Supporting information

Synthesis, Characterization and Theoretical Investigation of Ba$_4$GaS$_4$F$_3$: A New Chalcohalide with 3D Network Structure

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Table S1　Atomic coordinates and equivalent isotropic displacement parameters of $Ba_4GaS_4F_3$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Ba1	7055.7(2)	6820.9(2)	9711.0(2)	11.33(8)
Ba2	4632.8(2)	6160.7(2)	5174.1(2)	11.98(8)
Ba3	3725.1(2)	2852.0(2)	7941.0(2)	11.02(7)
Ba4	2281.4(2)	5475.2(2)	9425.6(2)	11.89(8)
Ga1	4496.3(3)	5836.1(3)	8367.8(3)	10.70(12)
S1	5753.3(7)	5638.4(8)	8882.7(7)	15.7(3)
S2	4653.7(7)	6183.7(7)	7070.1(7)	12.2(3)
S3	6313.1(8)	8232.4(7)	8880.2(7)	16.5(3)
S4	3810.2(7)	4657.2(7)	8566.8(7)	15.1(3)
F1	4698.7(15)	1656.0(16)	8089.5(15)	13.5(6)
F2	1856.1(16)	5584.1(16)	7961.4(15)	15.2(6)
F3	4267.8(16)	4929.7(16)	4318.6(15)	14.7(6)

Table S2　Symmetry, selected bond lengths and angles of Ba$_4$GaS$_4$F$_3$.

Ba(1)-S(1)#4	3.3862(19)	S(1)-Ba(1)-S(1)#4	134.55(4)	F(1)#3-Ba(3)-S(3)#12	137.10(6)
Ba(1)-S(1)	3.2514(15)	S(1)#11-Ba(3)-S(1)#8	96.53(3)	F(1)-Ba(3)-S(4)	131.68(6)
Ba(1)-S(2)#4	3.2084(15)	S(1)#11-Ba(3)-S(4)#11	65.30(3)	F(1)#13-Ba(3)-S(4)#11	125.89(6)
Ba(1)-S(3)	3.0101(14)	S(1)#8-Ba(3)-S(4)#11	82.02(4)	F(1)#3-Ba(3)-S(4)#11	67.29(6)
Ba(1)-F(1)#5	2.593(3)	S(1)-Ga(1)-S(2)	107.63(5)	F(1)-Ba(3)-S(4)#11	68.94(6)
Ba(1)-F(2)#3	2.616(3)	S(2)-Ba(2)-S(2)#2	81.45(3)	F(1)#13-Ba(3)-S(4)	69.38(6)
Ba(1)-F(3)#1	2.759(3)	S(2)#4-Ba(1)-S(1)	148.27(4)	F(1)#3-Ba(3)-S(4)	72.24(6)
Ba(2)-S(2)#9	3.2465(15)	S(2)#4-Ba(1)-S(1)#4	68.56(3)	F(1)#3-Ba(3)-F(1)#13	70.17(9)
Ba(2)-S(2)	3.250(2)	S(2)#5-Ba(4)-S3#15	79.13(3)	F(1)-Ba(3)-F(1)#3	73.04(9)
Ba(2)-S(2)#1	3.2795(15)	S(2)#5-Ba(4)-S(4)	142.03(3)	F(1)-Ba(3)-F(1)#13	67.83(10)
Ba(2)-S(3)#9	3.2315(18)	S(2)#5-Ba(4)-S(4)#5	73.09(3)	F(2)#3-Ba(1)-F(3)#2	70.49(8)
Ba(2)-F(2)#8	2.759(3)	S(2)#6-Ba(2)-S(2)	81.95(3)	F(2)-Ba(4)-S(2)#5	83.07(6)
Ba(2)-F(3)#6	2.718(3)	S(2)#6-Ba(2)-S(2)#2	87.84(3)	F(2)#5-Ba(4)-S(2)#5	116.29(6)
Ba(2)-F(3)	2.590(3)	S(3)-Ba(1)-S(1)#4	130.30(3)	F(2)-Ba(4)-S(3)#15	82.82(6)
Ba(3)-S(1)#8	3.3857(18)	S(3)-Ba(1)-S(1)	89.53(4)	F(2)#5-Ba(4)-S(3)#15	144.03(6)
Ba(3)-S(1)#10	3.3751(16)	S(3)-Ba(1)-S(2)#4	84.04(3)	F(2)#5-Ba(4)-S(4)#5	77.70(7)
Ba(3)-S(3)#11	3.2439(18)	S(3)#6-Ba(2)-S(2)#6	112.01(3)	F(2)-Ba(4)-S(4)	78.75(7)
Ba(3)-S(4)	3.1907(15)	S(3)#6-Ba(2)-S(2)#2	67.69(4)	F(2)-Ba(4)-S(4)#5	150.82(6)
Ba(3)-S(4)#10	3.4085(15)	S(3)#6-Ba(2)-S(2)	144.90(4)	F(2)#5-Ba(4)-S(4)	100.96(6)
Ba(3)-F(1)#12	2.757(3)	S(3)#12-Ba(3)-S(1)#11	116.18(3)	F(2)-Ba(4)-F(2)#5	129.16(7)
Ba(3)-F(1)	2.577(3)	S(3)#12-Ba(3)-S(1)#8	72.37(5)	F(2)-Ba(4)-F(3)#14	71.96(8)
Ba(3)-F(1)#3	2.620(3)	S(3)#12-Ba(3)-S(4)#11	154.38(3)	F(2)#5-Ba(4)-F(3)#14	69.30(8)
Ba(4)-S(2)#5	3.2289(15)	S(3)#15-Ga(1)-S(1)	119.85(6)	F(2)#3-Ba(1)-S(1)	86.20(6)
Ba(4)-S(3)#13	3.3098(16)	S(3)#15-Ga(1)-S(2)	105.85(5)	F(2)#3-Ba(1)-S(1)#4	73.78(6)
Ba(4)-S(4)#5	3.2728(19)	S(3)#15-Ga(1)-S(4)	103.57(5)	F(2)#3-Ba(1)-S(2)#4	80.65(6)
Ba(4)-S(4)	3.2372(15)	S(4)-Ba(3)-S(1)#11	74.89(3)	F(2)#3-Ba(1)-S(3)	142.95(6)
Ba(4)-F(2)#5	2.643(3)	S(4)-Ba(3)-S(1)#8	142.06(3)	F(2)#8-Ba(2)-S(2)#2	158.38(6)
Ba(4)-F(2)	2.614(3)	S(4)-Ba(3)-S(3)#12	78.55(4)	F(2)#8-Ba(2)-S(2)	80.52(6)
Ba(4)-F(3)#14	2.669(3)	S(4)-Ba(4)-S(3)#14	65.79(3)	F(2)#8-Ba(2)-S(2)#6	77.94(6)
Ga(1)-S(1)	2.2925(15)	S(4)#5-Ba(4)-S(3)#15	76.46(4)	F(2)#8-Ba(2)-S(3)#6	132.80(6)
Ga(1)-S(2)	2.3129(18)	S(4)-Ba(4)-S(4)#5	110.18(3)	F(3)#2-Ba(1)-S(1)#4	129.64(7)
Ga(1)-S(3)#13	2.2321(14)	S(4)-Ba(3)-S(4)#11	123.99(3)	F(3)#2-Ba(1)-S(2)#4	71.57(6)
Ga(1)-S(4)	2.2936(15)	S(4)-Ga(1)-S(2)	114.39(5)	F(3)-Ba(2)-S(2)#2	132.35(6)
		F(1)#5-Ba(1)-S(1)#4	86.02(7)	F(3)#10-Ba(2)-S(2)#6	149.30(6)
		F(1)#5-Ba(1)-S(1)	83.25(6)	F(3)-Ba(2)-S2#6	130.15(6)

F(1)#5-Ba(1)-S(2)#4	124.80(6)	F(3)-Ba(2)-S(2)	125.30(6)
F(1)#5-Ba(1)-S(3)	76.52(7)	F(3)#10-Ba(2)-S(2)#2	73.68(6)
F(1)#5-Ba(1)-F(2)#3	139.03(8)	F(3)-Ba(2)-F(2)#8	68.66(8)
F(1)#5-Ba(1)-F(3)#2	143.19(8)	F(3)#10-Ba(2)-F(2)#8	111.28(8)
F(1)-Ba(3)-S(3)#12	106.68(6)	F(3)-Ba(2)-F(3)#10	79.13(9)
F(1)-Ba(3)-S(1)#8	80.79(6)	F(3)#10-Ba(2)-S(2)	71.39(6)
F(1)-Ba(3)-S(1)#11	134.06(6)	F(3)#10-Ba(2)-S(3)#6	83.81(6)
F(1)#13-Ba(3)-S(1)#8	120.51(6)	F(3)-Ba(2)-S(3)#6	71.13(7)
F(1)#3-Ba(3)-S(1)#8	145.05(6)	F(3)#14-Ba(4)-S(2)#5	75.15(6)
F(1)#3-Ba(3)-S(1)#11	85.83(7)	F(3)#14-Ba(4)-S(3)#15	145.69(6)
F(1)#13-Ba(3)-S(1)#11	141.48(6)	F(3)#14-Ba(4)-S(4)	128.37(6)
F(1)#13-Ba(3)-S(3)#12	70.47(6)	F(3)#14-Ba(4)-S(4)#5	116.20(6)

[#1]1-X,1-Y,2-Z; [#2]5/4-Y,1/4+X,5/4-Z; [#3]1/4+Y,3/4-X,7/4-Z; [#4]1/4+Y,5/4-X,1/4+Z; [#5]3/4-Y,1/4+X,1/4+Z; [#6]-1/4+Y,5/4-X,5/4-Z; [#7]-1/2+X,+Y,3/2-Z; [#8]-1/4+Y,3/4-X,-1/4+Z; [#9]1/2-X,1-Y,-1/2+Z; [#10]1-X,1-Y,1-Z; [#11]3/4-Y,-1/4+X,7/4-Z; [#12]5/4-Y,-1/4+X,-1/4+Z; [#13]1-X,1/2-Y,+Z; [#14]1/2-X,1-Y,1/2+Z; [#15]1-X,3/2-Y,+Z

Table S3　Anisotropic displacement parameters of Ba$_4$GaS$_4$F$_3$.

| Atom	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
Ba1	10.05(15)	12.37(16)	11.56(14)	-0.22(12)	-0.30(11)	1.40(11)
Ba2	11.34(16)	12.14(16)	12.47(15)	-2.67(11)	0.95(12)	-0.25(11)
Ba3	12.24(16)	10.74(15)	10.09(15)	0.03(11)	-1.12(11)	-0.22(11)
Ba4	12.33(16)	13.15(16)	10.18(14)	1.32(12)	-0.68(12)	-0.54(12)
Ga1	11.6(3)	10.8(3)	9.7(3)	-1.3(2)	0.2(2)	1.3(2)
S1	12.1(6)	17.9(7)	17.1(6)	-3.6(5)	-3.3(5)	-0.6(5)
S2	12.1(6)	13.8(7)	10.7(6)	0.0(5)	0.9(5)	0.4(5)
S3	23.0(7)	12.8(7)	13.6(6)	0.1(5)	-4.6(5)	6.0(5)
S4	16.4(7)	9.4(6)	19.5(7)	0.3(5)	-1.8(5)	0.9(5)
F1	14.7(15)	13.3(15)	12.6(14)	-1.0(12)	0.7(12)	2.0(11)
F2	13.6(15)	18.2(16)	13.9(15)	0.4(12)	-0.8(12)	-0.4(12)
F3	14.7(15)	14.2(15)	15.1(15)	-0.7(12)	-0.2(12)	1.0(12)
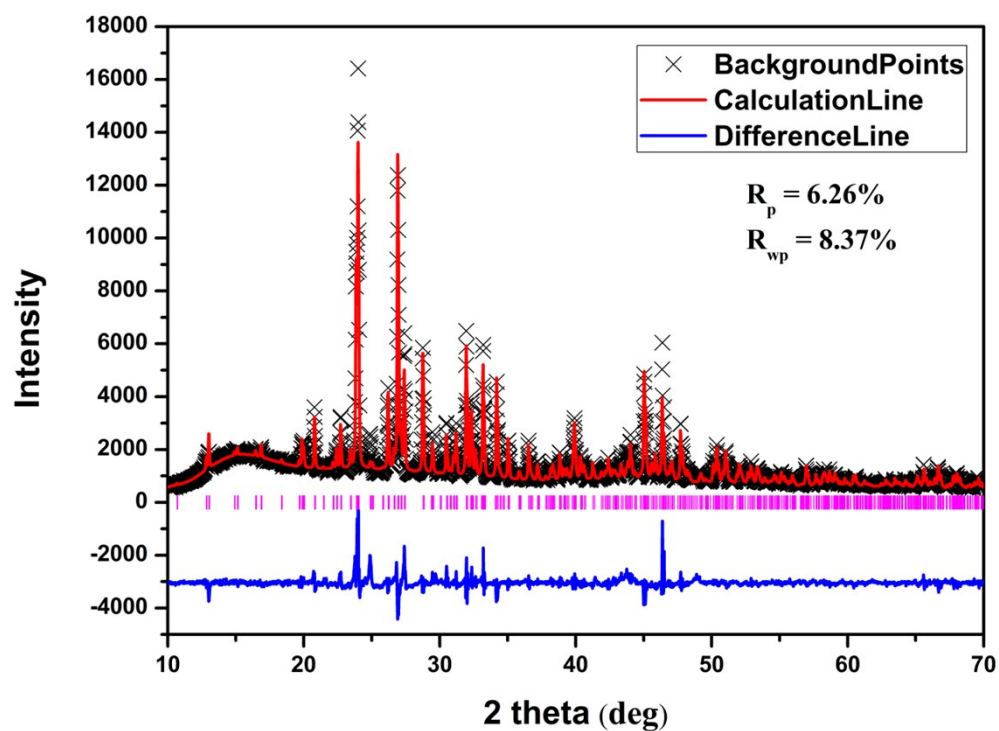
Figure S1   Experimental (black circles) and calculated (red line) PXRD patterns and the difference (blue line) for the PXRD Rietveld refinement of $Ba_4GaS_4F_3$.
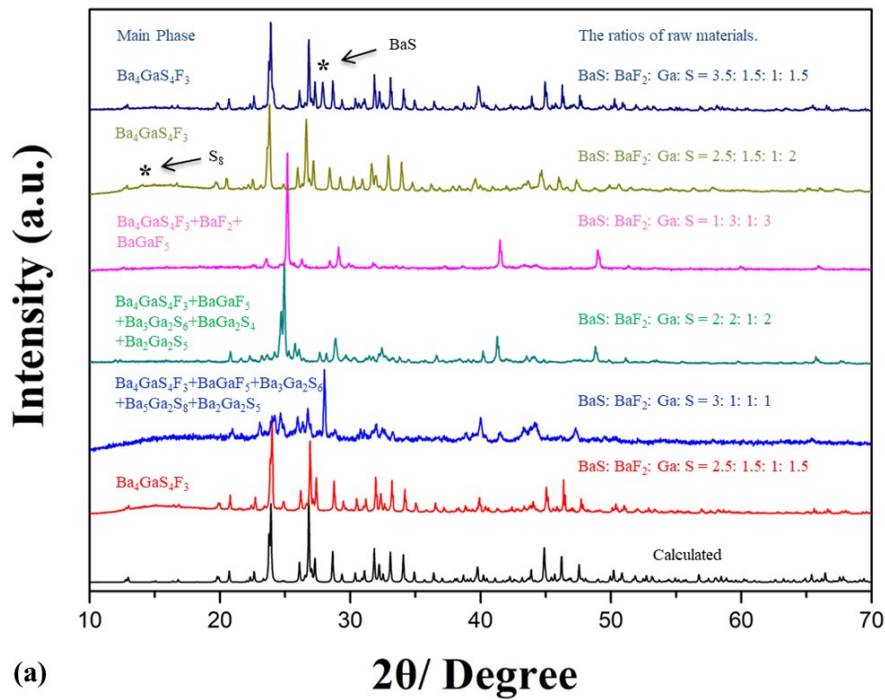
(a)
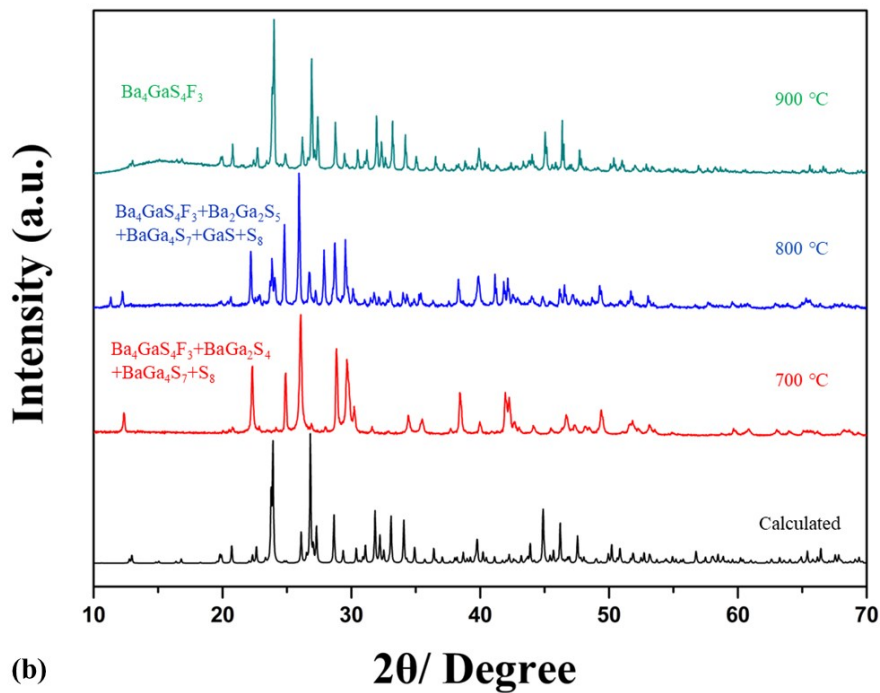
(b)

Figure S2 (a) The PXRD results of the obtained products under different raw materials ratios and (b) The PXRD results of the obtained products under different temperatures to synthesize the $Ba_4GaS_4F_3$ pure phase powders. The theoretical XRD pattern of $Ba_4GaS_4F_3$ is used as the reference.
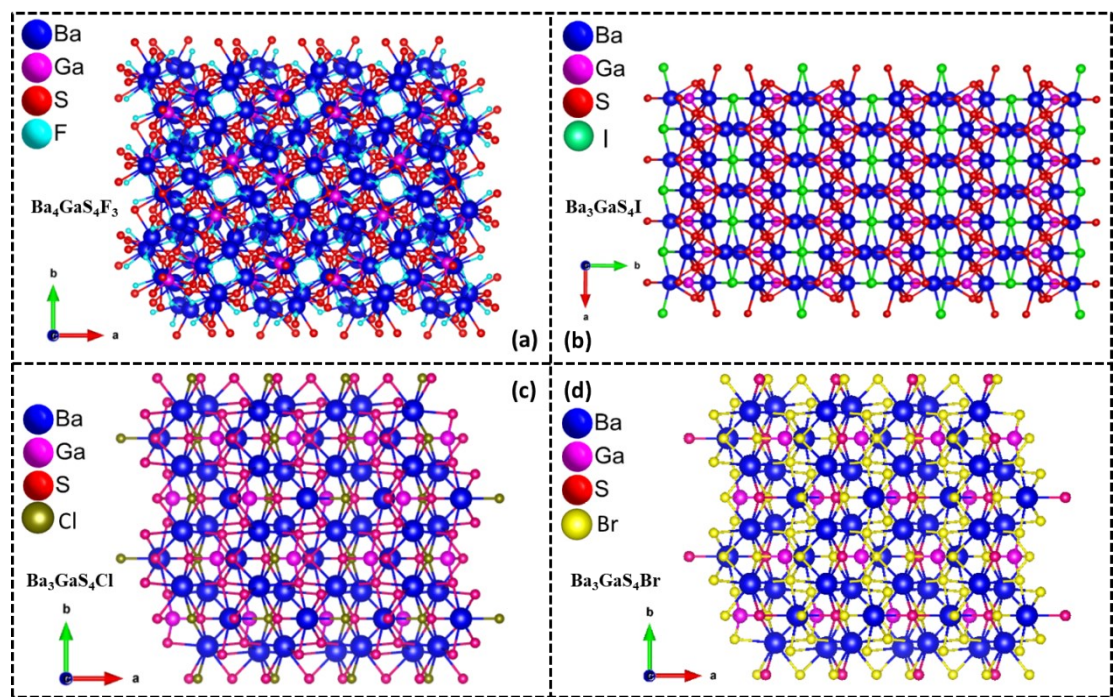
Figure S3　The structural contrast between $Ba_4GaS_4F_3$ and Ba_3GaS_4X (X = Cl, Br, I) along the *c*-axis. The 3D channel-like structure in $Ba_4GaS_4F_3$ (a), The pseudolayer structures in Ba_3GaS_4I (b), Ba_3GaS_4Cl (c) and Ba_3GaS_4Br (d).