Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

The Exploration of New Infrared Nonlinear Optical Crystals Based on Polymorphism of $BaGa_4S_7$

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Table S1a. Atomic coordinates and U_{eq} [Å^2] for β-$BaGa_4S_7$.

Atom	***x***	***y***	***z***	U_{eq}	**BVS**
Ba1	0.000000	0.4927(2)	0.39625(9)	0.0241(3)	1.80
Ba2	0.500000	0.86999(16)	0.14096(9)	0.0272(3)	1.78
Ga1	0.24978(8)	1.14517(18)	-0.15007(12)	0.0126(3)	3.08
Ga2	0.37943(7)	0.66207(19)	-0.15468(12)	0.0129(3)	3.03
Ga3	0.11946(7)	1.0108(2)	0.09209(10)	0.0120(3)	3.07
Ga4	0.24919(7)	0.4873(3)	0.10382(11)	0.0122(3)	3.07
S1	0.000000	0.8082(5)	0.1438(4)	0.0133(7)	1.91
S2	0.38529(17)	1.0116(5)	-0.1037(2)	0.0135(6)	1.94
S3	0.11530(18)	1.0143(5)	-0.0983(2)	0.0145(6)	1.94
S4	0.25341(17)	0.8472(4)	0.1536(2)	0.0104(5)	2.17
S5	0.38639(18)	0.3744(4)	0.1576(2)	0.0158(6)	1.95
S6	0.24478(17)	1.5029(4)	-0.0917(2)	0.0114(5)	2.18
S7	0.500000	0.5079(6)	-0.0722(3)	0.0159(8)	1.89
S8	0.11521(18)	1.3504(4)	0.1544(2)	0.0148(6)	1.96

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S1b. Atomic coordinates and U_{eq} [Å^2] for γ-$BaGa_4S_7$.

Atom	***x***	***y***	***z***	U_{eq}	**BVS**
Ba1	0.17944(18)	1.000000	0.8977(5)	0.0228(7)	1.80
Ba2	0.34781(15)	0.500000	0.6578(4)	0.0245(9)	1.74
Ba3	0.51031(16)	1.000000	1.1218(5)	0.0293(9)	1.78
Ga1	0.5398(2)	0.74924(18)	0.7820(6)	0.0102(7)	3.01
Ga2	0.5471(2)	0.61980(18)	0.3094(6)	0.0101(8)	3.03
Ga3	0.70729(17)	0.7509(2)	0.5551(5)	0.0104(9)	3.04
Ga4	0.21459(17)	0.6203(2)	0.0769(5)	0.0105(9)	2.99
Ga5	0.37846(18)	0.8802(3)	0.5285(4)	0.0116(9)	3.02
Ga6	0.37586(15)	0.7510(3)	0.0406(5)	0.0120(9)	2.99
S1	0.3427(4)	0.8845(5)	0.1562(10)	0.0131(16)	1.91
S2	0.6709(4)	0.7448(4)	0.8879(11)	0.0118(13)	1.93
S3	0.6737(4)	0.6160(4)	0.3988(13)	0.0152(14)	1.96
S4	0.3414(3)	0.6137(5)	0.1321(10)	0.0114(15)	1.95
S5	0.5065(3)	0.7542(5)	1.1187(9)	0.0108(15)	1.92
S6	0.8380(3)	0.7543(4)	0.6581(9)	0.0109(15)	2.07
S7	0.5053(3)	0.8850(5)	0.6361(10)	0.0133(17)	2.03
S8	0.6776(4)	0.8861(4)	0.3973(13)	0.0130(14)	1.96
S9	0.5068(4)	0.6145(5)	0.6240(10)	0.0139(17)	1.91
S10	0.5121(5)	0.500000	0.0825(13)	0.012(2)	1.90
S11	0.3383(5)	1.000000	0.6948(13)	0.012(2)	1.98
S12	0.1619(5)	0.500000	-0.1219(14)	0.017(2)	2.09

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S2a. Bond lengths and angles for *β*-$BaGa_4S_7$.

Atom–Atom	Length [Å]
Ba1–S8$^{\#1}$	3.456(3)
Ba1–S8$^{\#2}$	3.456(3)
Ba1–S1$^{\#3}$	3.493(4)
Ba1–S3$^{\#4}$	3.508(3)
Ba1–S3$^{\#5}$	3.508(3)
Ba1–S3$^{\#3}$	3.585(3)
Ba1–S3$^{\#6}$	3.585(3)
Ba1–S1	3.590(4)
Ba1–S6$^{\#4}$	3.599(3)
Ba1–S6$^{\#5}$	3.599(3)
Ba1–S8$^{\#4}$	3.642(3)
Ba1–S8$^{\#5}$	3.642(3)
Ba2–S7	3.395(4)
Ba2–S2	3.479(3)
Ba2–S2$^{\#7}$	3.479(3)
Ba2–S5	3.515(3)
Ba2–S5$^{\#7}$	3.515(3)
Ba2–S2$^{\#8}$	3.553(3)
Ba2–S2$^{\#4}$	3.553(3)
Ba2–S5$^{\#9}$	3.564(3)
Ba2–S5$^{\#10}$	3.564(3)
Ba2–S4$^{\#7}$	3.629(3)
Ba2–S4	3.629(3)
Ga1–S3	2.224(3)
Ga1–S2	2.227(3)
Ga1–S6	2.335(3)
Ga1–S4$^{\#11}$	2.338(3)
Ga2–S7	2.242(3)
Ga2–S5$^{\#12}$	2.248(3)
Ga2–S2	2.262(3)
Ga2–S6$^{\#2}$	2.337(3)
Ga3–S8	2.243(3)
Ga3–S1	2.248(2)
Ga3–S3	2.267(3)
Ga3–S4	2.334(3)
Ga4–S8$^{\#2}$	2.228(3)
Ga4–S5	2.229(3)
Ga4–S4	2.320(3)
Ga4–S6$^{\#2}$	2.330(3)

Atom–Atom–Atom	Angle [°]
S8–Ba1–S8	58.66(9)
S8–Ba1–S1	124.43(7)
S8–Ba1–S1	124.43(7)
S8–Ba1–S3	118.46(7)
S8–Ba1–S3	90.20(6)
S1–Ba1–S3	117.01(7)
S8–Ba1–S3	90.20(6)
S8–Ba1–S3	118.46(7)
S1–Ba1–S3	117.01(7)
S3–Ba1–S3	57.76(9)
S8–Ba1–S3	63.74(6)
S8–Ba1–S3	91.18(7)
S1–Ba1–S3	60.78(7)
S3–Ba1–S3	177.79(9)
S3–Ba1–S3	122.87(7)
S8–Ba1–S3	91.18(7)
S8–Ba1–S3	63.74(6)
S1–Ba1–S3	60.78(7)
S3–Ba1–S3	122.87(7)
S3–Ba1–S3	177.79(9)
S3–Ba1–S3	56.41(9)
S8–Ba1–S1	56.16(6)
S8–Ba1–S1	56.16(6)
S1–Ba1–S1	179.27(9)
S3–Ba1–S1	62.37(7)
S3–Ba1–S1	62.37(7)
S3–Ba1–S1	119.83(7)
S3–Ba1–S1	119.83(7)
S8–Ba1–S6	121.64(7)
S8–Ba1–S6	62.99(6)
S1–Ba1–S6	88.30(4)
S3–Ba1–S6	60.66(6)
S3–Ba1–S6	118.37(6)
S3–Ba1–S6	118.57(6)
S3–Ba1–S6	62.21(6)
S1–Ba1–S6	91.67(4)
S8–Ba1–S6	62.99(6)
S8–Ba1–S6	121.64(7)
S1–Ba1–S6	88.30(4)

S3–Ba1–S6	118.37(6)	S5–Ba2–S2	84.77(7)
S3–Ba1–S6	60.66(6)	S7–Ba2–S2	141.02(7)
S3–Ba1–S6	62.21(6)	S2–Ba2–S2	115.71(6)
S3–Ba1–S6	118.57(6)	S2–Ba2–S2	153.31(3)
S1–Ba1–S6	91.67(4)	S5–Ba2–S2	84.77(7)
S6–Ba1–S6	175.34(9)	S5–Ba2–S2	111.06(7)
S8–Ba1–S8	178.30(4)	S2–Ba2–S2	56.64(9)
S8–Ba1–S8	122.97(8)	S7–Ba2–S5	128.86(7)
S1–Ba1–S8	55.39(6)	S2–Ba2–S5	92.87(7)
S3–Ba1–S8	61.63(6)	S2–Ba2–S5	66.18(7)
S3–Ba1–S8	88.50(7)	S5–Ba2–S5	173.56(9)
S3–Ba1–S8	116.16(7)	S5–Ba2–S5	123.29(8)
S3–Ba1–S8	90.09(7)	S2–Ba2–S5	63.07(7)
S1–Ba1–S8	124.00(7)	S2–Ba2–S5	89.51(7)
S6–Ba1–S8	59.99(6)	S7–Ba2–S5	128.86(7)
S6–Ba1–S8	115.39(6)	S2–Ba2–S5	66.18(7)
S8–Ba1–S8	122.97(8)	S2–Ba2–S5	92.87(7)
S8–Ba1–S8	178.30(4)	S5–Ba2–S5	123.29(8)
S1–Ba1–S8	55.39(6)	S5–Ba2–S5	173.56(9)
S3–Ba1–S8	88.50(7)	S2–Ba2–S5	89.51(7)
S3–Ba1–S8	61.63(6)	S2–Ba2–S5	63.07(7)
S3–Ba1–S8	90.09(7)	S5–Ba2–S5	55.86(9)
S3–Ba1–S8	116.16(7)	S7–Ba2–S4	90.29(4)
S1–Ba1–S8	124.00(7)	S2–Ba2–S4	121.90(6)
S6–Ba1–S8	115.39(6)	S2–Ba2–S4	63.96(6)
S6–Ba1–S8	59.99(6)	S5–Ba2–S4	115.94(6)
S8–Ba1–S8	55.40(8)	S5–Ba2–S4	59.28(6)
S7–Ba2–S2	62.79(7)	S2–Ba2–S4	59.93(6)
S7–Ba2–S2	62.79(7)	S2–Ba2–S4	116.50(6)
S2–Ba2–S2	57.96(9)	S5–Ba2–S4	64.19(6)
S7–Ba2–S5	57.23(7)	S5–Ba2–S4	119.99(6)
S2–Ba2–S5	92.28(7)	S7–Ba2–S4	90.29(4)
S2–Ba2–S5	120.00(7)	S2–Ba2–S4	63.96(6)
S7–Ba2–S5	57.23(7)	S2–Ba2–S4	121.90(6)
S2–Ba2–S5	120.00(7)	S5–Ba2–S4	59.28(6)
S2–Ba2–S5	92.28(7)	S5–Ba2–S4	115.94(6)
S5–Ba2–S5	56.70(8)	S2–Ba2–S4	116.50(6)
S7–Ba2–S2	141.02(7)	S2–Ba2–S4	59.93(6)
S2–Ba2–S2	153.31(3)	S5–Ba2–S4	119.99(6)
S2–Ba2–S2	115.71(6)	S5–Ba2–S4	64.19(6)
S5–Ba2–S2	111.06(7)	S4–Ba2–S4	173.46(8)

S3–Ga1–S2	126.04(14)	S8–Ga3–S1	114.66(12)
S3–Ga1–S6	103.84(11)	S8–Ga3–S3	108.69(12)
S2–Ga1–S6	108.11(11)	S1–Ga3–S3	104.98(14)
S3–Ga1–S4	107.74(11)	S8–Ga3–S4	109.36(10)
S2–Ga1–S4	103.59(11)	S1–Ga3–S4	109.11(11)
S6–Ga1–S4	106.19(10)	S3–Ga3–S4	109.92(11)
S7–Ga2–S5	110.85(13)	S8–Ga4–S5	126.93(13)
S7–Ga2–S2	105.36(12)	S8–Ga4–S4	108.93(10)
S5–Ga2–S2	111.24(11)	S5–Ga4–S4	101.95(10)
S7–Ga2–S6	110.28(12)	S8–Ga4–S6	105.14(11)
S5–Ga2–S6	108.34(11)	S5–Ga4–S6	108.99(11)
S2–Ga2–S6	110.77(10)	S4–Ga4–S6	102.45(10)

Symmetry transformations used to generate equivalent atoms:

#1: -X, -1+Y, +Z; #2: +X, -1+Y, +Z; #3: -X, 1-Y, 0.5+Z; #4: +X, 2-Y, 0.5+Z; #5: -X, 2-Y, 0.5+Z; #6: +X, 1-Y, 0.5+Z; #7: 1-X, +Y, +Z; #8: 1-X, 2-Y, 0.5+Z; #9: 1-X, 1+Y, +Z; #10: +X, 1+Y, +Z; #11: +X, 2-Y, -0.5+Z; #12: +X, 1-Y, -0.5+Z; #13: -X, +Y, +Z; #14: -X, 1-Y, -0.5+Z; #15: 1-X, 2-Y, -0.5+Z; #16: -X, 2-Y, -0.5+Z;

Table S2b. Bond lengths and angles for *γ*-$BaGa_4S_7$.

Atom–Atom	Length [Å]
Ba1–S11	3.445(9)
Ba1–S1$^{\#1}$	3.484(8)
Ba1–S1$^{\#2}$	3.484(7)
Ba1–S3$^{\#3}$	3.526(8)
Ba1–S3$^{\#4}$	3.526(8)
Ba1–S10$^{\#5}$	3.529(10)
Ba1–S3$^{\#5}$	3.582(7)
Ba1–S3$^{\#6}$	3.582(7)
Ba1–S2$^{\#3}$	3.606(6)
Ba1–S2$^{\#4}$	3.606(6)
Ba1–S9$^{\#3}$	3.630(8)
Ba1–S9$^{\#4}$	3.630(8)
Ba2–S9	3.419(7)
Ba2–S9$^{\#7}$	3.419(7)
Ba2–S4$^{\#2}$	3.422(6)
Ba2–S4$^{\#8}$	3.422(6)
Ba2–S10$^{\#2}$	3.500(8)
Ba2–S8$^{\#9}$	3.572(8)
Ba2–S8$^{\#3}$	3.572(8)
Ba2–S6$^{\#9}$	3.620(7)
Ba2–S6$^{\#3}$	3.620(7)
Ba2–S4	3.654(6)
Ba2–S4$^{\#7}$	3.654(6)
Ba3–S7$^{\#10}$	3.449(7)
Ba3–S7	3.449(7)
Ba3–S12$^{\#11}$	3.475(10)
Ba3–S8$^{\#1}$	3.557(8)
Ba3–S8$^{\#2}$	3.557(8)
Ba3–S1$^{\#2}$	3.565(8)
Ba3–S1$^{\#1}$	3.565(8)
Ba3–S11	3.605(9)
Ba3–S5	3.619(7)
Ba3–S5$^{\#10}$	3.619(7)
Ba3–S7$^{\#1}$	3.644(6)
Ba3–S7$^{\#2}$	3.644(6)
Ga1–S7	2.223(7)
Ga1–S9	2.232(8)
Ga1–S5	2.323(7)
Ga1–S2	2.337(7)
Ga2–S10	2.254(6)
Ga2–S3	2.255(7)
Ga2–S9	2.256(8)
Ga2–S5$^{\#12}$	2.335(7)
Ga3–S8	2.228(7)
Ga3–S3	2.231(7)
Ga3–S2	2.327(8)
Ga3–S6	2.330(6)
Ga4–S12	2.242(6)
Ga4–S8$^{\#3}$	2.259(9)
Ga4–S4	2.271(7)
Ga4–S2$^{\#13}$	2.349(7)
Ga5–S1	2.254(6)
Ga5–S11	2.257(6)
Ga5–S7	2.263(7)
Ga5–S6$^{\#3}$	2.326(6)
Ga6–S1	2.228(6)
Ga6–S4	2.233(6)
Ga6–S6$^{\#13}$	2.317(6)
Ga6–S5$^{\#12}$	2.328(6)

Atom–Atom–Atom	Angle [°]
S11–Ba1–S1	57.33(17)
S11–Ba1–S1	57.33(17)
S1–Ba1–S1	58.4(3)
S11–Ba1–S3	61.64(17)
S1–Ba1–S3	118.95(19)
S1–Ba1–S3	90.64(17)
S11–Ba1–S3	61.64(17)
S1–Ba1–S3	90.64(17)
S1–Ba1–S3	118.95(19)
S3–Ba1–S3	58.0(2)
S11–Ba1–S10	177.6(2)
S1–Ba1–S10	124.61(18)
S1–Ba1–S10	124.61(18)
S3–Ba1–S10	116.34(17)
S3–Ba1–S10	116.34(17)
S11–Ba1–S3	121.65(17)
S1–Ba1–S3	64.33(16)
S1–Ba1–S3	91.84(17)

S3–Ba1–S3	176.7(2)	S3–Ba1–S9	61.54(16)
S3–Ba1–S3	122.43(18)	S10–Ba1–S9	54.83(16)
S10–Ba1–S3	60.35(16)	S3–Ba1–S9	89.00(17)
S11–Ba1–S3	121.65(17)	S3–Ba1–S9	115.17(17)
S1–Ba1–S3	91.84(17)	S2–Ba1–S9	115.24(15)
S1–Ba1–S3	64.33(16)	S2–Ba1–S9	59.93(15)
S3–Ba1–S3	122.43(18)	S9–Ba1–S9	55.3(2)
S3–Ba1–S3	176.7(2)	S9–Ba2–S9	59.1(2)
S10–Ba1–S3	60.35(16)	S9–Ba2–S4	91.10(15)
S3–Ba1–S3	57.0(2)	S9–Ba2–S4	120.07(17)
S11–Ba1–S2	91.77(10)	S9–Ba2–S4	120.07(17)
S1–Ba1–S2	121.62(16)	S9–Ba2–S4	91.10(15)
S1–Ba1–S2	63.21(16)	S4–Ba2–S4	58.5(2)
S3–Ba1–S2	60.60(15)	S9–Ba2–S10	56.91(17)
S3–Ba1–S2	118.50(14)	S9–Ba2–S10	56.91(17)
S10–Ba1–S2	88.16(10)	S4–Ba2–S10	63.22(16)
S3–Ba1–S2	118.74(14)	S4–Ba2–S10	63.22(16)
S3–Ba1–S2	61.84(15)	S9–Ba2–S8	150.34(18)
S11–Ba1–S2	91.77(10)	S9–Ba2–S8	113.96(17)
S1–Ba1–S2	63.21(16)	S4–Ba2–S8	114.47(19)
S1–Ba1–S2	121.62(16)	S4–Ba2–S8	87.43(17)
S3–Ba1–S2	118.50(14)	S10–Ba2–S8	147.49(14)
S3–Ba1–S2	60.60(15)	S9–Ba2–S8	113.96(17)
S10–Ba1–S2	88.16(10)	S9–Ba2–S8	150.34(18)
S3–Ba1–S2	61.84(15)	S4–Ba2–S8	87.43(17)
S3–Ba1–S2	118.74(14)	S4–Ba2–S8	114.47(19)
S2–Ba1–S2	175.1(2)	S10–Ba2–S8	147.49(14)
S11–Ba1–S9	123.18(19)	S8–Ba2–S8	56.0(2)
S1–Ba1–S9	178.45(19)	S9–Ba2–S6	122.37(15)
S1–Ba1–S9	123.14(15)	S9–Ba2–S6	63.31(16)
S3–Ba1–S9	61.54(16)	S4–Ba2–S6	118.42(15)
S3–Ba1–S9	88.46(17)	S4–Ba2–S6	59.96(15)
S10–Ba1–S9	54.83(16)	S10–Ba2–S6	91.91(9)
S3–Ba1–S9	115.17(17)	S8–Ba2–S6	59.55(13)
S3–Ba1–S9	89.00(17)	S8–Ba2–S6	115.55(14)
S2–Ba1–S9	59.93(15)	S9–Ba2–S6	63.31(16)
S2–Ba1–S9	115.24(15)	S9–Ba2–S6	122.37(15)
S11–Ba1–S9	123.18(19)	S4–Ba2–S6	59.96(15)
S1–Ba1–S9	123.14(15)	S4–Ba2–S6	118.42(15)
S1–Ba1–S9	178.45(19)	S10–Ba2–S6	91.91(9)
S3–Ba1–S9	88.46(17)	S8–Ba2–S6	115.55(13)

S8–Ba2–S6	59.55(13)	S1–Ba3–S1	57.0(2)
S6–Ba2–S6	174.31(19)	S7–Ba3–S11	61.25(16)
S9–Ba2–S4	64.09(14)	S7–Ba3–S11	61.25(16)
S9–Ba2–S4	90.82(15)	S12–Ba3–S11	109.2(2)
S4–Ba2–S4	123.3(2)	S8–Ba3–S11	148.96(13)
S4–Ba2–S4	175.80(19)	S8–Ba3–S11	148.96(13)
S10–Ba2–S4	120.90(16)	S1–Ba3–S11	55.23(15)
S8–Ba2–S4	88.38(16)	S1–Ba3–S11	55.23(15)
S8–Ba2–S4	62.72(16)	S7–Ba3–S5	119.32(15)
S6–Ba2–S4	117.83(15)	S7–Ba3–S5	60.54(14)
S6–Ba2–S4	63.40(14)	S12–Ba3–S5	90.82(9)
S9–Ba2–S4	90.82(15)	S8–Ba3–S5	119.18(14)
S9–Ba2–S4	64.09(14)	S8–Ba3–S5	62.90(14)
S4–Ba2–S4	175.80(19)	S1–Ba3–S5	60.50(15)
S4–Ba2–S4	123.3(2)	S1–Ba3–S5	117.46(15)
S10–Ba2–S4	120.90(16)	S11–Ba3–S5	89.06(9)
S8–Ba2–S4	62.72(16)	S7–Ba3–S5	60.54(14)
S8–Ba2–S4	88.38(16)	S7–Ba3–S5	119.32(15)
S6–Ba2–S4	63.40(14)	S12–Ba3–S5	90.81(9)
S6–Ba2–S4	117.83(15)	S8–Ba3–S5	62.90(14)
S4–Ba2–S4	54.5(2)	S8–Ba3–S5	119.17(14)
S7–Ba3–S7	58.8(2)	S1–Ba3–S5	117.46(15)
S7–Ba3–S12	58.11(15)	S1–Ba3–S5	60.50(15)
S7–Ba3–S12	58.11(15)	S11–Ba3–S5	89.06(9)
S7–Ba3–S8	91.68(17)	S5–Ba3–S5	177.84(19)
S7–Ba3–S8	119.49(19)	S7–Ba3–S7	122.8(2)
S12–Ba3–S8	61.44(18)	S7–Ba3–S7	176.66(18)
S7–Ba3–S8	119.49(19)	S12–Ba3–S7	125.18(17)
S7–Ba3–S8	91.68(17)	S8–Ba3–S7	63.77(17)
S12–Ba3–S8	61.44(18)	S8–Ba3–S7	89.78(18)
S8–Ba3–S8	56.3(2)	S1–Ba3–S7	87.95(15)
S7–Ba3–S1	116.47(17)	S1–Ba3–S7	61.39(14)
S7–Ba3–S1	88.71(16)	S11–Ba3–S7	116.50(15)
S12–Ba3–S1	144.99(15)	S5–Ba3–S7	117.69(14)
S8–Ba3–S1	148.5(2)	S5–Ba3–S7	62.33(14)
S8–Ba3–S1	113.77(17)	S7–Ba3–S7	176.66(18)
S7–Ba3–S1	88.71(16)	S7–Ba3–S7	122.8(2)
S7–Ba3–S1	116.47(17)	S12–Ba3–S7	125.18(16)
S12–Ba3–S1	144.99(15)	S8–Ba3–S7	89.78(18)
S8–Ba3–S1	113.77(17)	S8–Ba3–S7	63.77(17)
S8–Ba3–S1	148.5(2)	S1–Ba3–S7	61.39(14)

S1–Ba3–S7	87.95(15)	S3–Ga3–S6	107.3(3)
S11–Ba3–S7	116.50(16)	S2–Ga3–S6	104.6(3)
S5–Ba3–S7	62.33(15)	S12–Ga4–S8	105.9(3)
S5–Ba3–S7	117.69(14)	S12–Ga4–S4	109.8(3)
S7–Ba3–S7	55.4(2)	S8–Ga4–S4	112.2(3)
S7–Ga1–S9	126.7(3)	S12–Ga4–S2	109.9(3)
S7–Ga1–S5	103.3(3)	S8–Ga4–S2	109.8(3)
S9–Ga1–S5	108.9(3)	S4–Ga4–S2	109.0(3)
S7–Ga1–S2	108.2(3)	S1–Ga5–S11	113.8(3)
S9–Ga1–S2	104.5(3)	S1–Ga5–S7	109.1(2)
S5–Ga1–S2	102.9(3)	S11–Ga5–S7	105.4(3)
S10–Ga2–S3	104.9(3)	S1–Ga5–S6	110.1(2)
S10–Ga2–S9	114.4(3)	S11–Ga5–S6	109.8(2)
S3–Ga2–S9	108.5(3)	S7–Ga5–S6	108.4(2)
S10–Ga2–S5	109.6(3)	S1–Ga6–S4	126.9(2)
S3–Ga2–S5	109.3(3)	S1–Ga6–S6	109.0(2)
S9–Ga2–S5	109.9(3)	S4–Ga6–S6	101.5(2)
S8–Ga3–S3	126.1(4)	S1–Ga6–S5	105.2(2)
S8–Ga3–S2	109.6(3)	S4–Ga6–S5	107.8(2)
S3–Ga3–S2	104.2(3)	S6–Ga6–S5	104.7(2)
S8–Ga3–S6	103.2(3)		

Symmetry transformations used to generate equivalent atoms:

#1: +X, 2-Y, 1+Z; #2: +X, +Y, 1+Z; #3: -0.5+X, 1.5-Y, +Z; #4: -0.5+X, 0.5+Y, +Z; #5: -0.5+X, 0.5+Y, 1+Z; #6: -0.5+X, 1.5-Y, 1+Z; #7: +X, 1-Y, +Z; #8: +X, 1-Y, 1+Z; #9: -0.5+X, -0.5+Y, +Z; #10: +X, 2-Y, +Z; #11: 0.5+X, 0.5+Y, 1+Z; #12: +X, +Y, -1+Z; #13: -0.5+X, 1.5-Y, -1+Z; #14: 0.5+X, 1.5-Y, 1+Z; #15: 0.5+X, -0.5+Y, +Z; #16: 0.5+X, -0.5+Y, -1+Z; #17: 0.5+X, 1.5-Y, +Z; #18: 0.5+X, 0.5+Y, +Z; #19: -0.5+X, -0.5+Y, -1+Z;

Table S3a. Selected Bond Lengths, Experimental Bond Valences, Theoretical Bond Valences, Bond Valence Sums, and BSI and GII Indices for α-$BaGa_4S_7$.

							$V_i=\sum_i S_{ij}$
		Ba1		Ga1		Ga2	$z_i=\sum_i s_{ij}$
S1	R_{ij} (Å)	3.4358×2	3.6673×2	2.2317		2.2711	
	S_{ij} (vu)	0.1766	0.1179	0.8011		0.7384	1.9282
	s_{ij} (vu)	0.1623	0.1623	0.8053		0.6895	2
S2	R_{ij} (Å)	3.6264×2		2.334	2.3357	2.3215	
	S_{ij} (vu)	0.1266		0.6481	0.6459	0.6652	2.2009
	s_{ij} (vu)	0.0158		0.6947	0.6947	0.5789	2
S3	R_{ij} (Å)	3.5136×2	3.5714×2	2.2284		2.2586	
	S_{ij} (vu)	0.1542	0.1394	0.8065		0.7577	1.9268
	s_{ij} (vu)	0.1263	0.1263	0.8053		0.6895	2
S4	R_{ij} (Å)	3.4209×2				2.2567	
	S_{ij} (vu)	0.1813				0.7606	1.9035
	s_{ij} (vu)	0.4789				1.0421	2
$V_j=\sum_j S_{ij}$		1.8104		3.041		3.0615	BSI=0.124
$z_j=\sum_j S_{ij}$		2		3		3	GII=0.120

Table S3b. Selected Bond Lengths, Experimental Bond Valences, Theoretical Bond Valences, Bond Valence Sums, and BSI and GII Indices for *β*-$BaGa_4S_7$.

										$V_i=\sum_i S_{ij}$
		Ba1		Ba2		Ga1	Ga2	Ga3	Ga4	$z_i=\sum_i s_{ij}$
S1	R_{ij} (Å)	3.5904×2						2.2477		
	S_{ij} (vu)	0.1349						0.775		1.91
	s_{ij} (vu)	0.4771						1.0459		2
S2	R_{ij} (Å)			3.5530×2	3.4787×2	2.2272	2.2617			
	S_{ij} (vu)			0.144	0.1639	0.8085	0.7528			1.94
	s_{ij} (vu)			0.1463	0.1463	0.7974	0.6173			2
S3	R_{ij} (Å)	3.5846×2	3.5076×2			2.2243		2.2672		
	S_{ij} (vu)	0.1362	0.1558			0.8134		0.7443		1.94
	s_{ij} (vu)	0.1244	0.1244			0.8091		0.6932		2
S4	R_{ij} (Å)			3.6289×2		2.338		2.334	2.3201	
	S_{ij} (vu)			0.1261		0.6428		0.6482	0.6672	2.18
	s_{ij} (vu)			0.0325		0.6836		0.5677	0.6836	2
S5	R_{ij} (Å)			3.5635×2	3.5149×2		2.2481		2.229	
	S_{ij} (vu)			0.1413	0.1539		0.7743		0.8056	1.95
	s_{ij} (vu)			0.1463	0.1463		0.6173		0.7974	2
S6	R_{ij} (Å)	3.5994×2				2.3353	2.3365		2.33	
	S_{ij} (vu)	0.1328				0.6464	0.6448		0.6535	2.19
	s_{ij} (vu)	0.0252				0.7099	0.5298		0.7099	2
S7	R_{ij} (Å)			3.3952			2.2416			
	S_{ij} (vu)			0.1896			0.7849			1.89
	s_{ij} (vu)			0.7645			1.2355			2
S8	R_{ij} (Å)	3.4559×2	3.6416×2					2.2425	2.2279	
	S_{ij} (vu)	0.1706	0.1233					0.7833	0.8075	1.96
	s_{ij} (vu)	0.1244	0.1244					0.6932	0.8091	2
$V_j=\sum_i S_{ij}$		1.7986		1.7754		3.0306	3.0797	3.0881	3.0741	BSI=0.158
$z_j=\sum_i S_{ij}$		2		2		3	3	3	3	GII=0.123

Table S3c. Selected Bond Lengths, Experimental Bond Valences, Theoretical Bond Valences, Bond Valence Sums, and BSI and GII Indices for *γ*-$BaGa_4S_7$.

														$V_i=\sum_j S_{ij}$
		Ba1		Ba2		Ba3		Ga1	Ga2	Ga3	Ga4	Ga5	Ga6	$z_i=\sum_j s_{ij}$
S1	R_{ij} (Å)	3.4826×2				3.563×2						2.2494	2.2286	
	S_{ij} (vu)	0.1628				0.1415						0.7722	0.8062	1.88
	s_{ij} (vu)	0.1594				0.0894						0.6873	0.8151	2
S2	R_{ij} (Å)	3.608×2						2.3368		2.3314	2.3453			
	S_j (vu)	0.1308						0.6444		0.6517	0.6332			2.06
	s_{ij} (vu)	0						0.6617		0.7496	0.5887			2
S3	R_{ij} (Å)	3.5328×2	3.5762×2						2.2562	2.2334				
	S_{ij} (vu)	0.1491	0.1382						0.7614	0.7983				1.86
	s_{ij} (vu)	0.1149	0.1149						0.676	0.8645				2
S4	R_{ij} (Å)			3.6494×2	3.4227×2						2.2638		2.2391	
	S_{ij} (vu)			0.1217	0.1807						0.7495		0.7889	1.78
	s_{ij} (vu)			0.1633	0.1633						0.5589		0.7878	2
S5	R_{ij} (Å)					3.6216×2		2.3227	2.3353				2.3326	
	S_{ij} (vu)					0.1277		0.6636	0.6464				0.6501	2.09
	s_{ij} (vu)					-0.0177		0.714	0.6134				0.708	2
S6	R_{ij} (Å)			3.6204×2						2.3324		2.3229	2.3217	
	S_{ij} (vu)			0.128						0.6503		0.6632	0.6649	2.11
	s_{ij} (vu)			0.0645						0.621		0.5611	0.689	2
S7	R_{ij} (Å)					3.4545×2	3.6409×2	2.2208				2.2636		
	S_{ij} (vu)					0.171	0.1235	0.8194				0.7498		1.91
	s_{ij} (vu)					0.1117	0.1117	0.8435				0.7096		2
S8	R_{ij} (Å)			3.5715×2		3.5565×2				2.2266	2.2592			
	S_{ij} (vu)			0.1394		0.1431				0.8096	0.7567			1.85
	s_{ij} (vu)			0.2084		0.1072				0.7649	0.604			2
S9	R_{ij} (Å)	3.6333×2		3.4226×2				2.2324	2.2495					
	S_{ij} (vu)	0.1251		0.1808				0.8	0.7721					1.88
	s_{ij} (vu)	0.1191		0.1503				0.7808	0.6802					2
S10	R_{ij} (Å)	3.5254		3.5041					2.2546					
	S_{ij} (vu)	0.1511		0.1568					0.764					1.84
	s_{ij} (vu)	0.4692		0.5004					1.0303					2
S11	R_{ij} (Å)	3.4508				3.609						2.2515		
	S_{ij} (vu)	0.1721				0.1306						0.7689		1.84
	s_{ij} (vu)	0.5141				0.444						1.0419		2
S12	R_{ij} (Å)	3.4826×2				3.4854					2.2412			
	S_{ij} (vu)	0.1628				0.162					0.7855			1.90
	s_{ij} (vu)	0.1594				0.7516					1.2484			2
$V_j=\sum_i S_{ij}$		1.8032		1.795		1.7782		3.0701	3.0826	3.0321	3.0469	3.0945	3.0456	BSI=0.161
$z_j=\sum_i S_{ij}$		2		2		2		3	3	3	3	3	3	GII=0.133

Table S4a. Summary of the mode decomposition of α-$BaGa_4S_7$, indicating the amplitudes (Å) of all intervening irrep distortion components.

Irrep	Isotropy Subgroup	Dimension	Amplitude (Å)
Γ_1^+	*Pmmn* (No. 59)	12	0.4656
Γ_4^-	$Pmn2_1$ (No. 31)	7	1.4766

Table S4b. Summary of the mode decomposition of *β*-$BaGa_4S_7$, indicating the amplitudes (Å) of all intervening irrep distortion components.

Irrep	Isotropy Subgroup	Dimension	Amplitude (Å)
Γ_1^+	*Pnma* (No. 62)	19	9.1434
Γ_3^-	$Pmc2_1$ (No. 26)	19	8.2889

Table S5a. Occupied Wyckoff positions and site-symmetries for the paraelectric centrosymmetric α-$BaGa_4S_7$ structure in space group *Pmmn*.

Atom	Wyckoff Site	x	y	z
Ba(1)	2*a*	0.750000	0.750000	0.836820
Ga(1)	4*f*	0.496910	0.750000	0.189080
Ga(2)	4*f*	0.369250	0.750000	0.676620
S(1)	4*f*	0.637330	0.750000	0.311330
S(2)	4*f*	0.510390	0.750000	0.821230
S(3)	4*f*	0.354730	0.750000	0.318150
S(4)	2*b*	0.250000	0.750000	0.899810

Table S5b. Occupied Wyckoff positions and site-symmetries for the paraelectric centrosymmetric *β*-$BaGa_4S_7$ structure in space group *Pnma*.

Atom	Wyckoff Site	x	y	z
Ba(1)	4*c*	0.607250	0.250000	0.837830
Ga(1)	8*d*	0.093120	0.507520	0.311060
Ga(2)	8*d*	0.072610	0.635170	0.825950
S(1)	4*c*	0.368870	0.250000	0.113230
S(2)	8*d*	0.140810	0.642620	0.166960
S(3)	8*d*	0.122590	0.365530	0.180370

Table S6a. Atomic displacement in the distortion of the α-$BaGa_4S_7$.

WP		Atom	Atomic Displacements			
			$\mathbf{u_x}$	$\mathbf{u_y}$	$\mathbf{u_z}$	$\mathbf{\lvert u \rvert}$
2a	(0,y,z)	Ba1	0	0.0056	0.0236	0.14
4b	(x,y,z)	Ga1	0.0016	0.0013	-0.0627	0.37
4b	(x,y,z)	Ga2	0.0003	0.0041	-0.0794	0.47
4b	(x,y,z)	S1	-0.0024	0.0012	0.0372	0.22
4b	(x,y,z)	S2	-0.0066	-0.0065	0.0443	0.28
4b	(x,y,z)	S3	0.0091	-0.0075	0.0289	0.22
2a	(0,y,z)	S4	0	0.032	0.0402	0.31

Table S6b. Atomic displacement in the distortion of the *β*-$BaGa_4S_7$.

WP		Atom	Atomic Displacements			
			$\mathbf{u_x}$	$\mathbf{u_y}$	$\mathbf{u_z}$	**|u|**
2a	(0,y,z)	Ba1	0	-0.0951	-0.0541	0.87
2b	(1/2,y,z)	Ba1_2	0	0.0422	-0.0949	1.16
4c	(x,y,z)	Ga1	-0.1381	-0.0503	0.1558	2.76
4c	(x,y,z)	Ga1_2	0.1369	-0.2231	0.0953	2.69
4c	(x,y,z)	Ga2	-0.136	-0.0887	0.1881	3.05
4c	(x,y,z)	Ga2_2	0.1349	-0.2211	0.0794	2.59
2a	(0,y,z)	S1	0	-0.055	-0.0682	0.88
2b	(1/2,y,z)	S1_2	0	0.1447	-0.0465	1.05
4c	(x,y,z)	S2	-0.0073	0.0946	-0.0876	1.20
4c	(x,y,z)	S2_2	0.0078	-0.0666	-0.0479	0.71
4c	(x,y,z)	S3	-0.0002	0.0839	-0.064	0.92
4c	(x,y,z)	S3_2	0.0019	-0.056	-0.0629	0.82
4c	(x,y,z)	S4	-0.0047	-0.0828	-0.0755	1.03
4c	(x,y,z)	S4_2	0.0029	0.0729	-0.0488	0.73

Figure S1. The Powder XRD patterns of β-$BaGa_4S_7$.

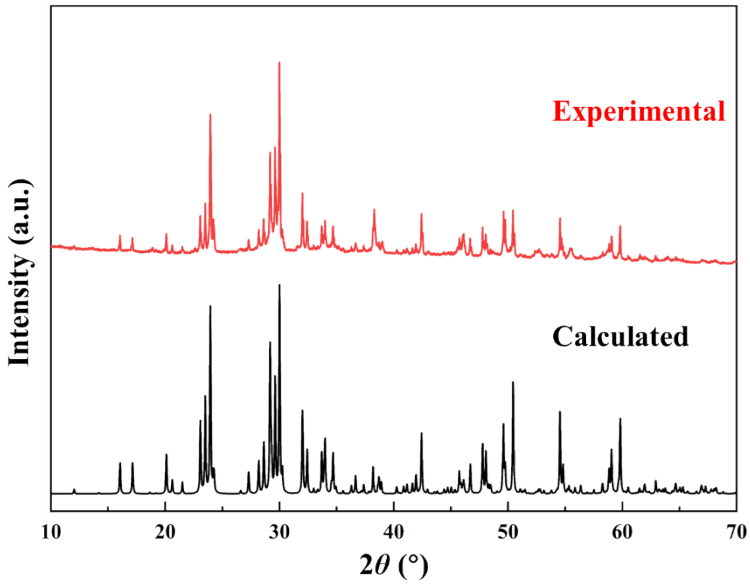
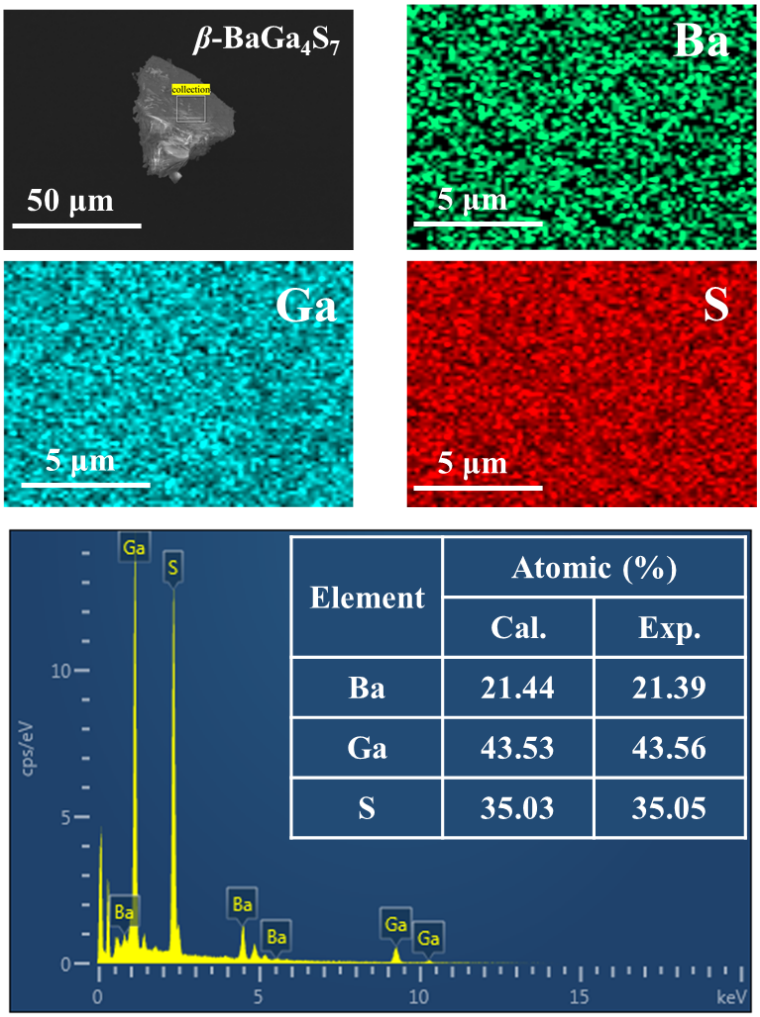
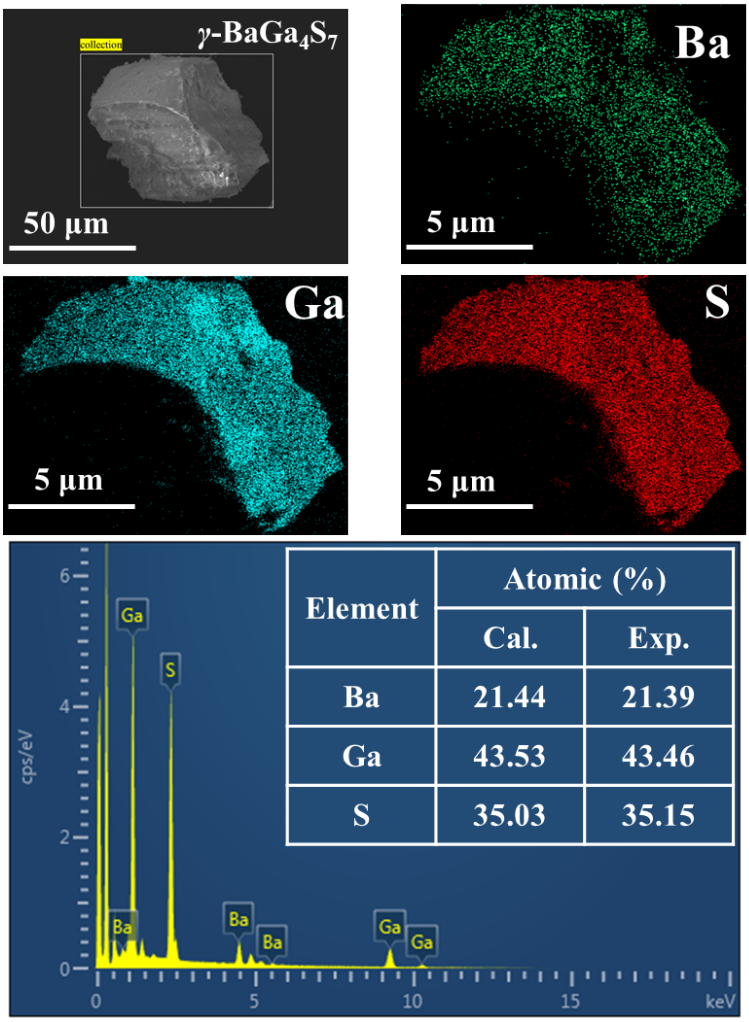


Figure S2a. The EDS spectra of *β*-$BaGa_4S_7$.



Element	Atomic (%)	
	Cal.	Exp.
Ba	21.44	21.39
Ga	43.53	43.56
S	35.03	35.05

Figure 2b. The EDS spectra of *γ*-$BaGa_4S_7$.



Element	Atomic (%)	
	Cal.	Exp.
Ba	21.44	21.39
Ga	43.53	43.46
S	35.03	35.15

Figure S3. the coordination of Ba atoms in the *α*-, *β*- and *γ*-$BaGa_4S_7$.

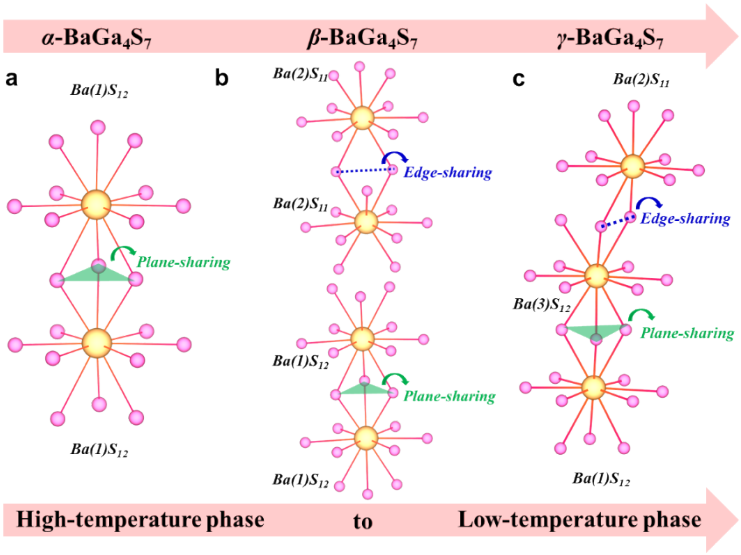


Figure S4a. Comparison between the centrosymmetric (*Pmmn*) and non-centrosymmetric ($Pmn2_1$) structures projected down the *a*-axis, **a** and **e**, the *b*-axis, **b** and **f**, and the c-axis, **c** and **g**, respectively.

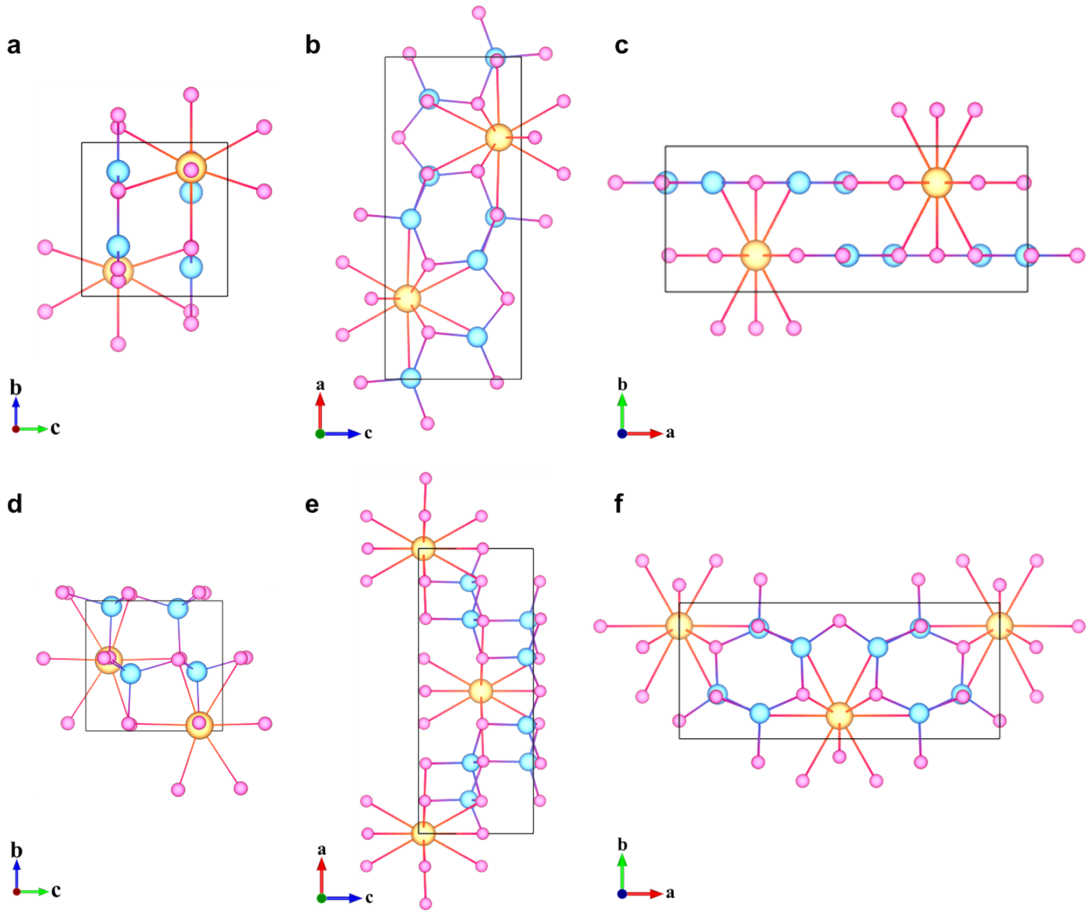


Figure S4b. Comparison between the centrosymmetric (*Pnma*) and non-centrosymmetric ($Pmc2_1$) structures projected down the a-axis, **a** and **e**, the *b*-axis, **f** and **g**, and the c-axis, **c** and **d**, respectively.

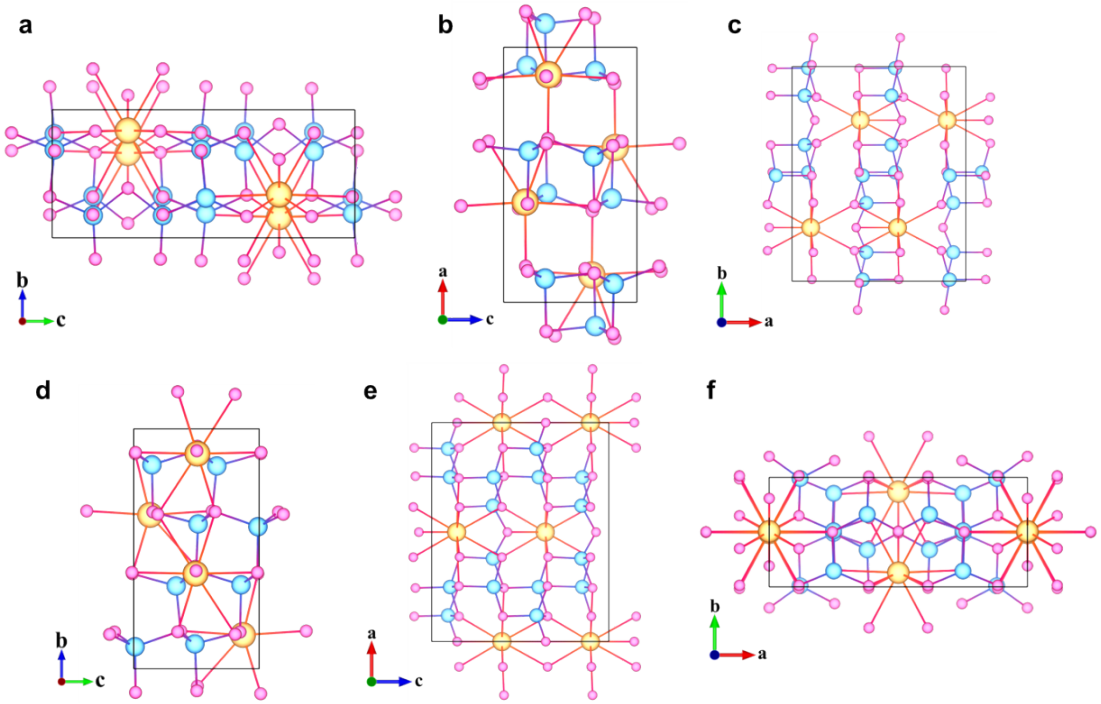


Figure S5a. Atomic displacements patterns from the centrosymmetric (top column) to polar *α*-$BaGa_4S_7$ structure (bottom column) for atoms belonging to the 2*a*, 2*b* and 4*f* Wyckoff positions projected about different crystallographic directions.

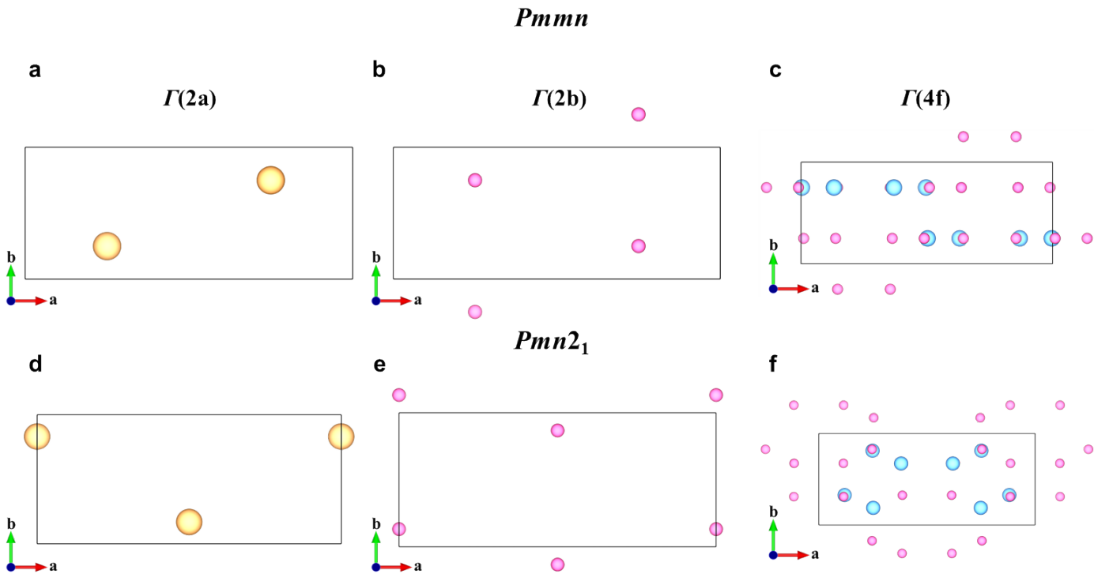


Figure S5b. Atomic displacements patterns from the centrosymmetric (top column) to polar *β*-$BaGa_4S_7$ structure (bottom column) for atoms belonging to the 4*c* and 8*d* Wyckoff positions projected about different crystallographic directions.