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$Ba_2GeF_2Q_3$ (Q = S, Se) and $Ba_3GeF_2Se_4$: New F-based Chalcohalides with Enhanced Birefringence

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CONTENTS

Experimetal Section:

Reagents

BaSe (Beijing Hawk Science and Technology Co. Ltd.), BaS (Beijing Hawk Science and Technology Co. Ltd.), BaF_2 (Aladdin Chemistry Co., Ltd.), Ge (Beijing Hawk Science and Technology Co. Ltd.) S (Aladdin Chemistry Co., Ltd.) and Se (Aladdin Chemistry Co., Ltd.) were used as received from commercial sources without any further purification.

Synthesis

Single crystals of $Ba_2GeF_2Q_3$ (Q = S, Se) and $Ba_3GeF_2Se_4$ were synthesized via the traditional high-temperature solid-state reaction. For $Ba_2GeF_2S_3$, mixture of BaF_2 (1 mmol, 0.175 g), BaS (1 mmol, 0.170 g), Ge (2 mmol, 0.146), and S (6 mmol, 0.192 g) at the ratio of 1:1:2:6 was transferred into a silica tube in a glovebox and further evacuated to be 1×10^{-3} Torr, and then sealed by flame. For $Ba_2GeF_2Se_3$, mixture of BaF_2 (1 mmol, 0.175 g), BaSe (1 mmol, 0.216 g), Ge (2 mmol, 0.146), and Se (5 mmol, 0.395 g) at the ratio of 1:1:2:5 was transferred into a silica tube in a glovebox and further evacuated to be 1×10^{-3} Torr, and then sealed by flame. Those tubes were placed into a muffle furnace heated from room temperature to 900 °C in 50 h and kept at 900 °C for 100 h and then cooled down to 350 °C in 130 h. The crystal of $Ba_2GeF_2S_3$ and $Ba_2GeF_2Se_3$ were obtained. For $Ba_3GeF_2Se_4$, mixture of BaF_2 (1 mmol, 0.175 g), BaS (2 mmol, 0.340 g), Ge (2 mmol, 0.146), and Se (5 mmol, 0.395 g) at the ratio of 1:2:2:5 was transferred into a silica tube in a glovebox and further evacuated to be 1×10^{-3} Torr, and then sealed by flame. The tube was placed into a muffle furnace heated from room temperature to 850 °C in 30 h and kept at 850 °C for 120 h and then cooled down to 350 °C in 80 h. The crystal of $Ba_3GeF_2Se_4$ was obtained. In addition, we directly attempted to mix $Ba_2GeF_2Se_3$ and BaSe in a 1:1 ratio, $Ba_3GeF_2Se_4$ can also be successfully synthesized under the same temperature conditions. And the yield was about 70% on the basis of Ge. For $Ba_3GeS_4F_2$, a series of experiments were conducted at different reaction temperatures by the high-temperature solid-state method. The powder XRD results of the sample indicate that at 800 and 850 °C, the powder sample is a mixture of BaF_2 and Ba_2GeS_4. When the sample was heated to 900 °C, the sample melted and the powder XRD results showed only BaF_2 (Fig. S4). The above results indicate sample with stoichiometric ratio was heated until the sample melt. The powder XRD of sample was not agreement with or similar with the theoretical XRD of $Ba_3GeSe_4F_2$. In the end, due to the lack of suitable flux, we did not obtain $Ba_3GeS_4F_2$ crystals.

Powder X-ray Diffraction. The PXRD measurements were collected using a SmartLab3KW X-ray diffractometer at room temperature (Cu Kα radiation). All the data were collected in the 2θ range of 10−60° with a step size of 0.01° and a step time of 2s. The XRD patterns are displayed in Figure S1.

Single-Crystal X-ray Diffraction. A Bruker SMART APEX III 4K CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) was used to collect the single-crystal XRD data at 298(2) K, and the data were integrated with the SAINT program. The crystal structure of $Ba_2GeF_2Q_3$ (Q = S, Se) and $Ba_3GeF_2Se_4$ were solved by the direct methods and refined using the SHELXTL system. All of the atomic positions were refined by full-matrix least-squares techniques. The structures were checked for missing symmetry elements with PLATON. The crystal data and structural refinement information are summarized in Table S1. The atomic coordinates and the equivalent isotropic displacement parameters are available in Table S1. The selected bond lengths and angles are listed in Table S2.

Infrared Spectroscopy. The IR spectra of $Ba_2GeF_2Q_3$ (Q = S, Se) and $Ba_3GeF_2Se_4$ were recorded on a Nicolet iS50 FT-IR spectrometer in the range 400−4000 cm^{-1}. The samples were placed on the test platform for testing.

Ultraviolet−Visible−Near-IR Diffuse Reflectance Spectroscopy. UV−vis−NIR diffuse reflectance data for $Ba_2GeF_2Q_3$ (Q = S, Se) and $Ba_3GeF_2Se_4$ were collected using a Hitachi UV−vis−NIR spectrophotometer equipped with an integrating sphere over the spectral range 240−2500 nm. $BaSO_4$ was used as a reference. Reflectance spectra were converted to absorbance with the Kubelka−Munk function, $F(R) = (1-R)^2/2R = K/S$, where R represents the reflectance, K represents the absorption, and S represents the scattering factor.

Band gap calculation. we calculated the band gap of the compounds by Tauc Plot method. Using the formula $(\alpha h\nu)^{1/n} = B(h\nu\text{-}Eg)$, where α is absorption coefficient, h is Planck-constant, ν is frequency, B is constant, Eg is the bandgap width of semiconductor, Exponential n is directly related to the type of semiconductor, direct bandgap n=1/2, indirect bandgap n=2. The title compounds are the indirect bandgap, so n=2, and the formula is $(\alpha h\nu)^{1/2}$=B (hν-Eg). The band-gaps of $Ba_2GeF_2Q_3$ (Q = S, Se) and $Ba_3GeF_2Se_4$ are 3.53, 2.45 and 2.57 eV, respectively.

Birefringence Measurement. The birefringence of $Ba_2GeF_2Q_3$ (Q = S, Se) and $Ba_3GeF_2Se_4$ were measured by using a cross-polarizing microscope. On the basis of the crystal optics, the birefringence was calculated from the following formula: $R = \Delta n \times d$, Δn can be obtained, where R, Δn and d are retardation, birefringence, and thickness, respectively.

Theoretical Calculation Details. The electronic structure calculations were performed by first-principles calculations in the CASTEP package, with the ultrasoft pseudopotentials. The Perdew−Burke−Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was applied for the exchange−correlation potential. The valence electrons of title compounds were calculated to be Ba $4d^{10}5p^{6}6s^{2}$, Ge $4s^{2}4p^{2}$, F $2s^{2}2p^{5}$, S $3s^{2}3p^{4}$ and Se $3d^{10}4s^{2}4p^{4}$. The plane-wave cutoff energy for $Ba_2GeF_2S_3$, $Ba_2GeF_2Se_3$ and $Ba_3GeF_2Se_4$ were set to 400 eV during the calculation, and the k-points sampling of 6 × 4 × 3, 6 × 4 × 3 and 2 × 6 × 3 for $Ba_2GeF_2S_3$, $Ba_2GeF_2Se_3$ and $Ba_3GeF_2Se_4$ respectively was selected to guarantee convergence for all computations. The other estimated parameters and convergent criteria matched the default CASTEP code values. Our experiments show that the computational parameters listed above are accurate enough for the current computations.

Table S1. Crystal data and structure refinement for $Ba_2GeF_2Q_3$ (Q = S, Se) and $Ba_3GeF_2Se_4$

Empirical formula	Ba_2GeF_2S3	Ba_2GeF_2Se3	$Ba_3GeF_2Se_4$
Formula weight	481.45	622.15	838.45
Space group	*Pnma*	*Pnma*	$P2_1/n$
a (Å)	12.626(14)	12.8823(15)	9.3777(3)
b (Å)	18.669(18)	19.118(3)	9.4571(3)
			β= 91.668(2)
c (Å)	6.316(7)	6.4566(10)	12.3301(5)
V (Å^3)	1489(3)	1590.2(4)	1093.04(7)
Z, ρ_{calcd} (mg/m^3)	8, 4.296	8, 5.198	4, 5.095
Completeness to θ (%)	99.90	99.50	99.80
GOOF on F^2	1.057	1.050	1.072
Final R indices	R_1 = 0.0445,	R_1 = 0.0255,	R_1 = 0.0348,
($F_o^2 > 2\sigma(F_o^2)$)	wR_2 = 0.1021	wR_2 = 0.0624	wR_2= 0.0620
Largest diff.peak and hole	4.840 and -3.641	1.558 and -2.650	2.001 and -4.555

[a]$R_1 = \Sigma||F_o|—|F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2—F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2(a). Selected bond distances (Å) and angles (degrees) for Ba_2GeF_2S3.

Ba(1)-F(1)#1	2.664(9)	S(2)#5-Ba(1)-S(2)#6	138.25(13)
Ba(1)-F(2)	2.673(9)	F(1)#1-Ba(1)-S(1)#6	71.4(3)
Ba(1)-F(1)#2	2.685(9)	F(2)-Ba(1)-S(1)#6	68.0(2)
Ba(1)-F(2)#1	2.695(10)	F(1)#2-Ba(1)-S(1)#6	136.1(2)
Ba(1)-S(3)#3	3.232(3)	F(2)#1-Ba(1)-S(1)#6	141.2(3)
Ba(1)-S(1)#4	3.295(5)	S(3)#3-Ba(1)-S(1)#6	63.12(13)
Ba(1)-S(2)#5	3.303(6)	S(1)#4-Ba(1)-S(1)#6	136.31(16)
Ba(1)-S(2)#6	3.458(6)	S(2)#5-Ba(1)-S(1)#6	78.73(10)
Ba(1)-S(1)#6	3.509(5)	S(2)#6-Ba(1)-S(1)#6	87.64(10)
Ba(1)-Ba(2)#7	4.311(4)	F(1)#9-Ba(2)-F(2)#7	72.6(4)
Ba(1)-Ba(2)#1	4.316(4)	F(1)#9-Ba(2)-F(1)	72.8(3)
Ba(1)-Ba(1)#8	4.319(3)	F(2)#7-Ba(2)-F(1)	113.6(2)
Ba(2)-F(1)#9	2.649(10)	F(1)#9-Ba(2)-F(2)	112.9(2)
Ba(2)-F(2)#7	2.673(9)	F(2)#7-Ba(2)-F(2)	71.6(3)
Ba(2)-F(1)	2.673(10)	F(1)-Ba(2)-F(2)	72.6(4)
Ba(2)-F(2)	2.675(10)	F(1)#9-Ba(2)-S(4)	115.9(2)
Ba(2)-S(4)	3.235(3)	F(2)#7-Ba(2)-S(4)	123.53(19)
Ba(2)-S(2)#5	3.292(5)	F(1)-Ba(2)-S(4)	122.3(2)
Ba(2)-S(1)#6	3.304(6)	F(2)-Ba(2)-S(4)	131.20(19)
Ba(2)-S(2)#10	3.477(5)	F(1)#9-Ba(2)-S(2)#5	140.6(2)
Ba(2)-S(1)#10	3.502(6)	F(2)#7-Ba(2)-S(2)#5	70.7(2)
Ba(2)-Ba(2)#9	4.283(4)	F(1)-Ba(2)-S(2)#5	136.2(2)
Ge(1)-S(1)	2.144(5)	F(2)-Ba(2)-S(2)#5	67.8(2)
Ge(1)-S(1)#10	2.144(5)	S(4)-Ba(2)-S(2)#5	74.74(13)
Ge(1)-S(3)	2.273(7)	F(1)#9-Ba(2)-S(1)#6	137.1(2)
Ge(1)-S(4)	2.285(6)	F(2)#7-Ba(2)-S(1)#6	140.0(2)
Ge(2)-S(2)	2.178(4)	F(1)-Ba(2)-S(1)#6	68.11(18)
Ge(2)-S(2)#10	2.178(4)	F(2)-Ba(2)-S(1)#6	71.41(18)
Ge(2)-S(3)	2.284(6)	S(4)-Ba(2)-S(1)#6	73.37(12)
Ge(2)-S(4)	2.295(7)	S(2)#5-Ba(2)-S(1)#6	81.91(10)
F(1)#1-Ba(1)-F(2)	72.9(3)	F(1)#9-Ba(2)-S(2)#10	70.9(2)
F(1)#1-Ba(1)-F(1)#2	113.13(15)	F(2)#7-Ba(2)-S(2)#10	141.1(2)
F(2)-Ba(1)-F(1)#2	72.0(4)	F(1)-Ba(2)-S(2)#10	67.2(2)
F(1)#1-Ba(1)-F(2)#1	72.4(4)	F(2)-Ba(2)-S(2)#10	136.2(2)
F(2)-Ba(1)-F(2)#1	113.40(15)	S(4)-Ba(2)-S(2)#10	64.08(13)
F(1)#2-Ba(1)-F(2)#1	72.2(3)	S(2)#5-Ba(2)-S(2)#10	137.81(14)
F(1)#1-Ba(1)-S(3)#3	115.4(2)	S(1)#6-Ba(2)-S(2)#10	78.13(10)
F(2)-Ba(1)-S(3)#3	122.5(2)	F(1)#9-Ba(2)-S(1)#10	71.7(2)
F(1)#2-Ba(1)-S(3)#3	131.4(2)	F(2)#7-Ba(2)-S(1)#10	68.65(19)
F(2)#1-Ba(1)-S(3)#3	123.48(19)	F(1)-Ba(2)-S(1)#10	141.5(2)
F(1)#1-Ba(1)-S(1)#4	141.6(2)	F(2)-Ba(2)-S(1)#10	136.1(2)
F(2)-Ba(1)-S(1)#4	135.6(2)	S(4)-Ba(2)-S(1)#10	63.40(12)

F(1)#2-Ba(1)-S(1)#4	68.1(2)	S(2)#5-Ba(2)-S(1)#10	81.99(9)
F(2)#1-Ba(1)-S(1)#4	71.9(3)	S(1)#6-Ba(2)-S(1)#10	136.45(14)
S(3)#3-Ba(1)-S(1)#4	74.41(14)	S(2)#10-Ba(2)-S(1)#10	87.47(10)
F(1)#1-Ba(1)-S(2)#5	137.2(2)	S(1)-Ge(1)-S(1)#10	129.5(3)
F(2)-Ba(1)-S(2)#5	67.69(19)	S(1)-Ge(1)-S(3)	106.34(13)
F(1)#2-Ba(1)-S(2)#5	69.88(19)	S(1)#10-Ge(1)-S(3)	106.34(13)
F(2)#1-Ba(1)-S(2)#5	139.3(2)	S(1)-Ge(1)-S(4)	106.39(16)
S(3)#3-Ba(1)-S(2)#5	74.65(12)	S(1)#10-Ge(1)-S(4)	106.39(16)
S(1)#4-Ba(1)-S(2)#5	80.78(10)	S(3)-Ge(1)-S(4)	97.3(2)
F(1)#1-Ba(1)-S(2)#6	71.08(18)	S(2)-Ge(2)-S(2)#10	132.1(2)
F(2)-Ba(1)-S(2)#6	141.4(2)	S(2)-Ge(2)-S(3)	105.54(15)
F(1)#2-Ba(1)-S(2)#6	136.0(2)	S(2)#10-Ge(2)-S(3)	105.53(15)
F(2)#1-Ba(1)-S(2)#6	67.73(17)	S(2)-Ge(2)-S(4)	105.73(11)
S(3)#3-Ba(1)-S(2)#6	64.05(11)	S(2)#10-Ge(2)-S(4)	105.73(11)
S(1)#4-Ba(1)-S(2)#6	82.62(10)	S(3)-Ge(2)-S(4)	96.7(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x-1/2,-y,z-1/2 #2 x,y,z-1 #3 x-1/2,y,-z+1/2

#4 x-1/2,-y+1/2,-z-1/2 #5 x,-y+1/2,z-1 #6 x-1/2,-y+1/2,-z+1/2

#7 -x,-y,-z #8 -x-1/2,-y,z+1/2 #9 -x,-y,-z+1

#10 x,-y+1/2,z #11 x+1/2,-y+1/2,-z-1/2 #12 x+1/2,-y+1/2,-z+1/2

#13 x,-y+1/2,z+1 #14 x+1/2,y,-z+1/2 #15 x,y,z+1

Table S2(b). Selected bond distances (Å) and angles (degrees) for Ba_2GeF_2Se3.

Ba(1)-F(2)#1	2.666(4)	Se(1)#5-Ba(1)-Se(1)#4	136.98(4)
Ba(1)-F(1)	2.701(4)	F(2)#1-Ba(1)-Se(2)#4	71.03(8)
Ba(1)-F(1)#2	2.702(4)	F(1)-Ba(1)-Se(2)#4	135.47(10)
Ba(1)-F(2)#3	2.703(4)	F(1)#2-Ba(1)-Se(2)#4	142.69(10)
Ba(1)-Se(2)	3.3587(9)	F(2)#3-Ba(1)-Se(2)#4	66.23(8)
Ba(1)-Se(4)#4	3.3769(9)	Se(2)-Ba(1)-Se(2)#4	136.61(4)
Ba(1)-Se(1)#5	3.3816(11)	Se(4)#4-Ba(1)-Se(2)#4	65.00(3)
Ba(1)-Se(1)#4	3.5521(11)	Se(1)#5-Ba(1)-Se(2)#4	77.29(2)
Ba(1)-Se(2)#4	3.5895(9)	Se(1)#4-Ba(1)-Se(2)#4	88.58(2)
Ba(1)-Ba(1)#6	4.2575(11)	F(2)#7-Ba(2)-F(1)#8	73.98(16)
Ba(1)-Ba(2)#1	4.2987(10)	F(2)#7-Ba(2)-F(1)#2	74.15(15)
Ba(1)-Ba(2)#2	4.2989(10)	F(1)#8-Ba(2)-F(1)#2	116.11(8)
Ba(2)-F(2)#7	2.640(4)	F(2)#7-Ba(2)-F(2)	115.59(8)
Ba(2)-F(1)#8	2.686(4)	F(1)#8-Ba(2)-F(2)	73.71(15)
Ba(2)-F(1)#2	2.702(4)	F(1)#2-Ba(2)-F(2)	72.65(16)
Ba(2)-F(2)	2.709(4)	F(2)#7-Ba(2)-Se(1)#4	142.09(10)
Ba(2)-Se(1)#4	3.3660(9)	F(1)#8-Ba(2)-Se(1)#4	134.94(10)
Ba(2)-Se(3)	3.3741(8)	F(1)#2-Ba(2)-Se(1)#4	70.56(8)
Ba(2)-Se(2)#8	3.3778(11)	F(2)-Ba(2)-Se(1)#4	66.08(8)
Ba(2)-Se(2)	3.5527(11)	F(2)#7-Ba(2)-Se(3)	117.51(8)
Ba(2)-Se(1)	3.5805(10)	F(1)#8-Ba(2)-Se(3)	121.29(8)
Ba(2)-Ba(2)#7	4.3063(10)	F(1)#2-Ba(2)-Se(3)	122.45(8)
Ge(1)-Se(2)	2.2957(11)	F(2)-Ba(2)-Se(3)	126.90(8)
Ge(1)-Se(2)#9	2.2957(11)	Se(1)#4-Ba(2)-Se(3)	72.55(3)
Ge(1)-Se(3)	2.4092(14)	F(2)#7-Ba(2)-Se(2)#8	137.08(10)
Ge(1)-Se(4)	2.4093(14)	F(1)#8-Ba(2)-Se(2)#8	66.82(9)
Ge(2)-Se(1)	2.2946(11)	F(1)#2-Ba(2)-Se(2)#8	139.25(10)
Ge(2)-Se(1)#9	2.2947(11)	F(2)-Ba(2)-Se(2)#8	69.61(9)
Ge(2)-Se(4)	2.4112(15)	Se(1)#4-Ba(2)-Se(2)#8	80.48(2)
Ge(2)-Se(3)	2.4137(14)	Se(3)-Ba(2)-Se(2)#8	72.08(3)
F(2)#1-Ba(1)-F(1)	115.61(11)	F(2)#7-Ba(2)-Se(2)	71.91(10)
F(2)#1-Ba(1)-F(1)#2	74.15(15)	F(1)#8-Ba(2)-Se(2)	143.06(10)
F(1)-Ba(1)-F(1)#2	72.76(17)	F(1)#2-Ba(2)-Se(2)	67.07(9)
F(2)#1-Ba(1)-F(2)#3	75.06(16)	F(2)-Ba(2)-Se(2)	134.93(9)
F(1)-Ba(1)-F(2)#3	73.18(15)	Se(1)#4-Ba(2)-Se(2)	81.864(19)
F(1)#2-Ba(1)-F(2)#3	116.76(11)	Se(3)-Ba(2)-Se(2)	65.28(3)
F(2)#1-Ba(1)-Se(2)	141.42(10)	Se(2)#8-Ba(2)-Se(2)	137.00(4)
F(1)-Ba(1)-Se(2)	66.99(8)	F(2)#7-Ba(2)-Se(1)	70.74(8)
F(1)#2-Ba(1)-Se(2)	70.23(8)	F(1)#8-Ba(2)-Se(1)	66.79(8)
F(2)#3-Ba(1)-Se(2)	135.08(9)	F(1)#2-Ba(2)-Se(1)	142.16(9)
F(2)#1-Ba(1)-Se(4)#4	117.01(8)	F(2)-Ba(2)-Se(1)	136.34(9)
F(1)-Ba(1)-Se(4)#4	127.38(8)	Se(1)#4-Ba(2)-Se(1)	136.68(4)

F(1)#2-Ba(1)-Se(4)#4	122.63(8)	Se(3)-Ba(2)-Se(1)	65.16(3)
F(2)#3-Ba(1)-Se(4)#4	120.49(8)	Se(2)#8-Ba(2)-Se(1)	78.19(2)
Se(2)-Ba(1)-Se(4)#4	72.64(3)	Se(2)-Ba(2)-Se(1)	88.71(2)
F(2)#1-Ba(1)-Se(1)#5	137.05(10)	Se(2)-Ge(1)-Se(2)#9	130.80(6)
F(1)-Ba(1)-Se(1)#5	69.90(9)	Se(2)-Ge(1)-Se(3)	105.23(3)
F(1)#2-Ba(1)-Se(1)#5	139.57(10)	Se(2)#9-Ge(1)-Se(3)	105.23(3)
F(2)#3-Ba(1)-Se(1)#5	65.89(9)	Se(2)-Ge(1)-Se(4)	105.56(3)
Se(2)-Ba(1)-Se(1)#5	81.29(2)	Se(2)#9-Ge(1)-Se(4)	105.56(3)
Se(4)#4-Ba(1)-Se(1)#5	71.93(3)	Se(3)-Ge(1)-Se(4)	100.75(5)
F(2)#1-Ba(1)-Se(1)#4	70.99(9)	Se(1)-Ge(2)-Se(1)#9	130.90(6)
F(1)-Ba(1)-Se(1)#4	135.92(10)	Se(1)-Ge(2)-Se(4)	105.27(3)
F(1)#2-Ba(1)-Se(1)#4	67.52(9)	Se(1)#9-Ge(2)-Se(4)	105.27(3)
F(2)#3-Ba(1)-Se(1)#4	142.88(9)	Se(1)-Ge(2)-Se(3)	105.52(3)
Se(2)-Ba(1)-Se(1)#4	81.98(2)	Se(1)#9-Ge(2)-Se(3)	105.52(3)
Se(4)#4-Ba(1)-Se(1)#4	65.29(3)	Se(4)-Ge(2)-Se(3)	100.57(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x-3/2,-y-1,z+1/2 #2 -x-2,-y-1,-z+1 #3 x-1/2,y,-z+3/2

#4 x,y,z+1 #5 x-1/2,y,-z+1/2 #6 -x-2,-y-1,-z+2

#7 -x-3/2,-y-1,z-1/2 #8 x+1/2,y,-z+1/2 #9 x,-y-1/2,z

#10 x,y,z-1 #11 x,-y-1/2,z-1 #12 x+1/2,y,-z+3/2

Table S2(c). Selected bond distances (Å) and angles (degrees) for $Ba_3GeF_2Se_4$.

Ba(1)-F(2)	2.598(5)	F(2)-Ba(2)-Se(1)#6	128.43(11)
Ba(1)-F(1)	2.611(5)	F(1)#5-Ba(2)-Se(1)#6	75.48(10)
Ba(1)-F(1)#1	2.653(4)	F(2)-Ba(2)-Se(2)#6	79.00(12)
Ba(1)-Se(4)#2	3.3350(10)	F(1)#5-Ba(2)-Se(2)#6	103.42(10)
Ba(1)-Se(4)#3	3.4058(10)	Se(1)#6-Ba(2)-Se(2)#6	69.05(2)
Ba(1)-Se(3)#3	3.4421(11)	F(2)-Ba(2)-Se(3)	74.99(10)
Ba(1)-Se(1)#2	3.4462(9)	F(1)#5-Ba(2)-Se(3)	80.86(10)
Ba(1)-Se(2)#4	3.4667(11)	Se(1)#6-Ba(2)-Se(3)	125.47(2)
Ba(1)-Ge(1)#3	3.7645(11)	Se(2)#6-Ba(2)-Se(3)	69.88(2)
Ba(1)-Ba(1)#1	4.0164(10)	F(2)-Ba(2)-Se(2)	88.99(12)
Ba(1)-Ba(3)	4.1882(7)	F(1)#5-Ba(2)-Se(2)	71.65(10)
Ba(1)-Ba(2)#4	4.3765(8)	Se(1)#6-Ba(2)-Se(2)	140.87(3)
Ba(2)-F(2)	2.540(5)	Se(2)#6-Ba(2)-Se(2)	139.146(19)
Ba(2)-F(1)#5	2.725(5)	Se(3)-Ba(2)-Se(2)	69.30(2)
Ba(2)-Se(1)#6	3.3124(10)	F(2)-Ba(2)-Se(1)#7	126.91(11)
Ba(2)-Se(2)#6	3.3571(10)	F(1)#5-Ba(2)-Se(1)#7	71.39(10)
Ba(2)-Se(3)	3.3593(10)	Se(1)#6-Ba(2)-Se(1)#7	63.33(3)
Ba(2)-Se(2)	3.3733(10)	Se(2)#6-Ba(2)-Se(1)#7	131.90(2)
Ba(2)-Se(1)#7	3.4443(11)	Se(3)-Ba(2)-Se(1)#7	147.71(3)
Ba(2)-Se(4)#2	3.5944(9)	Se(2)-Ba(2)-Se(1)#7	86.18(2)
Ba(2)-Ba(3)	4.5388(8)	F(2)-Ba(2)-Se(4)#2	66.54(10)
Ba(3)-F(2)	2.522(5)	F(1)#5-Ba(2)-Se(4)#2	140.07(10)
Ba(3)-F(1)#1	2.850(5)	Se(1)#6-Ba(2)-Se(4)#2	66.40(2)
Ba(3)-Se(1)	3.2941(10)	Se(2)#6-Ba(2)-Se(4)#2	74.19(2)
Ba(3)-Se(2)#4	3.3468(10)	Se(3)-Ba(2)-Se(4)#2	131.20(3)
Ba(3)-Se(3)	3.4417(11)	Se(2)-Ba(2)-Se(4)#2	135.61(2)
Ba(3)-Se(4)#4	3.4710(11)	Se(1)#7-Ba(2)-Se(4)#2	81.03(2)
Ba(3)-Se(3)#8	3.5003(9)	F(2)-Ba(3)-F(1)#1	63.26(15)
Ba(3)-Se(4)#8	3.6028(11)	F(2)-Ba(3)-Se(1)	101.47(13)
Ge(1)-Se(1)	2.3360(13)	F(1)#1-Ba(3)-Se(1)	74.24(9)
Ge(1)-Se(4)	2.3451(12)	F(2)-Ba(3)-Se(2)#4	78.87(12)
Ge(1)-Se(3)	2.3457(12)	F(1)#1-Ba(3)-Se(2)#4	73.58(10)
Ge(1)-Se(2)	2.3640(13)	Se(1)-Ba(3)-Se(2)#4	143.47(3)
F(2)-Ba(1)-F(1)	137.65(16)	F(2)-Ba(3)-Se(3)	73.65(11)
F(2)-Ba(1)-F(1)#1	65.24(14)	F(1)#1-Ba(3)-Se(3)	116.27(11)
F(1)-Ba(1)-F(1)#1	80.54(15)	Se(1)-Ba(3)-Se(3)	70.94(2)
F(2)-Ba(1)-Se(4)#2	70.56(11)	Se(2)#4-Ba(3)-Se(3)	140.47(3)
F(1)-Ba(1)-Se(4)#2	142.10(10)	F(2)-Ba(3)-Se(4)#4	131.85(11)
F(1)#1-Ba(1)-Se(4)#2	135.12(10)	F(1)#1-Ba(3)-Se(4)#4	73.32(11)
F(2)-Ba(1)-Se(4)#3	141.15(13)	Se(1)-Ba(3)-Se(4)#4	85.04(2)
F(1)-Ba(1)-Se(4)#3	77.25(11)	Se(2)#4-Ba(3)-Se(4)#4	69.53(2)
F(1)#1-Ba(1)-Se(4)#3	120.09(11)	Se(3)-Ba(3)-Se(4)#4	149.08(2)

Se(4)#2-Ba(1)-Se(4)#3	90.067(12)	F(2)-Ba(3)-Se(3)#8	145.57(11)
F(2)-Ba(1)-Se(3)#3	78.65(13)	F(1)#1-Ba(3)-Se(3)#8	135.50(9)
F(1)-Ba(1)-Se(3)#3	120.75(11)	Se(1)-Ba(3)-Se(3)#8	67.65(2)
F(1)#1-Ba(1)-Se(3)#3	80.28(12)	Se(2)#4-Ba(3)-Se(3)#8	129.85(3)
Se(4)#2-Ba(1)-Se(3)#3	84.03(3)	Se(3)-Ba(3)-Se(3)#8	71.93(3)
Se(4)#3-Ba(1)-Se(3)#3	65.74(2)	Se(4)#4-Ba(3)-Se(3)#8	81.20(2)
F(2)-Ba(1)-Se(1)#2	129.83(12)	F(2)-Ba(3)-Se(4)#8	120.75(13)
F(1)-Ba(1)-Se(1)#2	72.56(10)	F(1)#1-Ba(3)-Se(4)#8	145.73(11)
F(1)#1-Ba(1)-Se(1)#2	149.88(12)	Se(1)-Ba(3)-Se(4)#8	130.64(2)
Se(4)#2-Ba(1)-Se(1)#2	69.60(2)	Se(2)#4-Ba(3)-Se(4)#8	74.20(2)
Se(4)#3-Ba(1)-Se(1)#2	67.14(2)	Se(3)-Ba(3)-Se(4)#8	96.10(2)
Se(3)#3-Ba(1)-Se(1)#2	125.19(3)	Se(4)#4-Ba(3)-Se(4)#8	84.770(13)
F(2)-Ba(1)-Se(2)#4	75.64(13)	Se(3)#8-Ba(3)-Se(4)#8	63.08(2)
F(1)-Ba(1)-Se(2)#4	71.25(12)	Se(1)-Ge(1)-Se(4)	111.59(4)
F(1)#1-Ba(1)-Se(2)#4	73.83(12)	Se(1)-Ge(1)-Se(3)	113.29(5)
Se(4)#2-Ba(1)-Se(2)#4	102.77(3)	Se(4)-Ge(1)-Se(3)	104.82(4)
Se(4)#3-Ba(1)-Se(2)#4	142.84(3)	Se(1)-Ge(1)-Se(2)	107.09(4)
Se(3)#3-Ba(1)-Se(2)#4	149.25(2)	Se(4)-Ge(1)-Se(2)	111.35(5)
Se(1)#2-Ba(1)-Se(2)#4	84.72(2)	Se(3)-Ge(1)-Se(2)	108.74(4)
F(2)-Ba(2)-F(1)#5	153.27(14)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 x+1,y,z #3 -x+3/2,y+1/2,-z+1/2

#4 x+1/2,-y+1/2,z+1/2 #5 x-1/2,-y+1/2,z-1/2

#6 -x+3/2,y-1/2,-z+1/2 #7 x+1/2,-y+1/2,z-1/2

#8 -x+1,-y,-z+1 #9 x-1/2,-y+1/2,z+1/2 #10 x-1,y,z

Table S3(a). Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 ×10^3) for Ba_2GeF_2S3. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Ba(1)	-2519(1)	789(1)	-2445(1)	10(1)	1.92
Ba(2)	22(1)	786(1)	2530(1)	10(1)	1.90
Ge(1)	2094(2)	2500	3286(3)	14(1)	4.00
Ge(2)	405(2)	2500	6686(3)	14(1)	4.02
S(1)	2606(4)	3539(2)	2262(6)	20(1)	1.99
S(2)	-84(4)	3566(2)	7686(5)	12(1)	2.02
S(3)	2211(4)	2500	6877(10)	19(1)	2.06
S(4)	287(4)	2500	3059(10)	18(1)	2.10
F(1)	-1251(6)	14(3)	5030(20)	14(1)	0.99
F(2)	-1238(6)	10(3)	10(20)	13(1)	1.11

Table S3(b). Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 ×10^3) for Ba_2GeF_2Se3. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Ba(1)	-9965(1)	-4256(1)	7548(1)	12(1)	2.01
Ba(2)	-7534(1)	-4255(1)	2403(1)	11(1)	2.20
Ge(1)	-9589(1)	-2500	1678(1)	13(1)	3.97
Ge(2)	-7911(1)	-2500	-1717(1)	13(1)	4.09
Se(1)	-7395(1)	-3592(1)	-2776(1)	15(1)	1.98
Se(2)	-10105(1)	-3592(1)	2740(1)	16(1)	1.96
Se(3)	-7726(1)	-2500	2003(2)	18(1)	2.00
Se(4)	-9776(1)	-2500	-2035(2)	19(1)	2.19
F(1)	-11244(4)	-4988(2)	5039(6)	16(1)	1.03
F(2)	-6269(4)	-4981(2)	4973(6)	16(1)	0.98

Table S3(c). Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 ×10^3) for $Ba_3GeF_2Se_4$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Ba(1)	10896(1)	3662(1)	3954(1)	13(1)	1.84
Ba(2)	8431(1)	536(1)	1927(1)	15(1)	2.01
Ba(3)	7403(1)	1722(1)	5384(1)	15(1)	1.92
Ge(1)	4503(1)	1676(1)	3025(1)	12(1)	3.97
Se(1)	4522(1)	3340(1)	4426(1)	14(1)	1.98
Se(2)	5630(1)	2735(1)	1540(1)	15(1)	2.03
Se(3)	5717(1)	-417(1)	3488(1)	15(1)	2.10
Se(4)	2176(1)	953(1)	2550(1)	16(1)	2.12
F(1)	11656(5)	5595(5)	5368(5)	18(1)	1.01
F(2)	8951(5)	1717(5)	3746(5)	22(1)	1.00

Table S4. Comparison of response electron distribution anisotropy (REDA) for Ge_2Q_6(Q=S, Se) and $GeSe_4$ units.

Compounds	Polyhedras	Δρ	Δ*n* (at 1064 nm)
$[Ba_2F_2][GeS_3]$	Ge_2S_6	0.391	0.109
$[Ba_2F_2][GeSe_3]$	Ge_2Se_6	0.264	0.103
$[Ba_3F_2][GeSe_4]$	$GeSe_4$	0.027	0.063

Table S5. Ge-based compounds containing alkali metals or alkaline earth metals.

compound	Ge-based oligomers
$Na_4MgGe_2Se_6$	$GeSe_3$
Sr_2GeSe_4	$GeSe_4$
$Ba_3GeF_2Se_4$	$GeSe_4$
$Ba_2Ge_2Se_5$	Ge_2Se_5
Cs_2GeSe_3	Ge_2Se_6
$Ba_2GeF_2Se_3$	Ge_2Se_6
$Na_6Ge_2Se_7$	Ge_2Se_7
$Ba_4Ge_3Se_9Cl_2$	Ge_3Se_9
$Cs_2MgGe_3Se_8$	$[Ge_3Se_8]_\infty$ chain

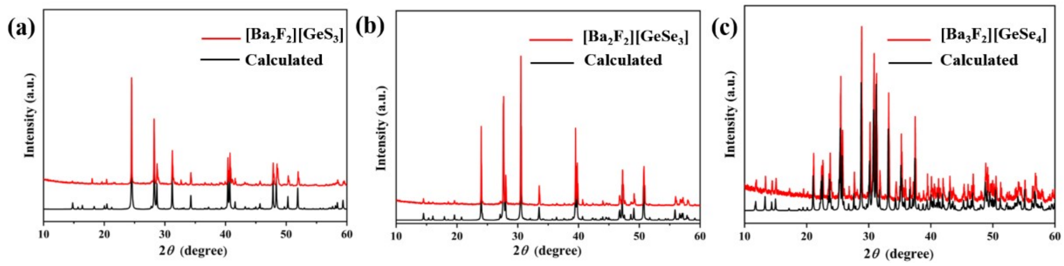

Fig. S1. Experimental and calculated XRD patterns for $Ba_2GeF_2Q_3$ (Q = S, Se) and $Ba_3GeF_2Se_4$

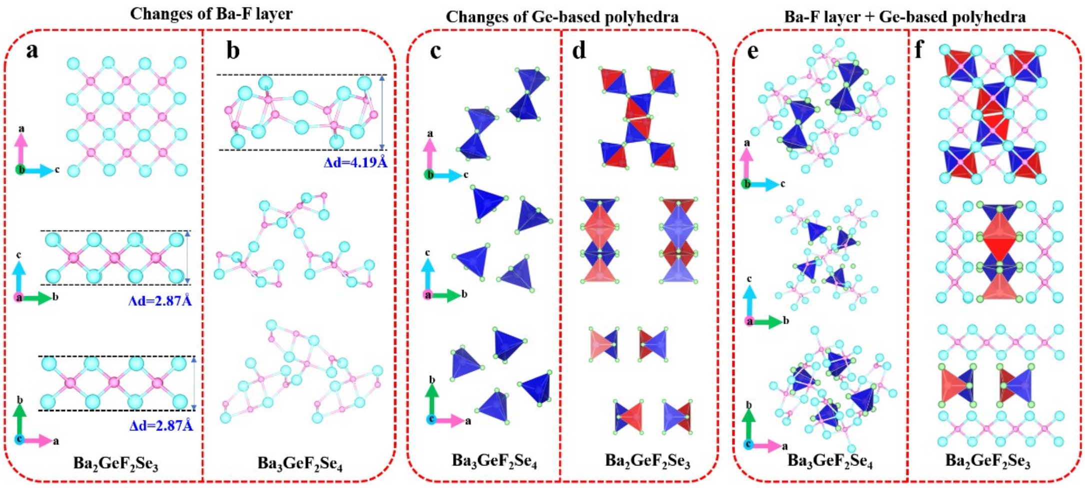

Fig. S2. Arrangement of Ba-F layer and Ge-based polyhedra in $Ba_2GeF_2Se_3$ and $Ba_3GeF_2Se_4$. (Δd is defined as distance of a single Ba-F layer).

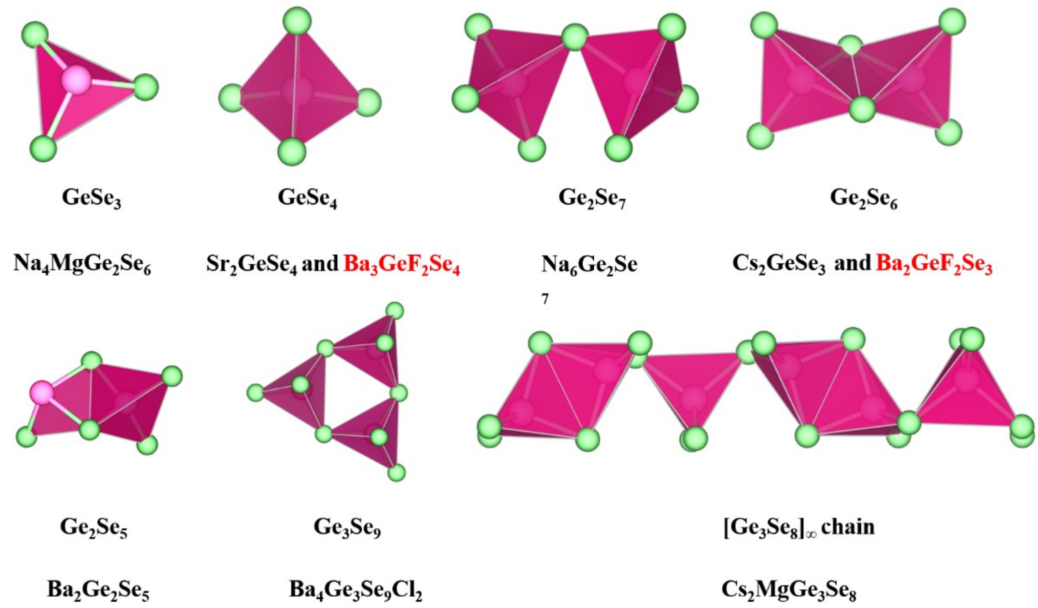

Fig. S3. Different Ge-based configuration in Ge-based compounds containing alkali metals or alkaline earth metals.

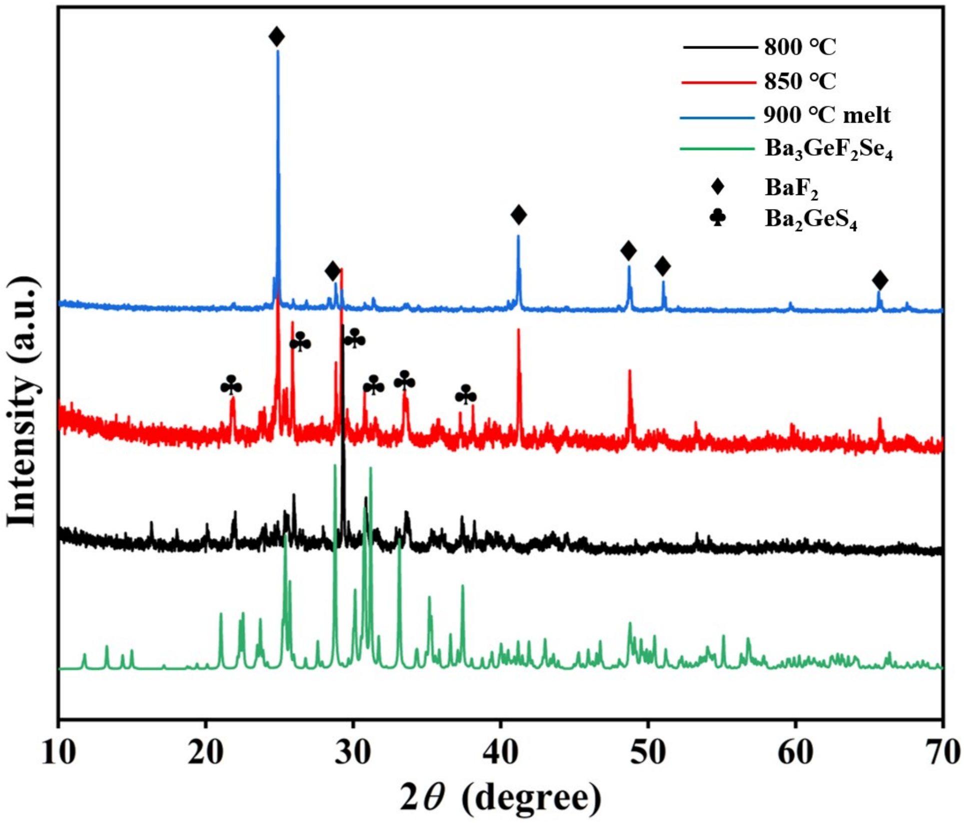

Fig. S4. Powder XRD patterns: calculated one for $Ba_3GeF_2Se_4$, annealed at 800, 850 and 900 °C for $Ba_3GeF_2S_4$, respectively.