)	0.25	0.81704(7)	0.0242(3)
Se2	-2	8d	1	0.06445(7)	0.0410(2)	0.18714(5)	0.0228(2)
Se3	-2	4c	1	0.49573(9)	0.25	0.49846(7)	0.0217(3)
Se4	-2	8d	1	0.06368(7)	0.5371(2)	0.40390(5)	0.0195(2)
Se5	-2	4c	1	0.28095(9)	0.25	0.31877(7)	0.0189(3)
Se6	-2	4c	1	0.28238(9)	0.25	0.06938(7)	0.0181(3)
Se7	-2	4c	1	0.2187(2)	0.25	0.57202(7)	0.0215(3)

[a]*U(eq)* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S1b. Atomic Coordinates and Equivalent Isotropic Displacement Parameters of $Ba_{10}Ga_2Sn_9Se_{22}$, **2**.

Atom	Oxidation	Wyckoff	SOF	*x*	*y*	*z*	U_{eq}(Å)[a]
Ba1	+2	8b	1	0.24605(9)	0.47676(2)	0.42605(8)	0.0143(2)
Ba2	+2	8b	1	0.24989(9)	0.08021(2)	0.40942(8)	0.0167(2)
Ba3	+2	8b	1	0.25029(9)	0.37902(2)	0.26907(7)	0.0159(2)
Ba4	+2	8b	1	0.24829(9)	0.17739(2)	0.24580(7)	0.0153(2)
Ba5	+2	8b	1	0.25421(9)	0.27662(2)	0.24078(8)	0.0131(2)
Ga1	+3	4a	1	0	0.44367(5)	0.1853(2)	0.0134(5)
Ga2	+3	4a	1	0	0.14825(5)	0.4881(2)	0.0146(5)
Sn1	+2	4a	0.5	0	0.33924(6)	0.0152(3)	0.0213(6)
Sn2	+2	4a	0.5	0	0.04288(7)	0.6547(3)	0.0254(7)
Sn3	+2	4a	1	0	0.52181(4)	0.1617(2)	0.0288(4)
Sn4	+2	4a	1	0	0.22773(4)	0.4998(2)	0.0288(4)
Sn5	+2	4a	1	0	0.02282(4)	0.1907(2)	0.0220(4)
Sn6	+2	4a	1	0	0.09954(3)	0.0671(2)	0.0188(3)
Sn7	+2	4a	1	0	0.31937(3)	0.4894(2)	0.0165(3)
Sn8	+2	4a	1	0	0.60281(3)	0.1054(2)	0.0190(3)
Sn9	+2	4a	1	0	0.26750(3)	0.0000(2)	0.0175(3)
Sn10	+2	4a	1	0	0.18288(3)	0.0110(2)	0.0242(3)
Se1	-2	8b	1	0.2085(2)	0.47388(3)	0.1502(2)	0.0163(3)
Se2	-2	8b	1	0.2204(2)	0.22819(3)	0.0142(2)	0.0132(3)
Se3	-2	8b	1	0.2122(2)	0.06174(3)	0.1518(2)	0.0150(3)
Se4	-2	8b	1	0.2861(2)	0.13963(3)	0.0235(2)	0.0150(3)
Se5	-2	8b	1	0.2928(2)	0.32057(3)	0.0184(2)	0.0167(3)
Se6	-2	4a	1	0	0.22809(5)	0.2911(2)	0.0130(5)
Se7	-2	4a	1	0	0.62924(5)	0.3065(2)	0.0157(4)
Se8	-2	4a	1	0	0.17396(4)	0.8053(2)	0.0127(4)
Se9	-2	4a	1	0	0.72655(5)	0.2907(2)	0.0129(4)
Se10	-2	4a	1	0	0.07178(5)	0.8690(2)	0.0158(4)
Se11	-2	4a	1	0	0.10358(5)	0.5919(2)	0.0170(4)
Se12	-2	4a	1	0	0.42720(5)	0.3703(2)	0.0121(4)
Se13	-2	4a	1	0	0.12912(5)	0.3064(2)	0.0130(4)
Se14	-2	4a	1	0	0.52768(4)	0.3685(2)	0.0130(5)
Se15	-2	4a	1	0	0.02705(5)	0.4026(2)	0.0178(5)
Se16	-2	4a	1	0	0.39848(4)	0.0830(2)	0.0148(4)
Se17	-2	4a	1	0	0.32547(5)	0.2777(2)	0.0172(5)

[a]*U(eq)* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2a. Selected Bond Lengths (Å) of $Ba_8Ga_2Sn_7Se_{18}$, **1**.

bond	dist.	bond	dist.	bond	dist.	bond	dist.
Ba1—Se6	3.282(2)	Ba2—Se4	3.325(2)	Ga1—Se2	2.421(2)	Sn2—Se2	2.891(2)
Ba1—Se1	3.296(2)	Ba2—Se1	3.356(2)	Ga1—Se2	2.421(2)	Sn2—Se2	2.891(2)
Ba1—Se7	3.307(2)	Ba2—Se5	3.361(2)	Sn1—Se3	2.766(3)	Sn3—Se7	2.751(2)
Ba1—Se4	3.321(2)	Ba2—Se3	3.412(2)	Sn1—Se2	2.831(2)	Sn3—Se4	2.802(2)
Ba1—Se5	3.329(2)	Ba2—Se6	3.448(2)	Sn1—Se2	2.831(2)	Sn3—Se4	2.802(2)
Ba1—Se2	3.443(3)	Ba2—Se7	3.465(2)	Sn1—Se7	2.966(3)	Sn4—Se1	2.631(3)
Ba1—Se2	3.576(2)	Ga1—Se3	2.384(2)	Sn1—Sn4	2.980(3)	Sn4—Se4	2.701(2)
Ba2—Se3	3.318(2)	Ga1—Se6	2.413(2)	Sn2—Se5	2.584(2)	Sn4—Se4	2.701(2)

Table S2b. Selected Bond Lengths (Å) of $Ba_{10}Ga_2Sn_9Se_{22}$, **2**.

bond	dist.	bond	dist.	bond	dist.	bond	dist.
Ba1–Se12	3.278(2)	Ba3–Se12	3.430(2)	Ga1–Se1	2.419(2)	Sn5–Se16	2.787(3)
Ba1–Se15	3.294(2)	Ba3–Se10	3.449(2)	Ga2–Se11	2.382(3)	Sn5–Se5	2.873(2)
Ba1–Se10	3.305(2)	Ba4–Se4	3.257(2)	Ga2–Se13	2.414(3)	Sn5–Se5	2.873(2)
Ba1–Se3	3.315(2)	Ba4–Se13	3.268(2)	Ga2–Se5	2.424(2)	Sn5–Se7	2.952(4)
Ba1–Se14	3.325(2)	Ba4–Se9	3.278(2)	Ga2–Se5	2.424(2)	Sn6–Se6	2.591(3)
Ba1–Se1	3.446(2)	Ba4–Se7	3.287(2)	Sn1–Se11	2.831(4)	Sn6–Se5	2.920(2)
Ba1–Se1	3.573(2)	Ba4–Se6	3.303(2)	Sn1–Se1	2.837(2)	Sn6–Se5	2.920(2)
Ba2–Se3	3.324(2)	Ba4–Se5	3.408(2)	Sn1–Se1	2.837(2)	Sn7–Se7	2.763(3)
Ba2–Se16	3.327(2)	Ba4–Se2	3.677(2)	Sn1–Se10	2.959(4)	Sn7–Se4	2.791(2)
Ba2–Se15	3.345(2)	Ba5–Se17	3.271(2)	Sn1–Sn4	2.979(3)	Sn7–Se4	2.791(2)
Ba2–Se14	3.364(2)	Ba5–Se9	3.278(2)	Sn2–Se14	2.581(3)	Sn8–Se17	2.643(3)
Ba2–Se11	3.425(2)	Ba5–Se6	3.289(2)	Sn2–Se1	2.910(2)	Sn8–Se4	2.755(2)
Ba2–Se13	3.456(2)	Ba5–Se8	3.297(2)	Sn2–Se1	2.910(2)	Sn8–Se4	2.755(2)
Ba2–Se7	3.461(2)	Ba5–Se2	3.410(2)	Sn3–Se10	2.756(3)	Sn9–Se9	2.613(3)
Ba3–Se4	3.286(2)	Ba5–Se5	3.411(2)	Sn3–Se3	2.818(2)	Sn9–Se2	2.723(2)
Ba3–Se11	3.307(2)	Ba5–Se2	3.567(2)	Sn3–Se3	2.818(2)	Sn9–Se2	2.723(2)
Ba3–Se17	3.360(2)	Ga1–Se16	2.391(3)	Sn4–Se15	2.638(3)	Sn10–Se8	2.585(3)
Ba3–Se8	3.367(2)	Ga1–Se12	2.413(3)	Sn4–Se3	2.691(2)	Sn10–Se2	2.900(2)
Ba3–Se16	3.408(2)	Ga1–Se1	2.419(2)	Sn4–Se3	2.691(2)	Sn10–Se2	2.900(2)

Table S3a. Selected Angles (deg) of $Ba_8Ga_2Sn_7Se_{18}$, **1**.

bond	angle	bond	angle
Se3–Ga1–Se6	103.95(8)	Se2–Sn1–Se3	104.89(5)
Se2–Ga1–Se2	107.78(9)	Se2–Sn2–Se2	85.15(7)
Se2–Ga1–Se6	110.46(5)	Se2–Sn2–Se5	96.82(4)
Se2–Ga1–Se6	110.46(5)	Se2–Sn2–Se5	96.82(4)
Se2–Ga1–Se3	112.10(5)	Se4–Sn3–Se4	90.63(7)
Se3–Ga1–Se5	112.10(5)	Se4–Sn3–Se7	94.22(5)
Se3–Sn1–Se7	80.38(7)	Se4–Sn3–Se7	94.22(5)
Se2–Sn1–Se7	97.76(5)	Se4–Sn4–Se4	95.08(7)
Se2–Sn1–Se7	97.76(5)	Se1–Sn4–Se4	97.83(4)
Se2–Sn1–Se2	148.26(9)	Se1–Sn4–Se4	97.83(4)
Se2–Sn1–Se3	104.89(5)		

Table S3b. Selected Angles (deg) of $Ba_{10}Ga_2Sn_9Se_{22}$, **2**.

bond	angle	bond	angle
Se12–Ga1–Se16	104.3(2)	Se3–Sn4–Se3	95.43(8)
Se1–Ga1–Se1	108.0(2)	Se3–Sn4–Se15	97.62(6)
Se1–Ga1–Se12	110.04(8)	Se3–Sn4–Se15	97.62(6)
Se1–Ga1–Se12	110.04(8)	Se7–Sn5–Se16	78.98(9)
Se1–Ga1–Se16	112.25(8)	Se5–Sn5–Se7	98.73(7)
Se1–Ga1–Se16	112.25(8)	Se5–Sn5–Se7	98.73(7)
Se11–Ga2–Se13	102.0(2)	Se5–Sn5–Se5	146.1(2)
Se5–Ga2–Se5	106.7(2)	Se5–Sn5–Se16	105.87(6)
Se5–Ga2–Se13	110.49(7)	Se5–Sn5–Se16	105.87(6)
Se5–Ga2–Se13	110.49(7)	Se5–Sn6–Se5	83.52(7)
Se5–Ga2–Se11	113.62(7)	Se5–Sn6–Se6	94.81(6)
Se5–Ga2–Se11	113.62(7)	Se5–Sn6–Se6	94.81(6)
Se10–Sn1–Se11	80.0(2)	Se4–Sn7–Se4	92.00(7)
Se1–Sn1–Se10	97.68(8)	Se4–Sn7–Se7	94.32(6)
Se1–Sn1–Se10	97.68(8)	Se4–Sn7–Se7	94.32(6)
Se1–Sn1–Se1	149.2(2)	Se4–Sn8–Se4	93.57(7)
Se1–Sn1–Se11	104.43(7)	Se4–Sn8–Se17	94.82(6)
Se1–Sn1–Se11	104.43(7)	Se4–Sn8–Se17	94.82(6)
Se1–Sn2–Se1	84.51(7)	Se2–Sn9–Se9	97.51(6)
Se1–Sn2–Se14	97.13(6)	Se2–Sn9–Se9	97.51(6)
Se1–Sn2–Se14	97.13(6)	Se2–Sn9–Se2	98.86(8)
Se3–Sn3–Se3	89.90(7)	Se2–Sn10–Se2	91.01(7)
Se3–Sn3–Se10	93.52(6)	Se2–Sn10–Se8	97.01(6)
Se3–Sn3–Se10	93.52(6)	Se2–Sn10–Se8	97.01(6)

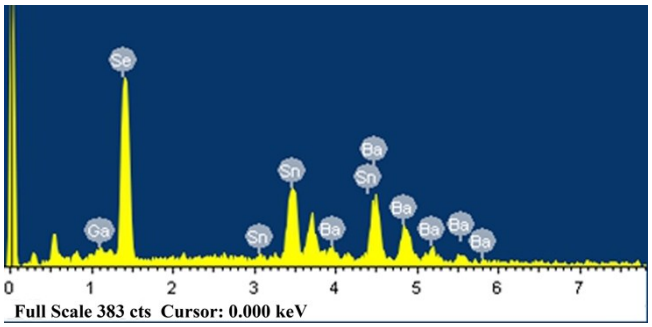

Figure S2a. EDX spectrum of $Ba_8Ga_2Sn_7Se_{18}$, **1**.

Table S4a. The EDX data of $Ba_8Ga_2Sn_7Se_{18}$, **1**.

Point-1				Point-2			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
Ga K	4.18	5.94	2.09	Ga K	3.53	5.23	1.77
Se L	41.36	51.91	18.28	Se L	34.41	44.97	15.21
Sn L	25.26	21.09	7.43	Sn L	27.71	23.47	8.15
Ba L	29.20	21.06	7.42	Ba L	35.05	26.33	8.91
Total	100.00			Total	100.00		
Point-3				Point-4			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
Ga K	4.22	6	2.11	Ga K	3.69	5.18	1.85
Se L	41.59	52.19	18.38	Se L	45.37	56.13	20.06
Sn L	23.89	19.94	7.02	Sn L	22.01	18.11	6.47
Ba L	30.31	21.87	7.70	Ba L	28.93	20.58	7.35
Total	100.00			Total	100.00		
Point-5							
Element	Weight%	Atomic%	Formula	Average formula: $Ba_{7.8(3)}Ga_{1.9(1)}Sn_{7.1(3)}Se_{18.4(8)}$			
Ga K	3.38	4.76	1.69				
Se L	45.22	56.17	19.99				
Sn L	20.99	17.35	6.17				
Ba L	30.41	21.72	7.73				
Total	100.00						

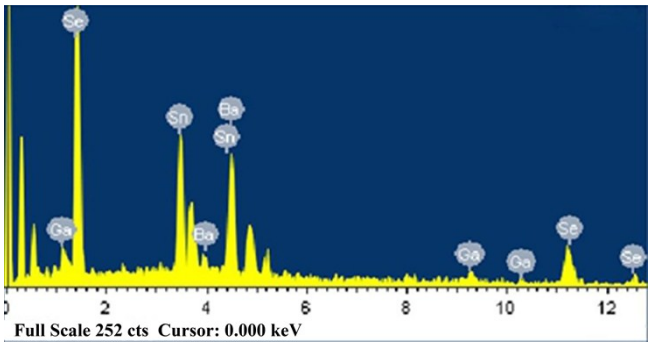

Figure S2b. EDX spectrum of $Ba_{10}Ga_2Sn_9Se_{22}$, **2**.

Table S4b. The EDX data of $Ba_{10}Ga_2Sn_9Se_{22}$, **2**.

Point-1				Point-2			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
Ga K	3.32	4.84	2.06	Ga K	2.82	4.19	1.75
Se L	37.71	48.52	20.62	Se L	34.42	45.17	18.82
Sn L	26.07	22.31	9.48	Sn L	27.71	24.19	10.08
Ba L	32.90	24.33	10.35	Ba L	35.05	26.44	11.02
Total	100.00			Total	100.00		
Point-3				Point-4			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
Ga K	3.42	4.95	2.12	Ga K	3.31	4.64	2.05
Se L	38.74	49.54	21.19	Se L	45.96	56.91	25.13
Sn L	25.80	21.95	9.39	Sn L	20.95	17.25	7.62
Ba L	32.04	23.56	10.08	Ba L	29.79	21.20	9.37
Total	100.00			Total	100.00		
Point-5							
Element	Weight%	Atomic%	Formula	Average formula: $Ba_{10.3(3)}Ga_{2.0(1)}Sn_{8.8(5)}Se_{21.7(9)}$			
Ga K	3.18	4.56	1.97				
Se L	41.80	52.97	22.86				
Sn L	20.82	17.55	7.57				
Ba L	34.20	24.92	10.75				
Total	100.00						

Table S5. The ICP data of $Ba_8Ga_2Sn_7Se_{18}$, **1** and $Ba_{10}Ga_2Sn_9Se_{22}$, **2**.

Compound	Element	Weight %	Formula
$Ba_8Ga_2Sn_7Se_{18}$	Ba	30.39	$Ba_{7.7}Ga_{2.0}Sn_{7.6}Se_{17.5}$
	Ga	4.12	
	Sn	26.14	
	Se	39.50	
$Ba_{10}Ga_2Sn_9Se_{22}$	Ba	33.14	$Ba_{10.4}Ga_{1.9}Sn_{9.7}Se_{20.5}$
	Ga	3.00	
	Sn	26.83	
	Se	37.42	

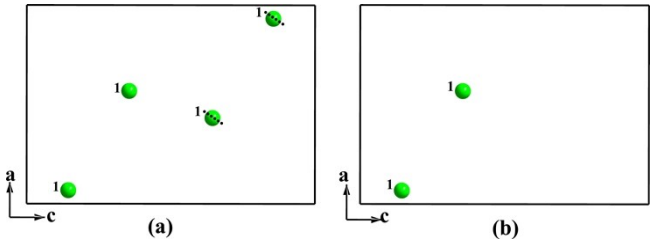

Figure S3. Schematic diagrams of one unit cell of $Ba_8Ga_2Sn_7Se_{18}$, **1** in [010] view. (a) To simulate the fractional occupancies of Sn(1) atoms, half of the partially occupied Sn(1) atoms will be removed and others will be fully occupied in the electronic calculations. The dashed lines mean those atoms will be removed. (b) The unit cell model of constructed for the electronic calculation, where Sn(1) are fully occupied. Only Sn(1) atoms are showing for clarity.

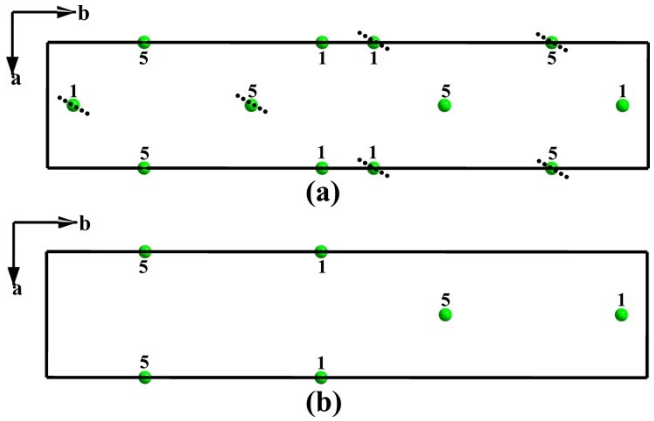

Figure S4. Schematic diagrams of one unit cell of $Ba_{10}Ga_2Sn_9Se_{22}$, **2** in [001] view. (a) The dashed lines mean those atoms will be removed in the electronic calculation because of half occupied Sn(1) and Sn(5) atoms. (b) The unit cell model of constructed for the electronic calculation, where Sn(1) and Sn(5) are fully occupied. Only Sn(1) and Sn(5) atoms are showing for clarity.

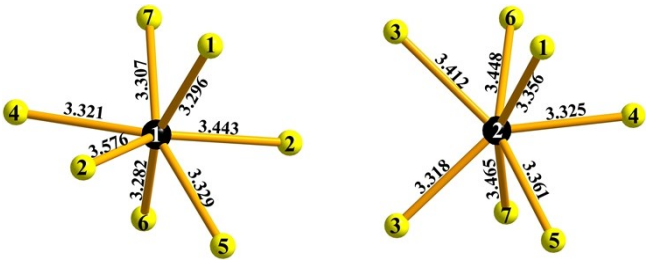

Figure S5. Coordination environments of Ba atoms in $Ba_8Ga_2Sn_7Se_{18}$, **1** with the bond distances marked. Black: Ba; Yellow: Se.

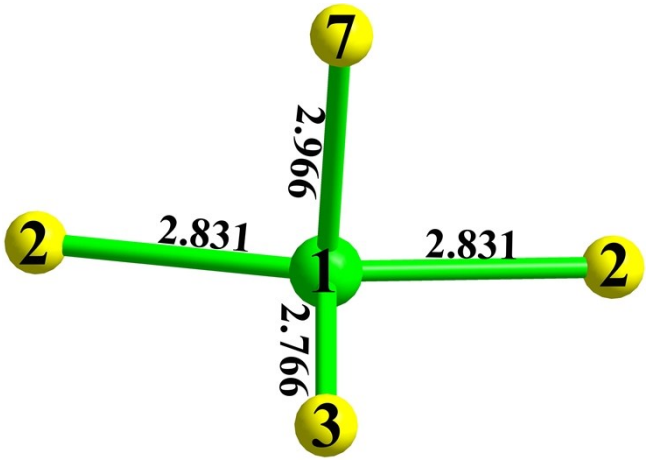

Figure S6. Coordination environments of Sn(1) atom in $Ba_8Ga_2Sn_7Se_{18}$, **1** with the bond distances marked. Green: Sn(1); Yellow: Se.

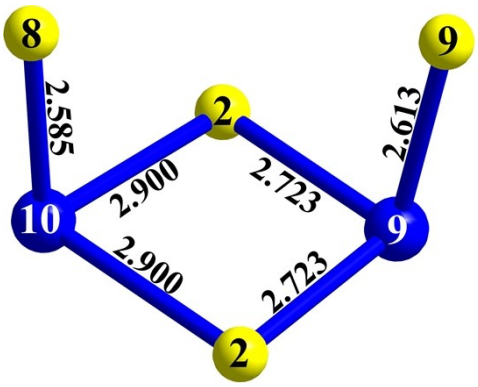

Figure S7. The isolated dimeric [Sn(9)Sn(10)Se_4] unit in $Ba_{10}Ga_2Sn_9Se_{22}$, **2** with the bond distances marked. Blue: Sn; Yellow: Se.

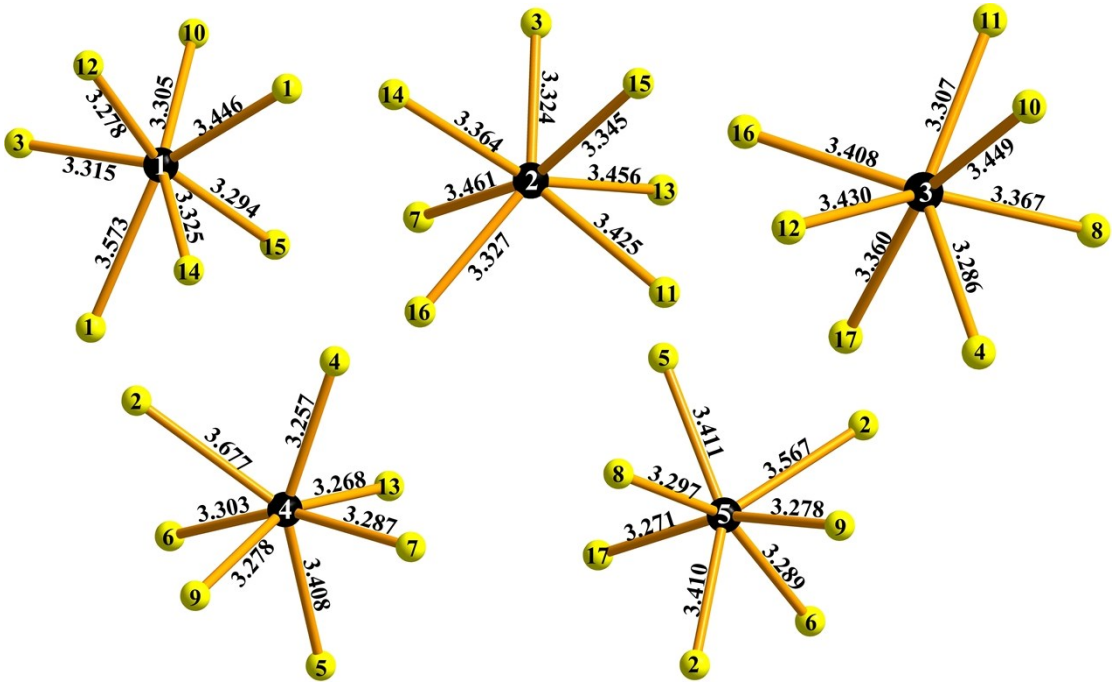

Figure S8. Coordination environments of Ba atoms in $Ba_{10}Ga_2Sn_9Se_{22}$, **2** with the bond distances marked. Black: Ba; Yellow: Se.

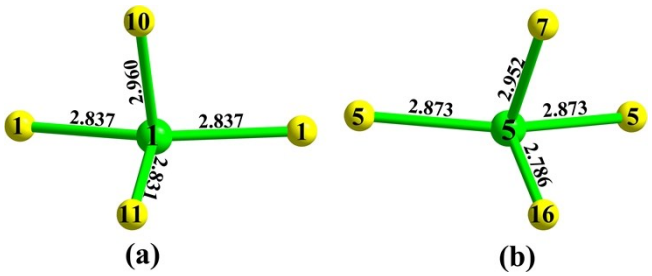

Figure S9. Coordination environments of Sn(1) and Sn(5) atoms in $Ba_{10}Ga_2Sn_9Se_{22}$, **2** with the bond distances marked. Green: Sn; Yellow: Se.

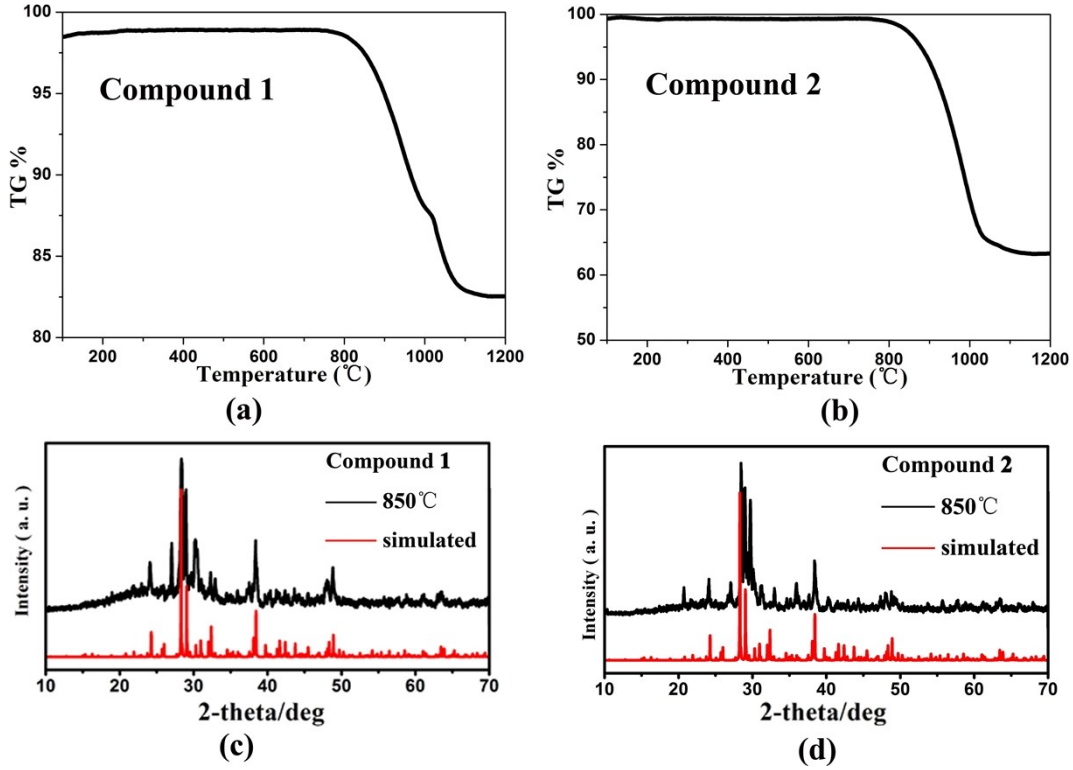

Figure S10. TG curves for $Ba_8Ga_2Sn_7Se_{18}$, **1** (a) and $Ba_{10}Ga_2Sn_9Se_{22}$, **2** (b). Experimental X-ray diffraction patterns heated at 850 °C for $Ba_8Ga_2Sn_7Se_{18}$, **1** (c) and $Ba_{10}Ga_2Sn_9Se_{22}$, **2** (d).

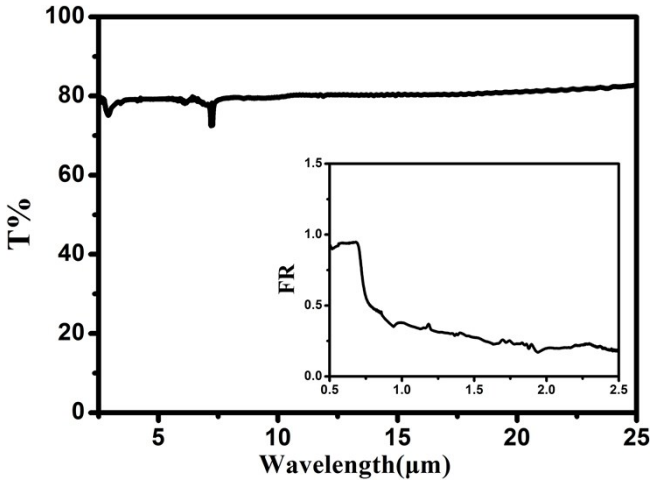

Figure S11. Reflection spectra and FT-IR spectra of $Ba_{10}Ga_2Sn_9Se_{22}$, **2**.

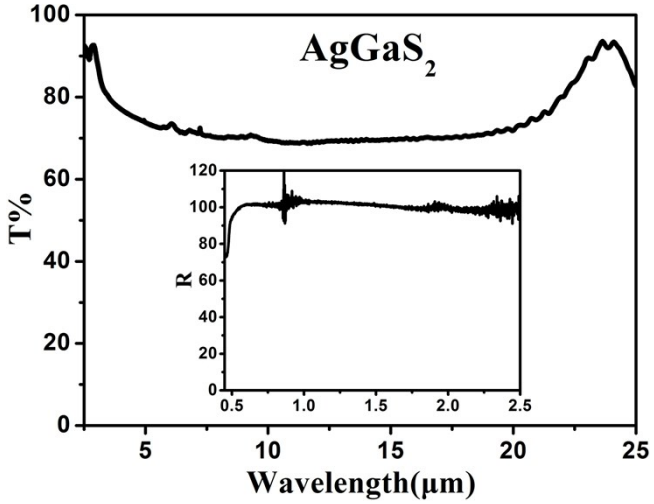

Figure S12. Reflection spectra and FT-IR spectra of $AgGaS_2$.