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Supporting Information

Cation and Anion Co-Partial Substitution Induced Centrosymmetric to Noncentrosymmetric Structural Transformation to Construct Nonlinear-Optical Rare-Earth Oxythiogermanates

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1. Tables

Table S1. Crystal data and structure refinement parameters for **1**–**3**.

Chemical formula	**$Eu_{18}Ge_9O_5S_{31}$ (1)**	**$Ca_{3.32}Eu_{14.68}Ge_9O_5S_{31}$ (2)**	**$Ba_3Eu_{15}Ge_9O_5S_{31}$ (3)**
Formula weight	4462.45	4091.01	4418.59
Temperature (K)		296	
Crystal system		trigonal	
Space group		*R*3	
a (Å)	16.8496(4)	16.7573(8)	16.8834(7)
c (Å)	17.9927(6)	17.9107(9)	18.0091(8)
γ/°		120	
V (Å^3)	4423.9(3)	4355.6(5)	4445.7(4)
Z		3	
D_{calc} (g/cm^3)	5.025	4.679	4.951
μ (mm^{-1})	24.431	21.588	23.148
F (000)	5874.0	5446.0	5811.0
2θ range (°)	4.836 to 56.706	4.862 to 61.032	3.588 to 50.036
Indep. reflns/R_{int}	4356/0.0319	5845/0.0438	3514/0.0379
GOF on F^2	0.974	1.047	1.187
Flack parameter	-0.001(9)	–0.009(8)	0.09(3)
R1[a], wR2[b] [$I \geq 2\sigma(I)$]	0.0189, 0.0310	0.0265, 0.0510	0.0283, 0.0693
R1[a], wR2[b] [all data]	0.0207, 0.0314	0.0291, 0.0516	0.0291, 0.0701
Largest diff. peak/hole/e Å^{-3}	0.84/–0.90	0.96/–2.39	2.29/–2.55

[a]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b]$wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (U_{eq}[a], Å^2 × 10^3) for **1**–**3**.

Atom	Wyck. site	Occupancy	*x*	*y*	*z*	U_{eq}
			1			
Eu(1)	9*b*	1	1341.3(3)	8239.2(3)	6710.7(2)	11.68(9)
Eu(2)	9*b*	1	3254.2(3)	8055.3(3)	8051.4(2)	12.18(9)
Eu(3)	9*b*	1	1283.1(3)	9902.3(3)	4854.7(2)	10.29(9)
Eu(4)	9*b*	1	-1467.2(3)	6728.5(3)	6671.2(2)	11.32(9)
Eu(5)	9*b*	1	1784.6(3)	6679.1(3)	5234.8(2)	12.00(9)
Eu(6)	9*b*	1	1773.0(3)	8325.7(3)	9993.8(2)	10.91(9)
Ge(1)	3*a*	1	0	10000	3359.5(7)	7.1(3)
Ge(2)	3*a*	1	3333.33	6666.67	3243.9(7)	7.9(3)
Ge(3)	9*b*	1	3263.6(5)	9828.1(5)	5416.3(4)	6.78(17)
Ge(4)	9*b*	1	4.1(5)	6540.1(5)	7972.5(4)	6.17(17)
Ge(5)	3*a*	1	3333.33	6666.67	6720.4(8)	6.9(3)
S(1)	3*a*	1	3333.33	6666.67	4469.4(17)	13.4(7)
S(2)	9*b*	1	3312.8(12)	7899.5(12)	6330.8(10)	11.2(4)
S(3)	9*b*	1	3167.4(12)	9934.1(12)	6640.3(9)	10.0(4)
S(4)	9*b*	1	-1261.0(12)	5327.1(13)	7573.9(10)	9.1(4)
S(5)	9*b*	1	1993.7(12)	8803.8(13)	8385.8(10)	9.5(4)
S(6)	9*b*	1	1253.7(12)	6581.7(12)	7521.5(10)	9.9(4)
S(7)	9*b*	1	3295.0(13)	11084.1(12)	5015.5(9)	9.6(4)
S(8)	9*b*	1	3414.6(13)	7979.9(13)	9713.5(11)	12.5(4)

S(9)	9*b*	1	2017.3(12)	8604.1(12)	5041.7(10)	10.3(4)
S(10)	9*b*	1	99.5(13)	6786.6(13)	9183.3(10)	9.0(4)
S(11)	9*b*	1	-68.6(13)	8757.3(12)	6102.3(10)	11.7(4)
O(1)	3*a*	1	0	10000	4354(4)	8.7(18)
O(2)	3*a*	1	3333.33	6666.67	7724(4)	6.6(17)
O(3)	9*b*	1	-19(3)	7482(3)	7535(2)	8.3(10)
			2			
Eu(1)	9*b*	0.848	1353.5(3)	8243.4(4)	6712.0(3)	13.59(15)
Eu(2)	9*b*	0.750	3261.8(4)	8058.7(4)	8049.9(3)	12.97(18)
Eu(3)	9*b*	0.762	1283.4(4)	9905.5(4)	4848.1(3)	11.18(17)
Eu(4)	9*b*	1	-1466.3(3)	6734.7(3)	6668.5(2)	12.33(12)
Eu(5)	9*b*	0.705	1787.8(4)	6678.4(4)	5232.8(4)	13.28(19)
Eu(6)	9*b*	0.829	1767.3(4)	8329.2(4)	9994.7(3)	11.76(15)
Ca(1)	9*b*	0.152	1353.5(3)	8243.4(4)	6712.0(3)	13.59(15)
Ca(2)	9*b*	0.250	3261.8(4)	8058.7(4)	8049.9(3)	12.97(18)
Ca(3)	9*b*	0.238	1283.4(4)	9905.5(4)	4848.1(3)	11.18(17)
Ca(5)	9*b*	0.295	1787.8(4)	6678.4(4)	5232.8(4)	13.28(19)
Ca(6)	9*b*	0.171	1767.3(4)	8329.2(4)	9994.7(3)	11.76(15)
Ge(1)	9*b*	1	0	10000	3358.0(8)	7.4(3)
Ge(2)	9*b*	1	3333.33	6666.67	3250.5(8)	8.6(3)
Ge(3)	3*a*	1	3264.0(6)	9832.0(6)	5419.9(5)	7.71(19)
Ge(4)	3*a*	1	7.6(6)	6548.8(6)	7976.7(5)	6.60(18)
Ge(5)	3*a*	1	3333.33	6666.67	6723.8(9)	8.4(3)

S(1)	9*b*	1	3333.33	6666.67	4475(2)	18.1(8)
S(2)	9*b*	1	3309.7(15)	7903.7(14)	6330.3(12)	13.5(4)
S(3)	9*b*	1	3168.8(15)	9931.7(14)	6649.5(12)	12.7(4)
S(4)	9*b*	1	-1258.8(14)	5330.2(14)	7567.7(11)	8.8(4)
S(5)	9*b*	1	1997.6(14)	8795.7(14)	8389.8(11)	10.9(4)
S(6)	9*b*	1	1258.7(14)	6584.4(14)	7523.0(12)	10.9(4)
S(7)	9*b*	1	3288.8(15)	11088.4(14)	5015.8(11)	11.6(4)
S(8)	9*b*	1	3410.1(14)	7980.1(14)	9706.7(12)	12.6(4)
S(9)	9*b*	1	2007.8(13)	8604.1(14)	5043.1(12)	11.3(4)
S(10)	9*b*	1	94.6(14)	6795.3(14)	9191.1(11)	9.3(4)
S(11)	9*b*	1	-59.2(15)	8761.2(14)	6097.0(12)	13.6(4)
O(1)	9*b*	1	0	10000	4352(5)	8(2)
O(2)	3*a*	1	3333.33	6666.67	7740(5)	10(2)
O(3)	3*a*	1	-7(4)	7506(4)	7536(3)	8.5(11)
			3			
Ba(1)	9*b*	1	8452.5(7)	8443.2(7)	5309.7(7)	5.5(3)
Eu(1)	9*b*	1	6886.4(8)	8237.3(7)	3453.6(5)	14.3(3)
Eu(2)	9*b*	1	4797.7(7)	8053.9(7)	4798.4(6)	13.6(3)
Eu(3)	9*b*	1	8196.7(8)	6726.6(9)	3413.7(6)	13.6(3)
Eu(4)	9*b*	1	7953.0(7)	4714.7(7)	4928.6(6)	12.0(3)
Eu(5)	9*b*	1	9893.0(7)	4986.4(8)	3406.3(6)	13.5(3)
Ge(1)	3*a*	1	3333.33	6666.67	6776.6(19)	7.0(7)
Ge(2)	3*a*	1	10000	10000	3329(2)	9.1(8)

Ge(3)	9*b*	1	6541.8(14)	6547.2(14)	4721.4(12)	6.3(4)
Ge(4)	9*b*	1	9933.0(14)	6769.5(14)	5494.1(12)	9.3(5)
Ge(5)	3*a*	1	10000	10000	6804(2)	7.0(7)
S(1)	3*a*	1	10000	10000	4542(5)	15.7(18)
S(2)	9*b*	1	6584(3)	5330(3)	4323(3)	10.6(10)
S(3)	9*b*	1	3419(3)	8748(3)	4274(3)	11.1(10)
S(4)	9*b*	1	8824(3)	8767(4)	2845(3)	15.8(11)
S(5)	9*b*	1	9980(3)	8748(3)	6411(3)	11.7(10)
S(6)	9*b*	1	8683(3)	6744(3)	5121(3)	12.0(10)
S(7)	9*b*	1	9960(3)	5545(3)	5088(3)	11.4(10)
S(8)	9*b*	1	4570(3)	7968(3)	6454(3)	13.5(10)
S(9)	9*b*	1	6807(3)	8806(3)	5128(3)	11.4(10)
S(10)	9*b*	1	6696(3)	6790(3)	5927(3)	9.5(10)
S(11)	9*b*	1	9843(3)	6584(3)	6718(3)	12.2(10)
O(1)	9*b*	1	7508(10)	7502(9)	4272(7)	13(3)
O(2)	3*a*	1	3333.33	6666.67	7778(12)	7.8(18)
O(3)	3*a*	1	10000	10000	7823(12)	9(5)

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

Table S3. Bond distances for **1**–**3**.

Bond	Distance/Å	Bond	Distance/Å
		1	
Eu(1)–S(3)	2.9752(18)	Eu(5)–S(5)^{2}	3.1358(18)
Eu(1)–S(5)	3.1863(18)	Eu(5)–S(9)	3.0860(19)
Eu(1)–S(6)	3.0883(19)	Eu(5)–S(10)^{2}	3.088(19)
Eu(1)–S(9)	3.1611(19)	Eu(5)–O(3)^{2}	2.457(5)
Eu(1)–S(10)^{2}	3.0031(19)	Eu(6)–S(2)^{6}	3.4314(19)
Eu(1)–S(11)	3.1110(19)	Eu(6)–S(3)^{6}	2.961(19)
Eu(1)–O(3)	2.482(4)	Eu(6)–S(4)^{1}	2.8952(18)
Eu(2)–S(2)	3.1127(18)	Eu(6)–S(5)	2.9763(18)
Eu(2)–S(5)	3.0237(18)	Eu(6)–S(6)^{1}	3.0407(18)
Eu(2)–S(6)^{3}	3.2258(19)	Eu(6)–S(7)^{12}	3.1607(17)
Eu(2)–S(6)	3.1729(19)	Eu(6)–S(8)	3.1397(19)
Eu(2)–S(7)^{6}	2.9640(19)	Eu(6)–S(10)	3.0807(19)
Eu(2)–S(8)	3.011(2)	Ge(1)–S(8)^{13}	2.2200(19)
Eu(2)–O(2)	2.4803(18)	Ge(1)–S(8)^{14}	2.2200(18)
Eu(3)–S(4)^{2}	3.1498(18)	Ge(1)–S(8)^{9}	2.2199(19)
Eu(3)–S(4)^{10}	3.2744(18)	Ge(1)–O(1)	1.789(7)
Eu(3)–S(7)	2.9649(19)	Ge(2)–S(1)	2.205(3)
Eu(3)–S(8)^{9}	3.254(2)	Ge(2)–S(11)^{2}	2.2104(19)
Eu(3)–S(9)	3.0223(19)	Ge(2)–S(11)^{15}	2.2106(19)
Eu(3)–S(11)	3.091(19)	Ge(2)–S(11)^{5}	2.2105(19)
Eu(3)–S(11)^{8}	3.1276(19)	Ge(3)–S(3)	2.2219(19)

Eu(3)–O(1)	2.423(3)	Ge(3)–S(5)^{5}	2.2089(19)
Eu(4)–S(3)^{7}	3.0679(18)	Ge(3)–S(7)	2.2112(19)
Eu(4)–S(4)	3.0256(18)	Ge(3)–S(9)	2.1878(19)
Eu(4)–S(7)^{7}	3.2246(17)	Ge(4)–S(4)	2.209(2)
Eu(4)–S(8)^{11}	3.328(19)	Ge(4)–S(6)	2.225(2)
Eu(4)–S(9)^{1}	3.1704(19)	Ge(4)–S(10)	2.2086(19)
Eu(4)–S(10)^{2}	3.0367(19)	Ge(4)–O(3)	1.789(5)
Eu(4)–S(11)	3.1986(19)	Ge(5)–S(2)^{3}	2.2090(19)
Eu(4)–O(3)	2.623(5)	Ge(5)–S(2)	2.2089(19)
Eu(5)–S(1)	2.9600(15)	Ge(5)–S(2)^{4}	2.2089(19)
Eu(5)–S(2)^{4}	3.1395(19)	Ge(5)–O(2)	1.806(8)
Eu(5)–S(2)	3.0745(19)		

2

Eu(1)/Ca(1)–S(3)	2.943(2)	Eu(5)/Ca(5)–S(5)^{1}	3.130(2)
Eu(1)/Ca(1)–S(5)	3.171(2)	Eu(5)/Ca(5)–S(9)	3.078(2)
Eu(1)/Ca(1)–S(6)	3.070(2)	Eu(5)/Ca(5)–S(10)^{1}	3.066(2)
Eu(1)/Ca(1)–S(9)	3.137(2)	Eu(5)/Ca(5)–O(3)^{1}	2.425(6)
Eu(1)/Ca(1)–S(10)^{1}	2.980(2)	Eu(6)/Ca(6)–S(2)^{2}	3.398(2)
Eu(1)/Ca(1)–S(11)	3.102(2)	Eu(6)/Ca(6)–S(3)^{2}	2.941(2)
Eu(1)/Ca(1)–O(3)	2.467(5)	Eu(6)/Ca(6)–S(4)^{7}	2.880(2)
Eu(2)/Ca(2)–S(2)	3.095(2)	Eu(6)/Ca(6)–S(5)	2.953(2)
Eu(2)/Ca(2)–S(5)	3.000(2)	Eu(6)/Ca(6)–S(6)^{7}	3.021(2)
Eu(2)/Ca(2)–S(6)	3.157(2)	Eu(6)/Ca(6)–S(7)^{11}	3.141(2)
Eu(2)/Ca(2)–S(6)^{3}	3.194(2)	Eu(6)/Ca(6)–S(8)	3.130(2)

Eu(2)/Ca(2)–S(7)^{2}	2.953(2)	Eu(6)/Ca(6)–S(10)	3.055(2)
Eu(2)/Ca(2)–S(8)	2.986(2)	Ge(1)–S(8)^{5}	2.214(2)
Eu(2)/Ca(2)–O(2)	2.458(2)	Ge(1)–S(8)^{12}	2.214(2)
Eu(3)/Ca(3)–S(4)^{1}	3.139(2)	Ge(1)–S(8)^{13}	2.214(2)
Eu(3)/Ca(3)–S(4)^{4}	3.256(2)	Ge(1)–O(1)	1.781(9)
Eu(3)/Ca(3)–S(7)	2.941(2)	Ge(2)–S(1)	2.194(4)
Eu(3)/Ca(3)–S(8)^{5}	3.240(2)	Ge(2)–S(11)^{14}	2.208(2)
Eu(3)/Ca(3)–S(9)	3.000(2)	Ge(2)–S(11)^{15}	2.208(2)
Eu(3)/Ca(3)–S(11)	3.070(2)	Ge(2)–S(11)^{1}	2.208(2)
Eu(3)/Ca(3)–S(11)^{6}	3.119(2)	Ge(3)–S(3)	2.220(2)
Eu(3)/Ca(3)–O(1)	2.404(3)	Ge(3)–S(5)^{14}	2.203(2)
Eu(4)–S(3)^{8}	3.051(2)	Ge(3)–S(7)	2.207(2)
Eu(4)–S(4)	3.012(2)	Ge(3)–S(9)	2.188(2)
Eu(4)–S(7)^{8}	3.198(2)	Ge(4)–S(4)	2.208(2)
Eu(4)–S(8)^{9}	3.320(2)	Ge(4)–S(6)	2.221(2)
Eu(4)–S(9)^{7}	3.160(2)	Ge(4)–S(10)	2.205(2)
Eu(4)–S(10)^{1}	3.031(2)	Ge(4)–O(3)	1.798(6)
Eu(4)–S(11)	3.183(2)	Ge(5)–S(2)^{10}	2.208(2)
Eu(4)–O(3)	2.627(5)	Ge(5)–S(2)^{3}	2.208(2)
Eu(5)/Ca(5)–S(1)	2.9324(18)	Ge(5)–S(2)	2.208(2)
Eu(5)/Ca(5)–S(2)	3.057(2)	Ge(5)–O(2)	1.820(10)
Eu(5)/Ca(5)–S(2)^{10}	3.127(2)		

3

Ba(1)–S(1)	2.963(4)	Eu(4)–S(6)	3.026(5)

Ba(1)–S(5)[1]	3.145(5)	Eu(4)–S(7)	2.963(5)
Ba(1)–S(5)	3.086(5)	Eu(4)–S(8)[10]	3.258(5)
Ba(1)–S(6)	3.101(5)	Eu(4)–O(2)[10]	2.419(8)
Ba(1)–S(9)	3.147(5)	Eu(5)–S(2)[12]	2.894(5)
Ba(1)–S(10)	3.089(5)	Eu(5)–S(3)[2]	3.035(5)
Ba(1)–O(1)	2.455(14)	Eu(5)–S(5)[9]	3.433(5)
Eu(1)–S(3)[6]	3.093(5)	Eu(5)–S(7)	3.157(5)
Eu(1)–S(4)	3.127(5)	Eu(5)–S(8)[10]	3.148(5)
Eu(1)–S(6)[5]	3.154(5)	Eu(5)–S(9)[10]	2.988(5)
Eu(1)–S(9)	3.188(5)	Eu(5)–S(10)[10]	3.076(5)
Eu(1)–S(10)[5]	3.000(5)	Eu(5)–S(11)[9]	2.962(5)
Eu(1)–S(11)[5]	2.975(5)	Ge(1)–S(8)[7]	2.222(5)
Eu(1)–O(1)	2.473(13)	Ge(1)–S(8)[6]	2.222(5)
Eu(2)–S(3)	3.226(5)	Ge(1)–S(8)	2.222(5)
Eu(2)–S(3)[6]	3.179(5)	Ge(1)–O(2)	1.80(2)
Eu(2)–S(5)[5]	3.116(5)	Ge(2)–S(1)	2.184(9)
Eu(2)–S(7)[1]	2.971(5)	Ge(2)–S(4)[1]	2.213(5)
Eu(2)–S(8)	3.001(5)	Ge(2)–S(4)	2.213(5)
Eu(2)–S(9)	3.028(5)	Ge(2)–S(4)[2]	2.213(5)
Eu(2)–O(3)[8]	2.473(5)	Ge(3)–S(2)	2.212(5)
Eu(3)–S(2)	3.039(5)	Ge(3)–S(3)[6]	2.229(5)
Eu(3)–S(4)	3.224(5)	Ge(3)–S(10)	2.202(5)
Eu(3)–S(6)	3.179(5)	Ge(3)–O(1)	1.813(14)
Eu(3)–S(7)[9]	3.234(5)	Ge(4)–S(6)	2.194(5)

Eu(3)–S(8)[10]	3.353(5)	Ge(4)–S(7)	2.215(5)
Eu(3)–S(10)[5]	3.052(5)	Ge(4)–S(9)[2]	2.205(5)
Eu(3)–S(11)[9]	3.092(5)	Ge(4)–S(11)	2.220(5)
Eu(3)–O(1)	2.641(13)	Ge(5)–S(5)[2]	2.214(5)
Eu(4)–S(2)[12]	3.274(5)	Ge(5)–S(5)[1]	2.214(5)
Eu(4)–S(2)	3.163(5)	Ge(5)–S(5)	2.214(5)
Eu(4)–S(4)[13]	3.142(5)	Ge(5)–O(3)	1.830(2)
Eu(4)–S(4)[3]	3.089(5)		

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

Table S4. LIDTs of **1**, **2** and AGS for their powder samples (75−110 μm).

Compound	Damage energy (mJ)	Spot area (cm^2)	Damage threshold (MW/cm^2)	Relative value
1	2.3	0.02	11.44	3.3
2	2.3	0.02	11.44	3.3
AGS	0.6	0.02	3.48	1

Table S5. Thermal expansion coefficients (TECs, αL) ($\times 10^{-5}$ K^{-1}) of **1**, **2** and the reference AGS along *a*-, *b*- and *c*-axis, and the thermal expansion anisotropy (TEA, δ) of **1**, **2** and AGS.

Compound	a [10^{-5} K^{-1}]	b [10^{-5} K^{-1}]	c [10^{-5} K^{-1}]	δ
1	−1.58	−1.58	−4.08	2.58
2	1.49	1.49	0.77	1.94
AGS	3.08	3.08	−9.158	2.97

Table S6. NLO properties of **1**–**3** and other reported rare-earth oxychalcogenides.

Compound	Space group	E_g (eV)	SHG (× AGS)	LIDT (× AGS)	Δn	PM/NPM	Reference
$Sm_3NbO_4S_3$	$Pna2_1$	2.68	0.3	12.5	-	PM	1
$Gd_3NbO_4S_3$	$Pna2_1$	2.74	0.4	4.5	-	PM	1
$La_3Ga_3Ge_2O_{10}S_3$	$P\bar{6}2c$	4.7	2 KDP	-	0.11	PM	2
$LaCaGa_3OS_6$	$P\bar{4}2_1m$	3.27	0.9	14.0	0.163	PM	3
$LaSrGa_3OS_6$	$P\bar{4}2_1m$	3.21	1.0	14.0	0.138	PM	3
Eu_3GeOS_4	$Pca2_1$	2.05	0.24	8.86	0.019	NPM	4
$Nd_3[Ga_3O_3S_3][Ge_2O_7]$	$P\bar{6}2c$	4.35	0.8	23.0	0.091	PM	5
$Eu_2MnGe_2OS_6$	$P\bar{4}2_1m$	2.40	0.3	8.3	0.13	PM	6
$Eu_2FeGe_2OS_6$	$P\bar{4}2_1m$	2.11	0.3	2.8	0.12	PM	6
$Eu_2CoGe_2OS_6$	$P\bar{4}2_1m$	2.14	0.5	3.2	0.17	PM	6
$Eu_{18}Ge_9O_5S_{31}$	$R3$	2.18	0.5	3.3	0.0749	PM	this work
$Ca_{3.32}Eu_{14.68}Ge_9O_5S_{31}$	$R3$	2.23	0.6	3.3	0.0543	PM	this work
$Ba_3Eu_{15}Ge_9O_5S_{31}$	$R3$	2.24	-	-	0.0282	-	this work

"-" indicates no available data.

PM: phase-matchable; NPM: non-phase-matchable.

Table S7. The calculated dipole moments (esu cm $Å^{-3}$) in one unit cell of **1** and **2**.

Structural unit	GeS_4	$GeOS_3$	Total
		1	
Dipole moment (esu cm $Å^{-3}$)	0.085	0.116	0.201
		2	
Dipole moment (esu cm $Å^{-3}$)	0.096	0.120	0.216

Table S8. Distortion degrees of polyhedral units in **1** and **2**.

Unite	DI (M-S/O)	DI (S-M-S/O)	DI (S-S/O)
		1	
$Ge(1)OS_3$	0.076503	0.04179	0.96841
$Ge(2)S_4$	0.000917	0.03069	0.96704
$Ge(3)S_4$	0.004062	0.02791	0.96708
$Ge(4)OS_3$	0.072664	0.03683	0.96841
$Ge(5)OS_3$	0.071673	0.00882	0.9696
		2	
$Ge(1)OS_3$	0.07711	0.03986	0.9685
$Ge(2)S_4$	0.002381	0.03582	0.96713
$Ge(3)S_4$	0.004083	0.02714	0.96712
$Ge(4)OS_3$	0.073529	0.03711	0.96848
$Ge(5)OS_3$	0.068925	0.00777	0.96846

Distortion degree: the average deviation of bond lengths, bond angles and side lengths from their means.

2. Figures

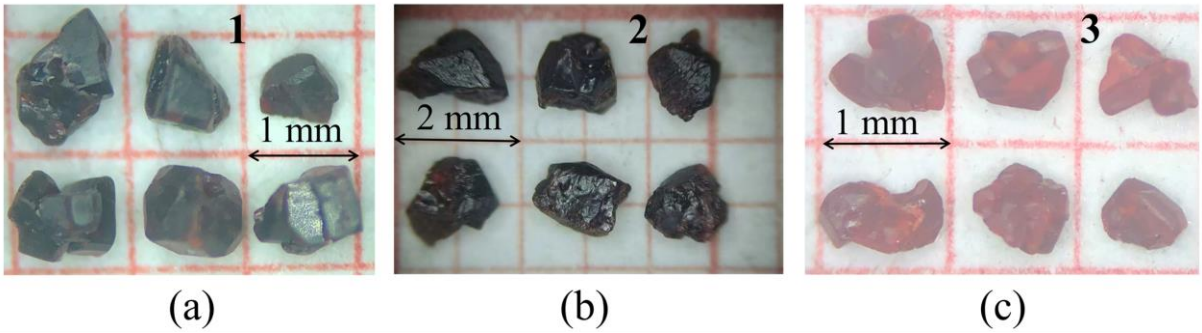

Figure S1. The crystals' photographs of **1** (a), **2** (b) and **3** (c).

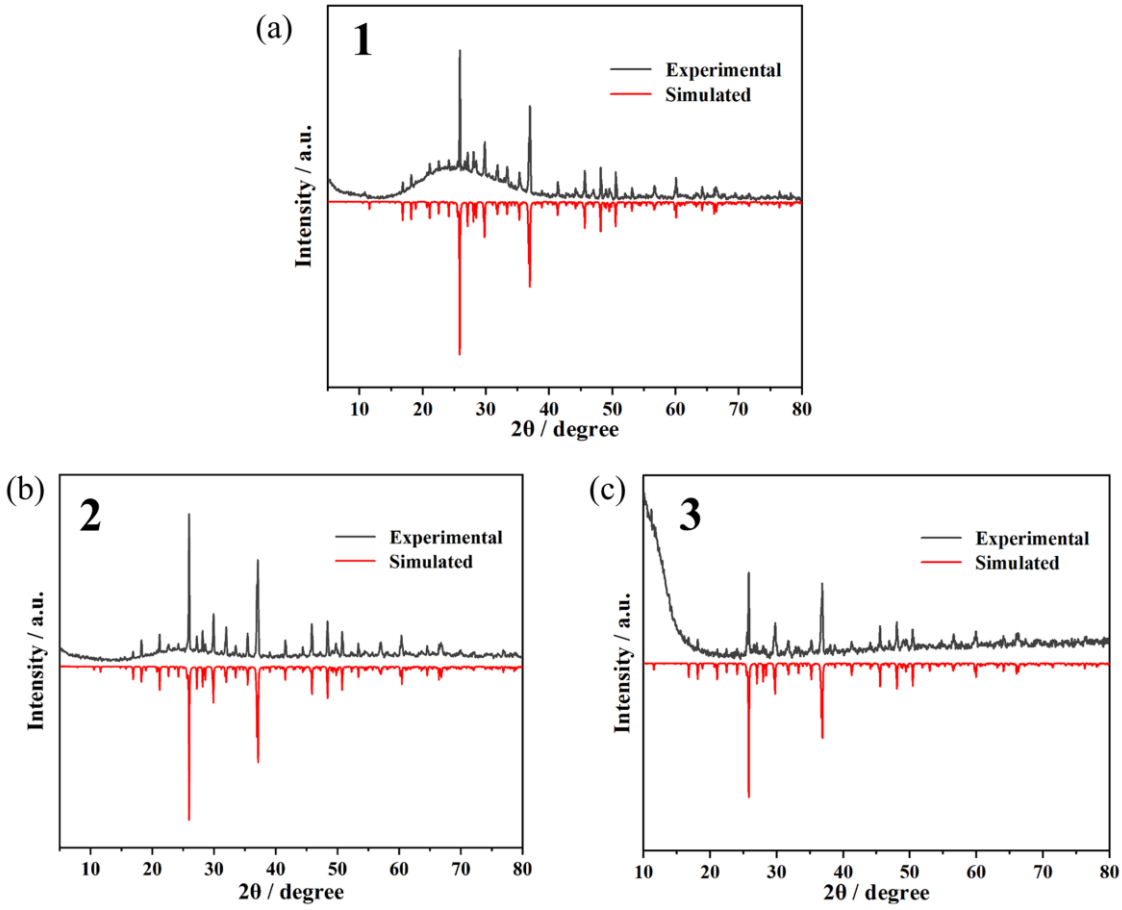

Figure S2. The powder XRD patterns of **1** (a), **2** (b) and **3** (c).

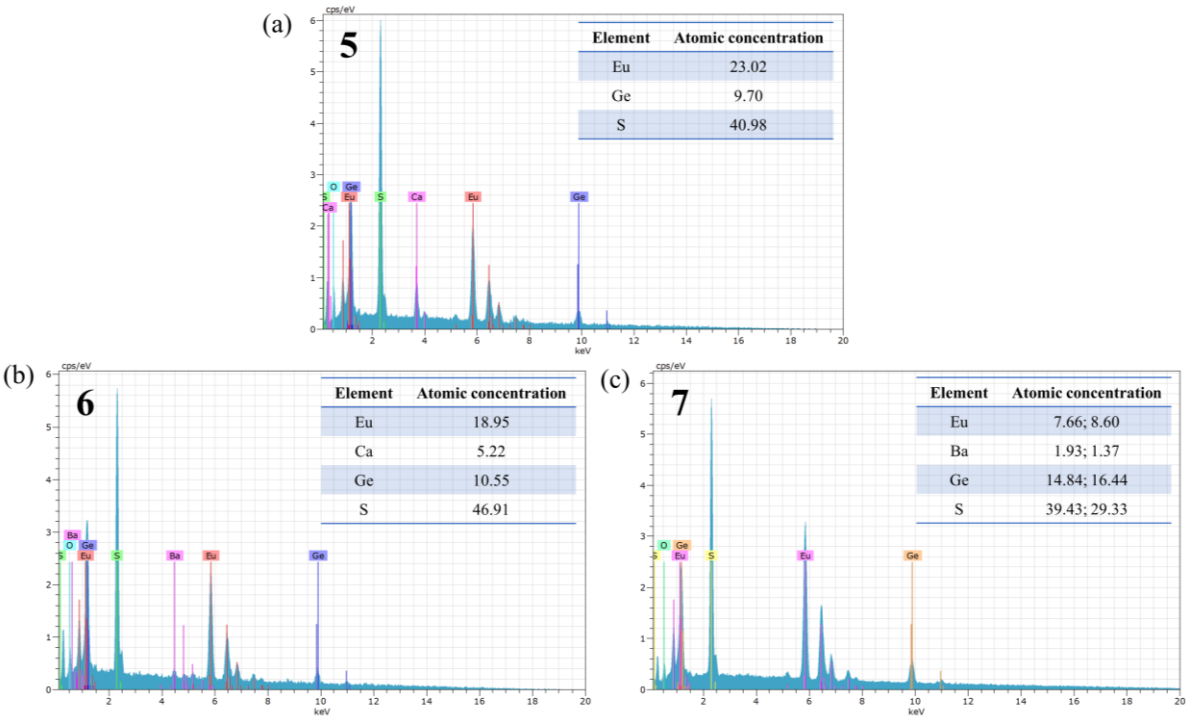

Figure S3. The EDS images for single crystals of **1** (a), **2** (b) and **3** (c).

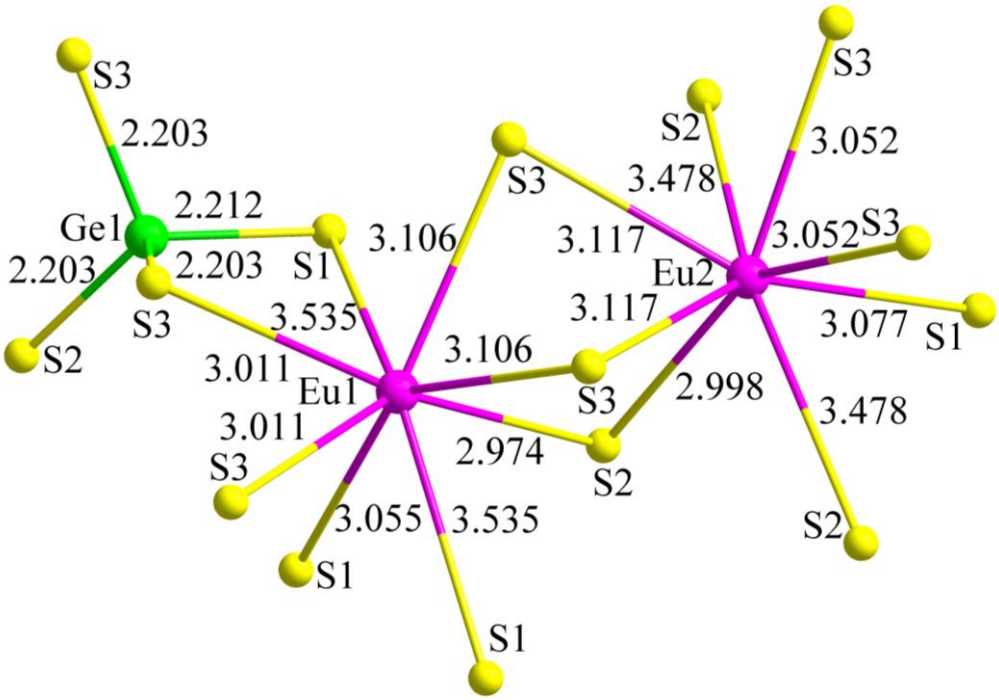

Figure S4. Coordination geometry of **0**.

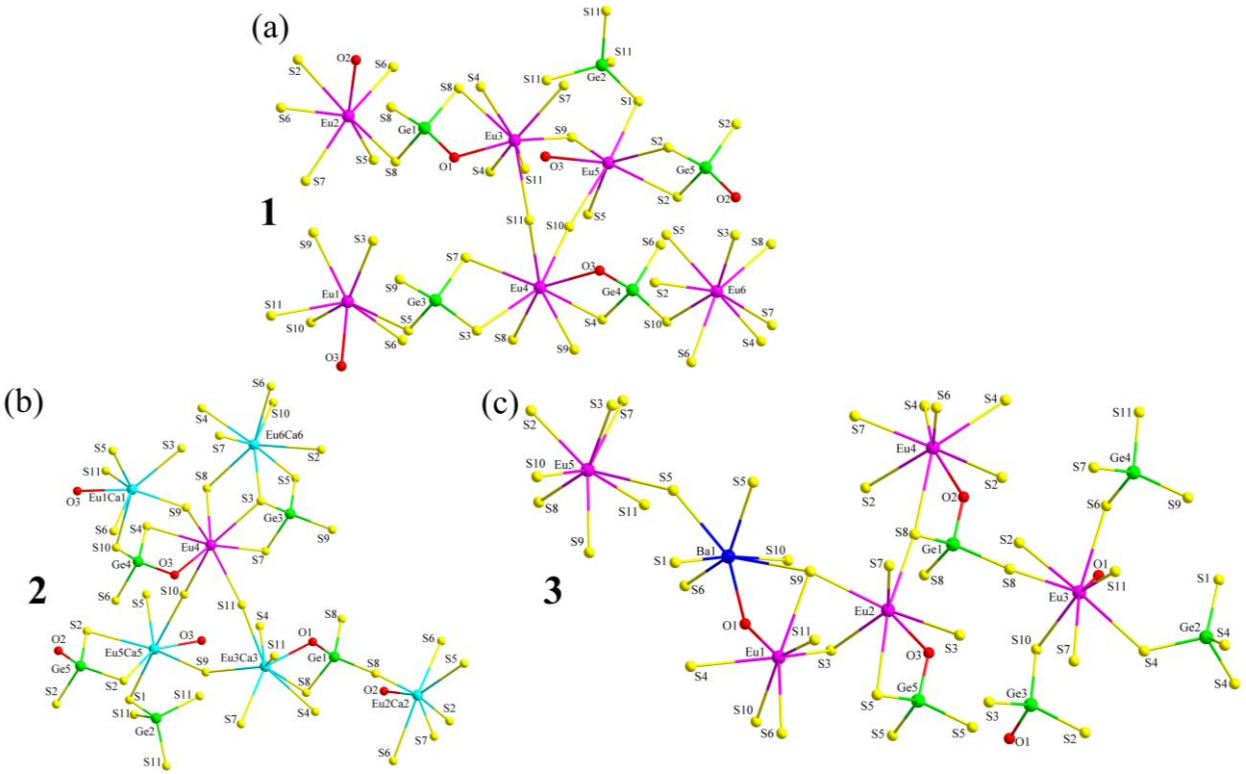

Figure S5. Coordination geometries of **1** (a), **2** (b) and **3** (c).

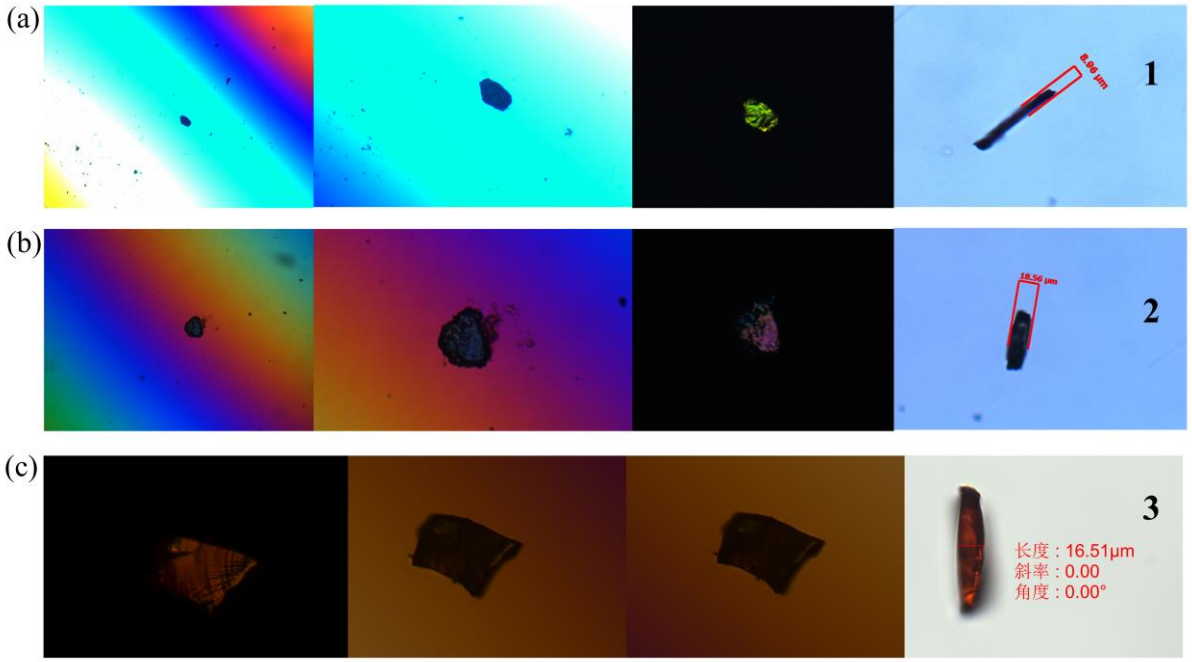

Figure S6. Photographs of **1** (a), **2** (b) and **3** (c) for the measurements of birefringence with polarizing microscope.

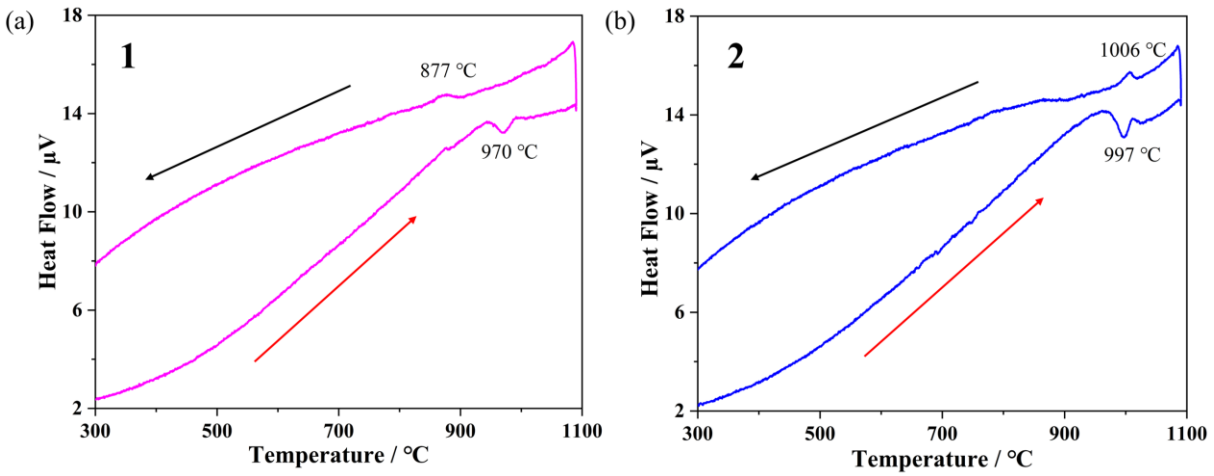

Figure S7. DSC curves of **1** and **2**. The red and black arrows represent the heating and cooling processes, respectively.

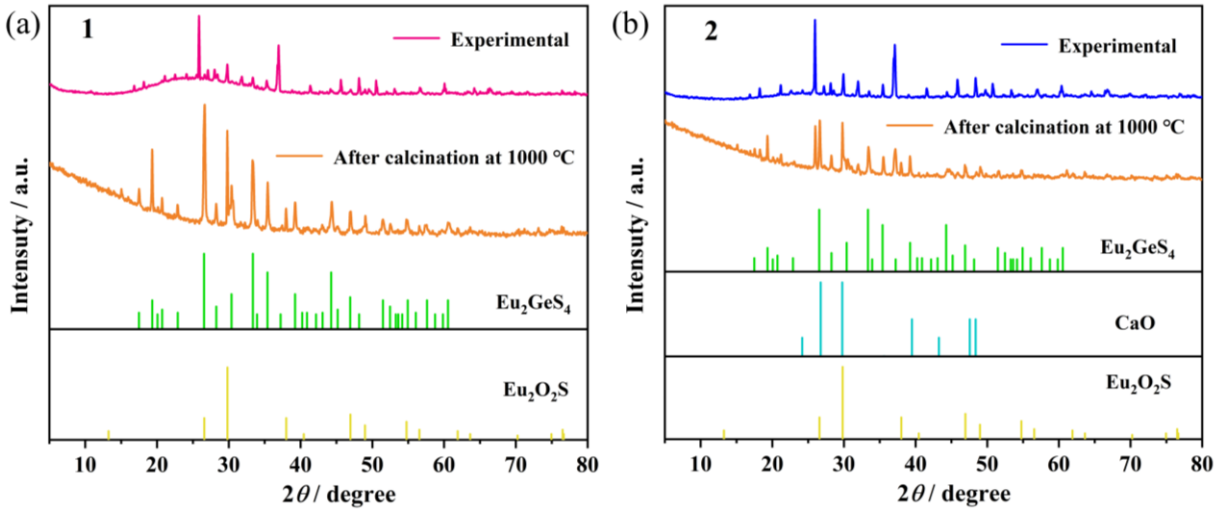

Figure S8. The powder XRD patterns of **1** and **2** after calcination.

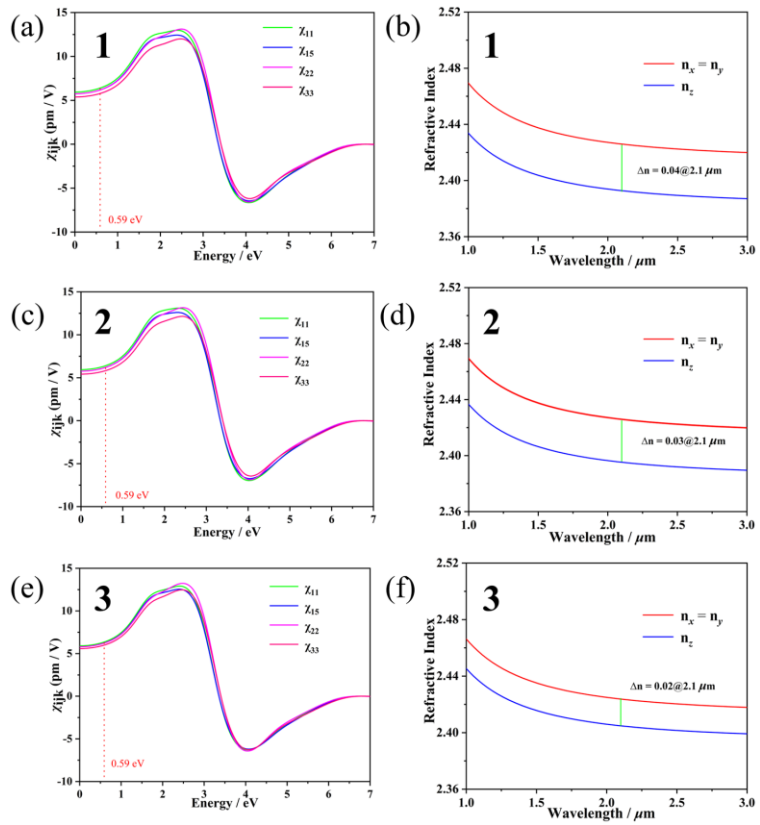

Figure S9. The calculated SHG tensors (a, c, e) and birefringences (b, d, f) of **1**–**3**.

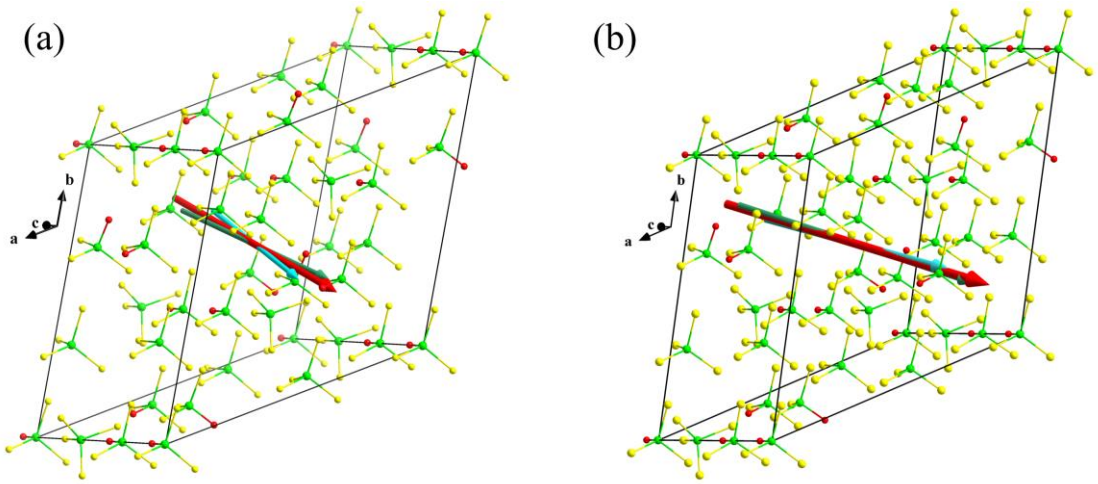

Figure S10. The calculated dipole moments for one unit cell of **1** (a) and **2** (b) (Red: total; blue: GeS_4 tetrahedra; green: $GeOS_3$ tetrahedra).

3. References

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