Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Applying Band Gap Engineering to Tune Linear Optical and Nonlinear Optical Properties of Noncentrosymmetric Chalcogenides $La_4Ge_3Se_xS_{12-x}$ (x = 0, 2, 4, 6, 8, 10)

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Supporting Information

Table S1. Selected crystal data and unit cell parameters for $La_4Ge_3Se_xS_{12-x}$ (x = 0, 2, 4, 6, 8, 10)

Empirical Formula	$La_4Ge_3S_{12}$	$La_4Ge_3Se_2S_{10}$	$La_4Ge_3Se_4S_8$	$La_4Ge_3Se_6S_6$	$La_4Ge_3Se_8S_4$	$La_4Ge_3Se_{10}S_2$
Formula weight	1158.13	1247.40	1356.28	1423.43	1521.60	1616.26
Temperature	200(2) K	296(2) K	296(2) K	296(2) K	296(2) K	296(2) K
Radiation, wavelength	Mo-Kα, 0.71073 Å	Mo-Kα, 0.71073 Å	Mo-Kα, 0.71073 Å	Mo-Kα, 0.71073 Å	Mo-Kα, 0.71073 Å	Mo-Kα, 0.71073 Å
Crystal system	Rhombohedral					
Space group	*R3c* (No. 161)					
Unit cell dimensions	a=19.427(3) Å c=8.0753(13) Å	a=19.5575(6) Å c=8.1468(19) Å	a=19.6679(12) Å c=8.1950(6) Å	a=19.7766(11) Å c= 8.2448(4) Å	a=19.8976(12) Å c=8.2984(4) Å	a=20.0723(12) Å c=8.3460(5) Å
Unit cell volume	2639.2(10) $Å^3$	2698.64(19) $Å^3$	2745.3(4) $Å^3$	2792.6(3) $Å^3$	2845.3(4) $Å^3$	2912.1(4) $Å^3$
Z	6					
Density (calc)	4.372 g/cm^3	4.605 g/cm^3	4.922 g/cm^3	5.078 g/cm^3	5.328 g/cm^3	5.530 g/cm^3
Absorption coefficient	15.942 mm^{-1}	19.221 mm^{-1}	23.427 mm^{-1}	25.491 mm^{-1}	28.806 mm^{-1}	31.713 mm^{-1}
Final R indices [$I>2\sigma_{(I)}$]	R_1 = 0.0323, wR_2 = 0.0634	R_1 = 0.0351, wR_2 = 0.0618	R_1 = 0.0323, wR_2 = 0.0518	R_1 = 0.0296, wR_2 = 0.0439	R_1 = 0.0391, wR_2 = 0.0709	R_1 = 0.0368, wR_2 = 0.0632
Final R indices [all data]	R_1 = 0.0383, wR_2 = 0.0763	R_1 = 0.0520, wR_2 = 0.0812	R_1 = 0.0415, wR_2 = 0.0597	R_1 = 0.0374, wR_2 = 0.0457	R_1 = 0.0646, wR_2 = 0.0840	R_1 = 0.0515, wR_2 = 0.0680

Table S2. Refined atomic coordinates and isotropic displacement parameters for $La_4Ge_3Se_xS_{12-x}$ (x = 0, 2, 4, 6, 8, 10)

Atoms	Wyckoff	*x*	*y*	*z*	Occupancy	U_{eq} (Å^2)
			$La_4Ge_3S_{12}$			
La1	*18b*	0.56401(7)	0.66945(9)	0.97069(15)	1	0.0113(3)
La2	*6a*	0.3333	0.6667	0.6736(2)	1	0.0092(5)
Ge1	*18b*	0.34629(12)	0.47923(13)	1.0210(3)	1	0.0074(5)
S1	*18b*	0.2470(3)	0.4661(3)	1.1771(7)	1	0.0110(11)
S2	*18b*	0.3939(3)	0.6029(3)	0.9226(6)	1	0.0101(11)
S3	*18b*	0.6039(3)	0.6631(3)	1.3253(6)	1	0.0117(12)
S4	*18b*	0.5113(3)	0.5572(3)	0.6789(6)	1	0.0123(11)
			$La_4Ge_3Se_2S_{10}$			
La1	*18b*	0.43819(6)	0.33469(7)	0.97798(14)	1	0.0188(3)
La2	*6a*	0.6667	0.3333	1.1813(2)	1	0.0138(4)
Ge1	*18b*	0.68003(10)	0.53332(11)	1.0269(2)	1	0.0125(4)
S1	*18b*	0.57954(18)	0.44671(19)	1.1871(4)	0.687(16)	0.0165(10)
Se1	*18b*	0.57954(18)	0.44671(19)	1.1871(4)	0.313(16)	0.0165(10)
S2	*18b*	0.4454(2)	0.4896(2)	1.0171(4)	0.796(15)	0.0178(12)
Se2	*18b*	0.4454(2)	0.4896(2)	1.0171(4)	0.204(15)	0.0178(12)
S3	*18b*	0.3916(2)	0.3286(2)	1.3313(5)	0.880(15)	0.0191(13)
Se3	*18b*	0.3916(2)	0.3286(2)	1.3313(5)	0.120(15)	0.0191(13)
S4	*18b*	0.5423(2)	0.2691(3)	0.9298(5)	1	0.0129(8)
			$La_4Ge_3Se_4S_8$			
La1	*18b*	0.43797(5)	0.33346(6)	0.02593(9)	1	0.01817(19)
La2	*6a*	0.6667	0.3333	0.32203(13)	1	0.0112(3)
Ge1	*18b*	0.65285(8)	0.51901(8)	-0.02245(15)	1	0.0114(3)
S1	*18b*	0.75416(10)	0.53323(10)	-0.1847(2)	0.366(11)	0.0153(6)
Se1	*18b*	0.75416(10)	0.53323(10)	-0.1847(2)	0.634(11)	0.0153(6)
S2	*18b*	0.60615(18)	0.39664(18)	0.0732(3)	0.977(11)	0.0118(9)
Se2	*18b*	0.60615(18)	0.39664(18)	0.0732(3)	0.023(11)	0.0118(9)
S3	*18b*	0.39643(13)	0.33939(14)	-0.3276(3)	0.724(10)	0.0150(7)

Atoms	Wyckoff	*x*	*y*	*z*	Occupancy	U_{eq} (Å^2)
Se3	*18b*	0.39643(13)	0.33939(14)	-0.3276(3)	0.276(10)	0.0150(7)
S4	*18b*	0.49060(11)	0.44729(11)	0.3208(2)	0.522(11)	0.0156(6)
Se4	*18b*	0.49060(11)	0.44729(11)	0.3208(2)	0.478(11)	0.0156(6)
			$La_4Ge_3Se_6S_6$			
La1	*18b*	0.56130(4)	0.66595(5)	0.97383(8)	1	0.01846(18)
La2	*6a*	0.3333	0.6667	0.67836(12)	1	0.0115(2)
Ge1	*18b*	0.34722(7)	0.48143(6)	1.02229(14)	1	0.0118(3)
S1	*18b*	0.24572(7)	0.46723(8)	1.18522(16)	0.240(9)	0.0142(5)
Se1	*18b*	0.24572(7)	0.46723(8)	1.18522(16)	0.760(9)	0.0142(5)
S2	*18b*	0.39365(15)	0.60361(14)	0.9275(3)	0.965(9)	0.0119(9)
Se2	*18b*	0.39365(15)	0.60361(14)	0.9275(3)	0.035(9)	0.0119(9)
S3	*18b*	0.60387(9)	0.66028(10)	1.3274(2)	0.535(9)	0.0170(6)
Se3	*18b*	0.60387(9)	0.66028(10)	1.3274(2)	0.465(9)	0.0170(6)
S4	*18b*	0.50915(8)	0.55226(8)	0.67890(18)	0.374(8)	0.0150(5)
Se4	*18b*	0.50915(8)	0.55226(8)	0.67890(18)	0.626(8)	0.0150(5)
			$La_4Ge_3Se_8S_4$			
La1	*18b*	0.43908(7)	0.33400(8)	0.02710(15)	1	0.0200(3)
La2	*6a*	0.6667	0.3333	0.3209(2)	1	0.0155(5)
Ge1	*18b*	0.65278(12)	0.51812(12)	-0.0231(3)	1	0.0142(5)
S1	*18b*	0.75433(12)	0.53228(13)	-0.1854(3)	0.067(19)	0.0175(8)
Se1	*18b*	0.75433(12)	0.53228(13)	-0.1854(3)	0.933(19)	0.0175(8)
S2	*18b*	0.6063(2)	0.3959(2)	0.0723(5)	0.864(18)	0.0143(14)
Se2	*18b*	0.6063(2)	0.3959(2)	0.0723(5)	0.136(18)	0.0143(14)
S3	*18b*	0.39621(13)	0.34008(15)	-0.3270(3)	0.320(18)	0.0178(9)
Se3	*18b*	0.39621(13)	0.34008(15)	-0.3270(3)	0.680(18)	0.0178(9)
S4	*18b*	0.49129(13)	0.44805(12)	0.3201(3)	0.165(18)	0.0178(8)
Se4	*18b*	0.49129(13)	0.44805(12)	0.3201(3)	0.835(18)	0.0178(8)
			$La_4Ge_3Se_{10}S_2$			
La1	*18b*	0.56213(6)	0.66732(6)	0.97182(13)	1	0.0187(3)
La2	*6a*	0.3333	0.6667	0.6788(2)	1	0.0156(4)

Atoms	Wyckoff	*x*	*y*	*z*	Occupancy	U_{eq} (Å^2)
Ge1	*18b*	0.34685(10)	0.48149(10)	1.0251(2)	1	0.0129(4)
Se1	*18b*	0.24530(9)	0.46716(10)	1.1854(2)	1	0.0166(4)
S2	*18b*	0.39433(14)	0.60466(14)	0.9272(3)	0.577(15)	0.0131(9)
Se2	*18b*	0.39433(14)	0.60466(14)	0.9272(3)	0.423(15)	0.0131(9)
S3	*18b*	0.60401(9)	0.65991(11)	1.3267(2)	0.135(14)	0.0154(6)
Se3	*18b*	0.60401(9)	0.65991(11)	1.3267(2)	0.865(14)	0.0154(6)
S4	*18b*	0.50909(10)	0.55265(9)	0.6819(2)	0.032(14)	0.0166(6)
Se4	*18b*	0.50909(10)	0.55265(9)	0.6819(2)	0.968(14)	0.0166(6)

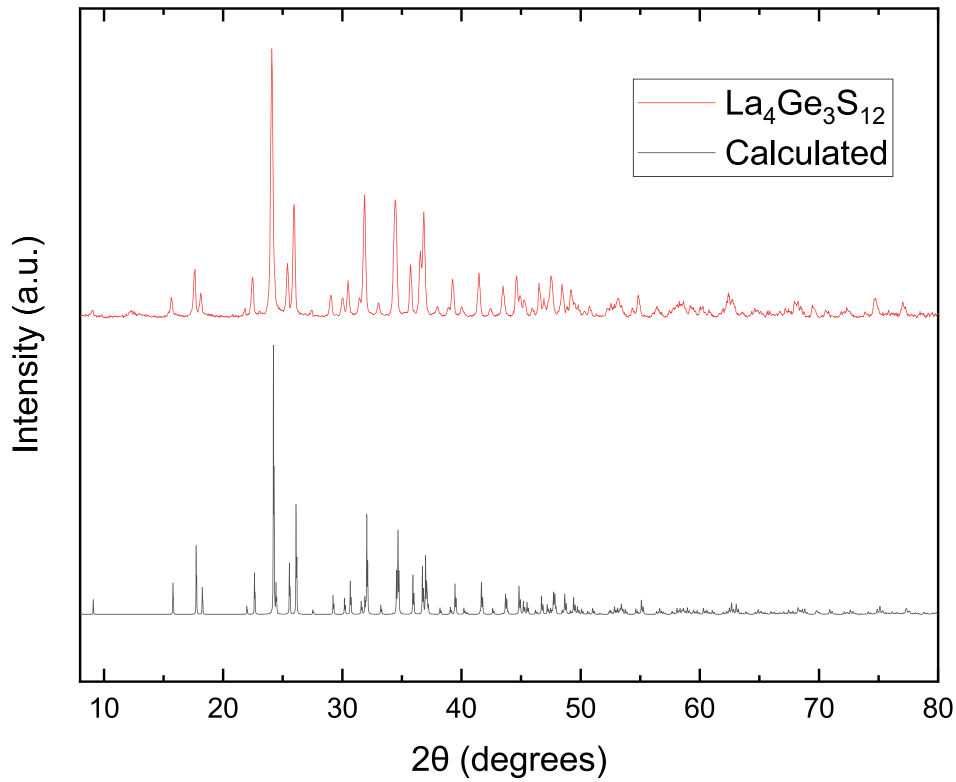
Table S3. Selected important interatomic distances (Å) in $La_4Ge_3Se_xS_{12-x}$ (x = 0, 2, 4, 6, 8, 10)

Atom Pairs		Distances (Å)	Atom Pairs		Distances (Å)
		$La_4Ge_3S_{12}$			
La1	S3	2.868(5)	La2	S2	2.901(5)
	S2	2.911(5)		S2	2.901(5)
	S4	2.945(6)		S2	2.901(5)
	S3	2.985(5)		S2	2.913(5)
	S1	3.013(5)		S2	2.913(5)
	S4	3.021(6)		S2	2.913(5)
	S1	3.089(5)		S1	3.386(6)
Ge1	S4	2.197(6)		S1	3.386(6)
	S3	2.200(5)		S1	3.386(6)
	S1	2.209(6)			
	S2	2.244(6)			
		$La_4Ge_3Se_2S_{10}$			
La1	Se3	2.888(4)	La2	S4	2.922(4)
	S3	2.888(4)		S4	2.922(4)
	S4	2.924(4)		S4	2.922(4)
	S2	2.979(4)		S4	2.939(4)
	S3	3.004(4)		S4	2.939(4)
	S1	3.048(3)		S4	2.939(4)
	Se2	3.073(4)		Se1	3.406(3)
	S2	3.073(4)		Se1	3.406(3)
	S1	3.118(3)			
Ge1	Se3	2.229(4)			
	S3	2.229(4)			
	S4	2.237(5)			
	S2	2.244(4)			
	Se2	2.244(4)			
	S1	2.260(4)			

Atom Pairs		Distances (Å)	Atom Pairs		Distances (Å)
		$La_4Ge_3Se_4S_8$			
La1	Se3	2.908(2)	La2	Se2	2.934(3)
	S3	2.908(2)		S2	2.934(3)
	S2	2.920(3)		Se2	2.934(3)
	Se4	3.023(2)		S2	2.934(3)
	S4	3.023(2)		S2	2.934(3)
	S3	3.028(2)		Se2	2.947(3)
	S1	3.0745(18)		S2	2.947(3)
	Se1	3.0745(18)		Se2	2.947(3)
	S4	3.100(2)		S2	2.947(3)
Ge1	S2	2.245(3)		Se2	2.947(3)
	Se3	2.255(3)		S2	2.947(3)
	S3	2.255(3)			
	Se4	2.279(2)			
	S4	2.279(2)			
	S1	2.293(2)			
		$La_4Ge_3Se_6S_6$			
La1	Se3	2.9257(17)	La2	Se2	2.947(3)
	S3	2.9257(17)		S2	2.947(3)
	S2	2.928(3)		Se2	2.947(3)
	S3	3.0514(18)		S2	2.947(3)
	Se4	3.0540(16)		S2	2.947(3)
	S4	3.0540(16)		Se2	2.957(3)
	S1	3.0928(14)		S2	2.957(3)
	Se1	3.0928(14)		Se2	2.957(3)
	S4	3.1166(16)		S2	2.957(3)
Ge1	S2	2.253(3)		Se2	2.957(3)
	Se3	2.280(2)		S2	2.957(3)
	S3	2.280(2)			
	Se4	2.2986(18)			

Atom Pairs		Distances (Å)	Atom Pairs		Distances (Å)
	S4	2.2986(18)			
Ge1	S1	2.3128(18)			
		$La_4Ge_3Se_8S_4$			
La1	S2	2.937(4)	La2	Se2	2.957(4)
	Se3	2.954(3)		S2	2.957(4)
	S3	2.954(3)		Se2	2.957(4)
	S3	3.079(3)		S2	2.957(4)
	Se4	3.083(3)		S2	2.957(4)
	S4	3.083(3)		Se2	2.973(4)
	S1	3.109(2)		S2	2.973(4)
	Se1	3.109(2)		Se2	2.973(4)
	S4	3.128(3)		S2	2.973(4)
Ge1	S2	2.269(4)		Se2	2.973(4)
	Se3	2.309(3)		S2	2.973(4)
	S3	2.309(3)			
	Se4	2.319(3)			
	S4	2.319(3)			
	S1	2.325(3)			
		$La_4Ge_3Se_{10}S_2$			
La1	S2	2.971(3)	La2	Se2	2.978(3)
	Se3	2.9745(19)		S2	2.978(3)
	S3	2.9745(19)		Se2	2.978(3)
	Se4	3.086(2)		S2	2.978(3)
	S4	3.086(2)		S2	2.978(3)
	S3	3.103(2)		Se2	2.997(3)
	Se1	3.1272(19)		S2	2.997(3)
	S4	3.136(2)		Se2	2.997(3)
	Se1	3.188(2)		S2	2.997(3)
Ge1	S2	2.309(3)		Se2	2.997(3)
	Se4	2.332(2)		S2	2.997(3)

Atom Pairs		Distances (Å)	Atom Pairs	Distances (Å)
	S4	2.332(2)		
	Se1	2.333(2)		
Ge1	Se3	2.339(3)		
	S3	2.339(3)		



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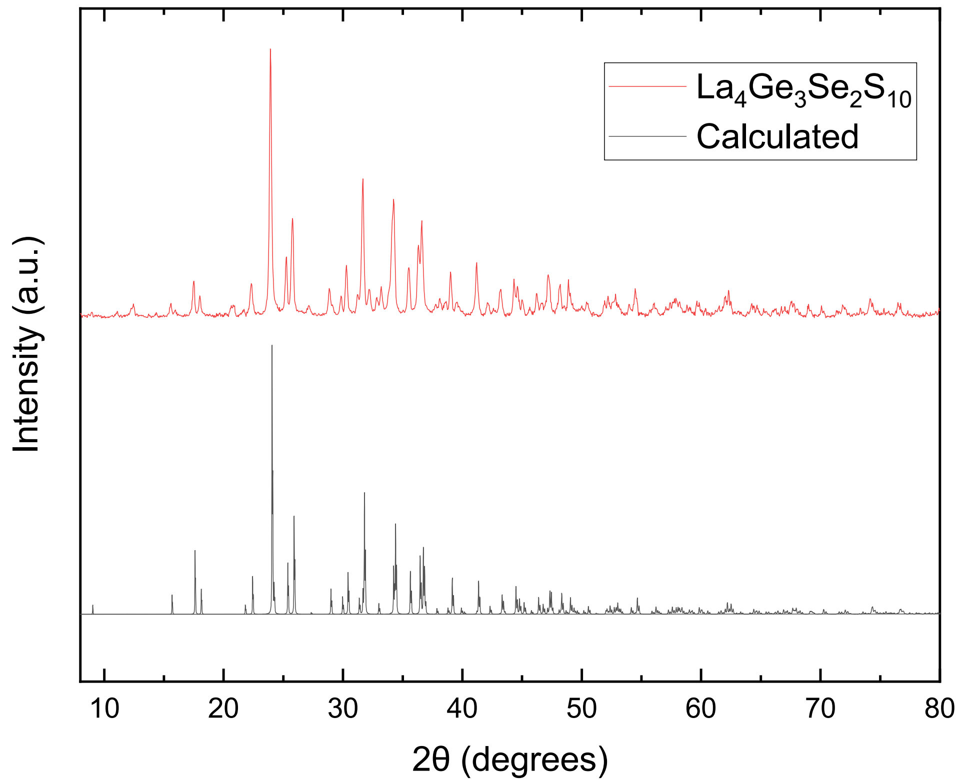
gure S1. The calculated and experimental X-ray diffraction patterns of $La_4Ge_3S_{12.}$



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gure S2. The calculated and experimental X-ray diffraction patterns of $La_4Ge_3Se_2S_{10}$.

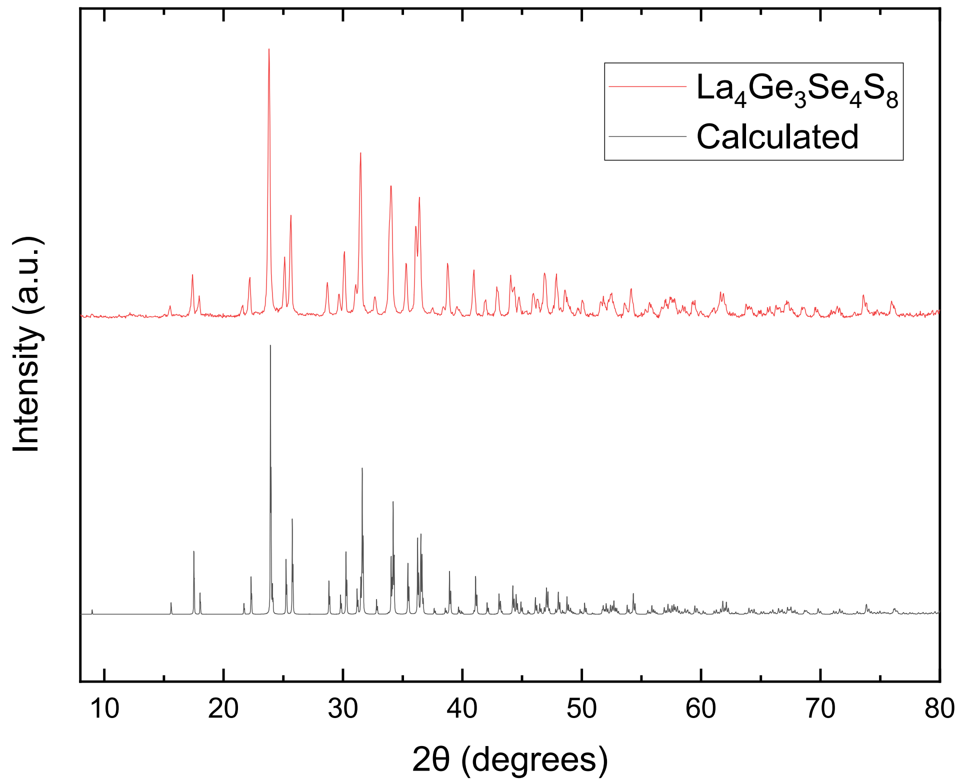
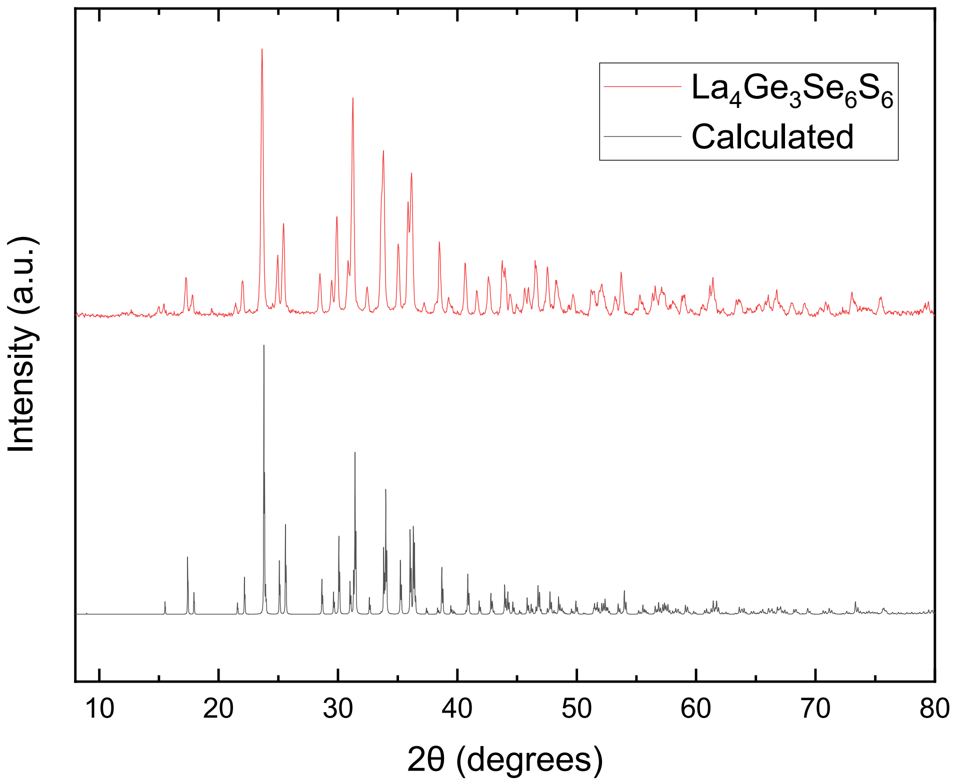


Figure S3. The calculated and experimental X-ray diffraction patterns of $La_4Ge_3Se_4S_8$.



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gure S4. The calculated and experimental X-ray diffraction patterns of $La_4Ge_3Se_6S_6$.

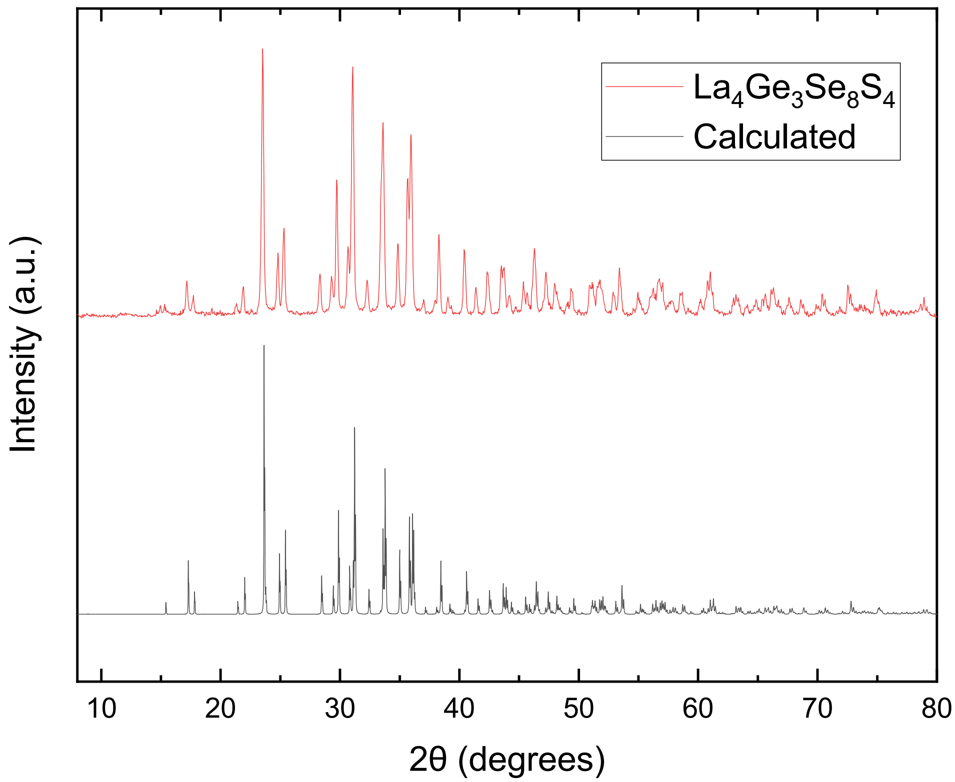


Figure S5. The calculated and experimental X-ray diffraction patterns of $La_4Ge_3Se_8S_4$.

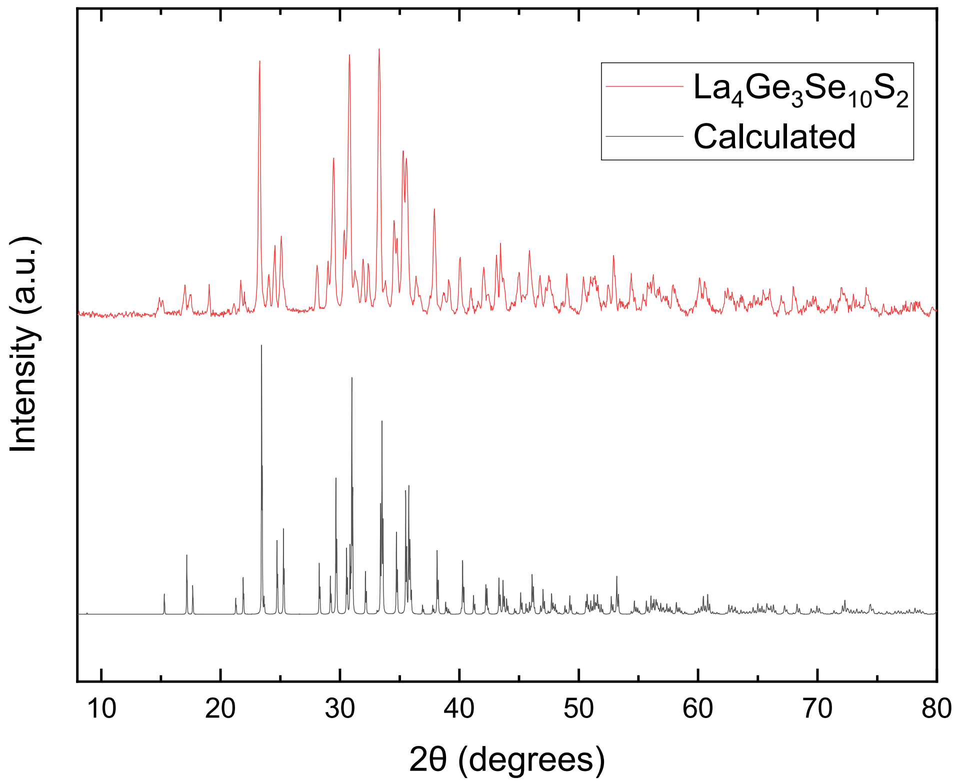


Figure S6. The calculated and experimental X-ray diffraction patterns of $La_4Ge_3Se_{10}S_2$.

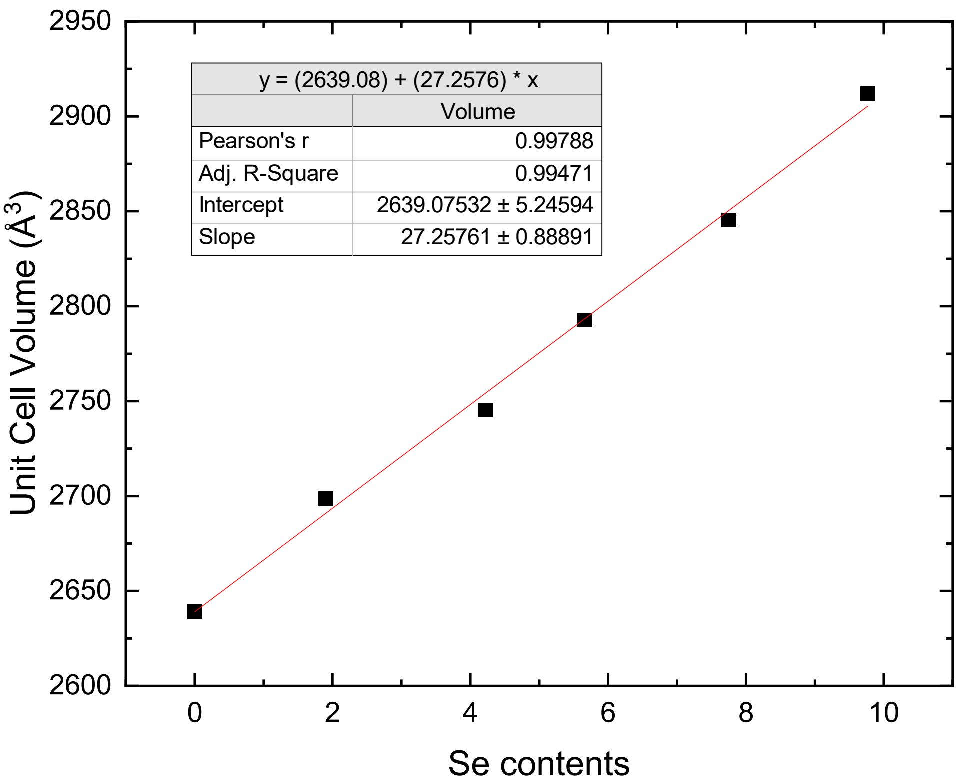
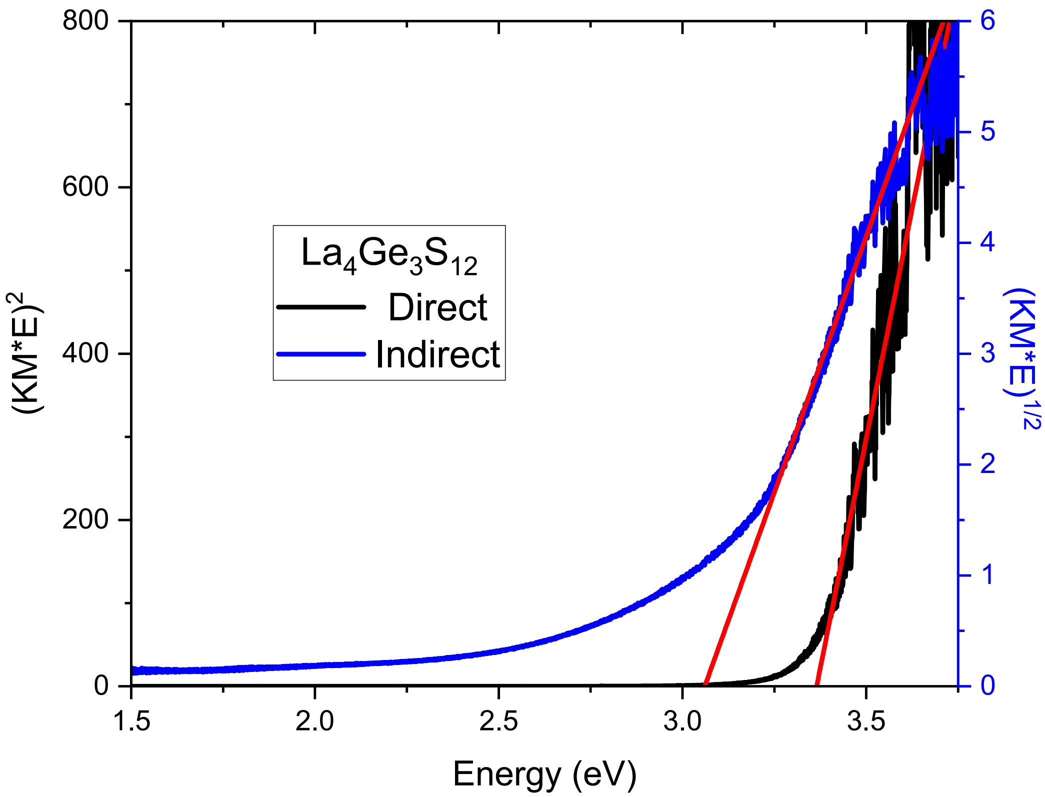


Figure S7. A comparison of Se contents and unit cell volume in $La_4Ge_3Se_xS_{12-x}$ (x = 0, 2, 4, 6, 8, 10), emphasizing the linear increase of volume as Se is incorporated into the crystal structure.



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gure S8. Tauc plots for allowed direct and indirect transitions of $La_4Ge_3S_{12}$.

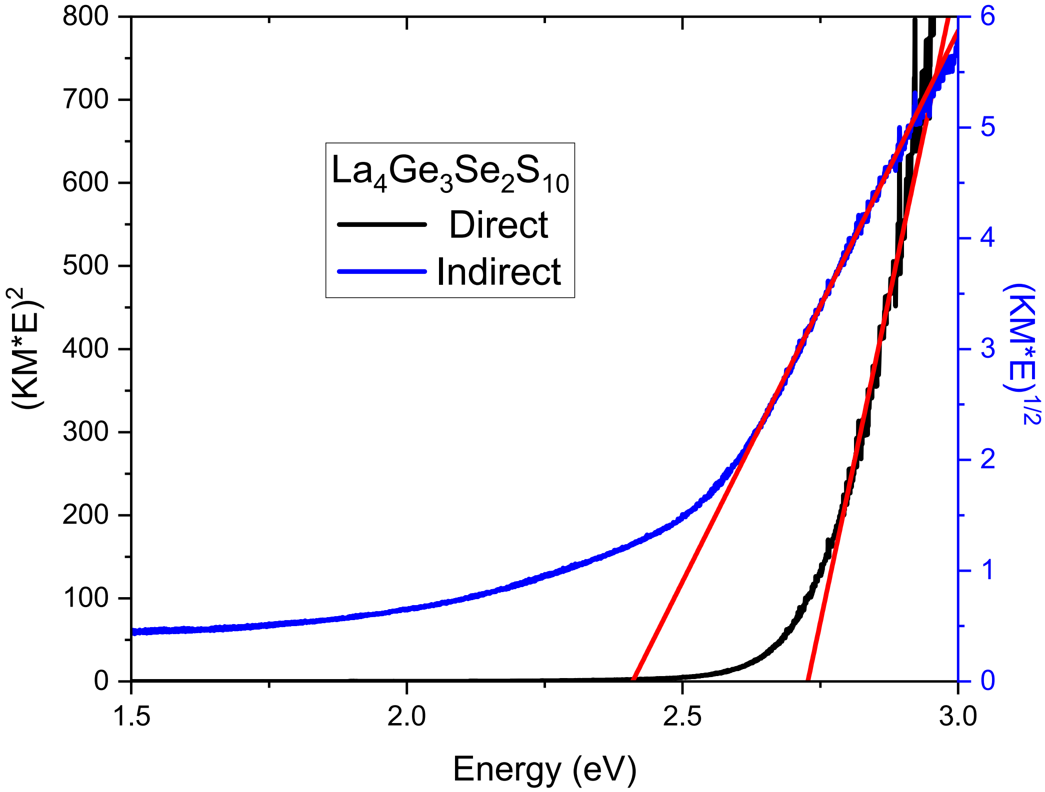
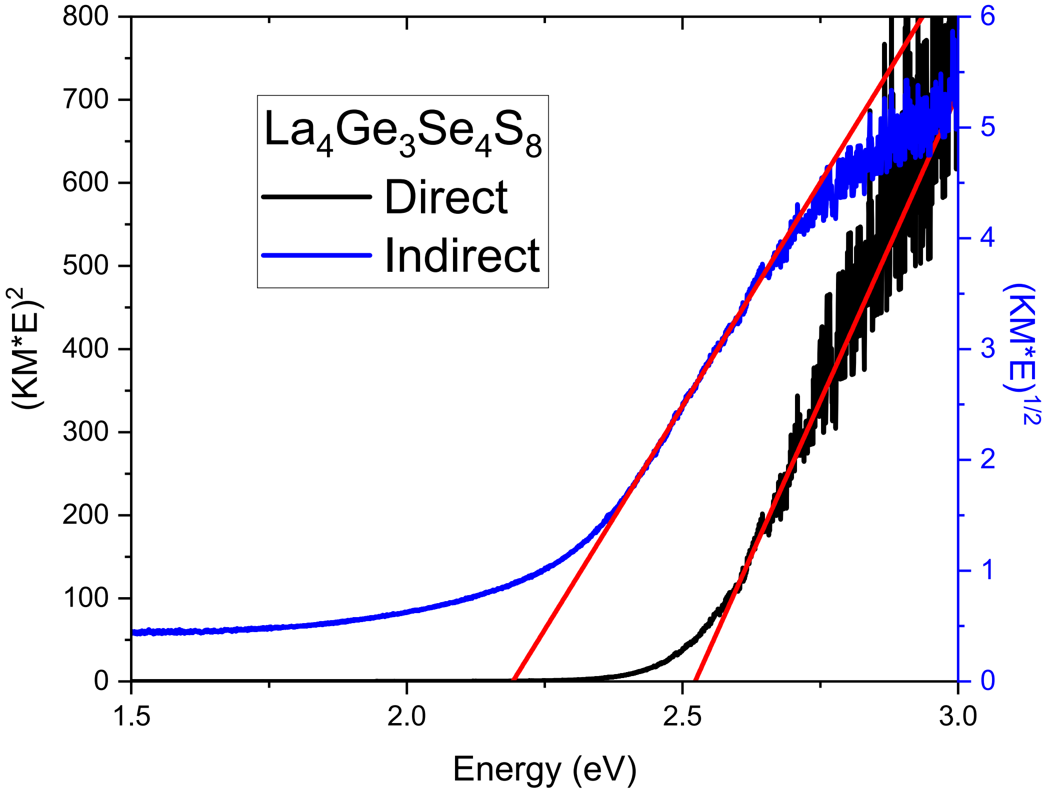


Figure S9. Tauc plots for allowed direct and indirect transitions of $La_4Ge_3Se_2S_{10}$.



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gure S10. Tauc plots for allowed direct and indirect transitions of $La_4Ge_3Se_4S_8$.

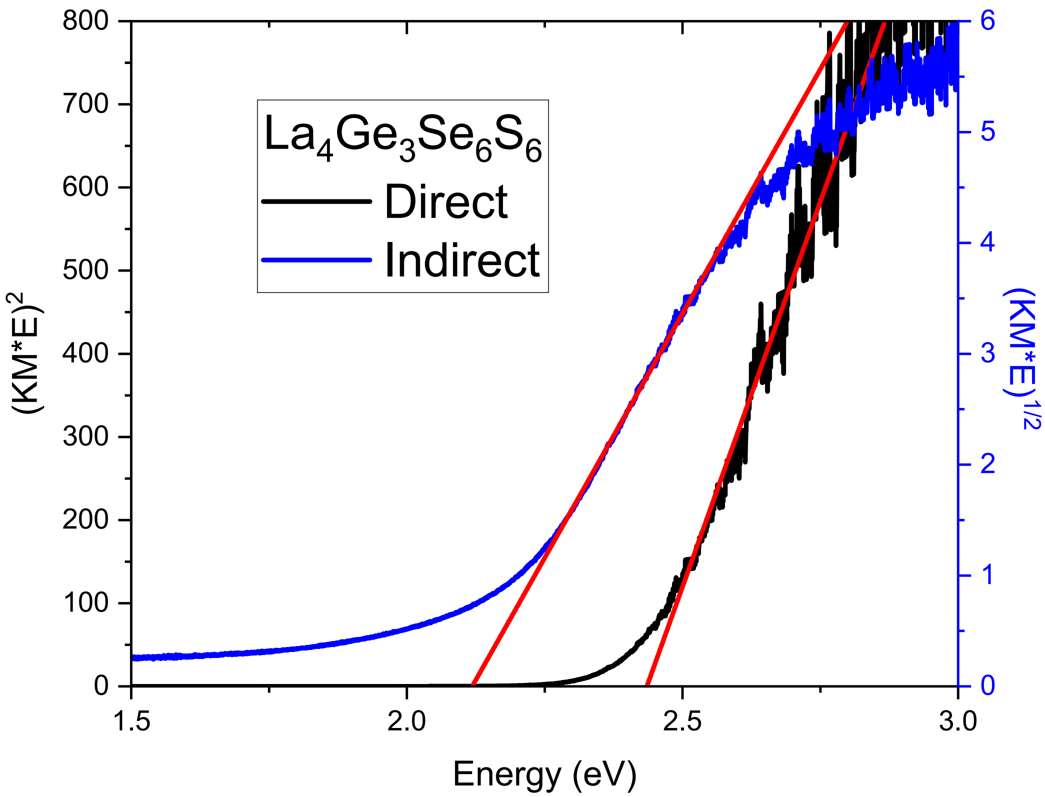


Figure S11. Tauc plots for allowed direct and indirect transitions of $La_4Ge_3Se_6S_6$.

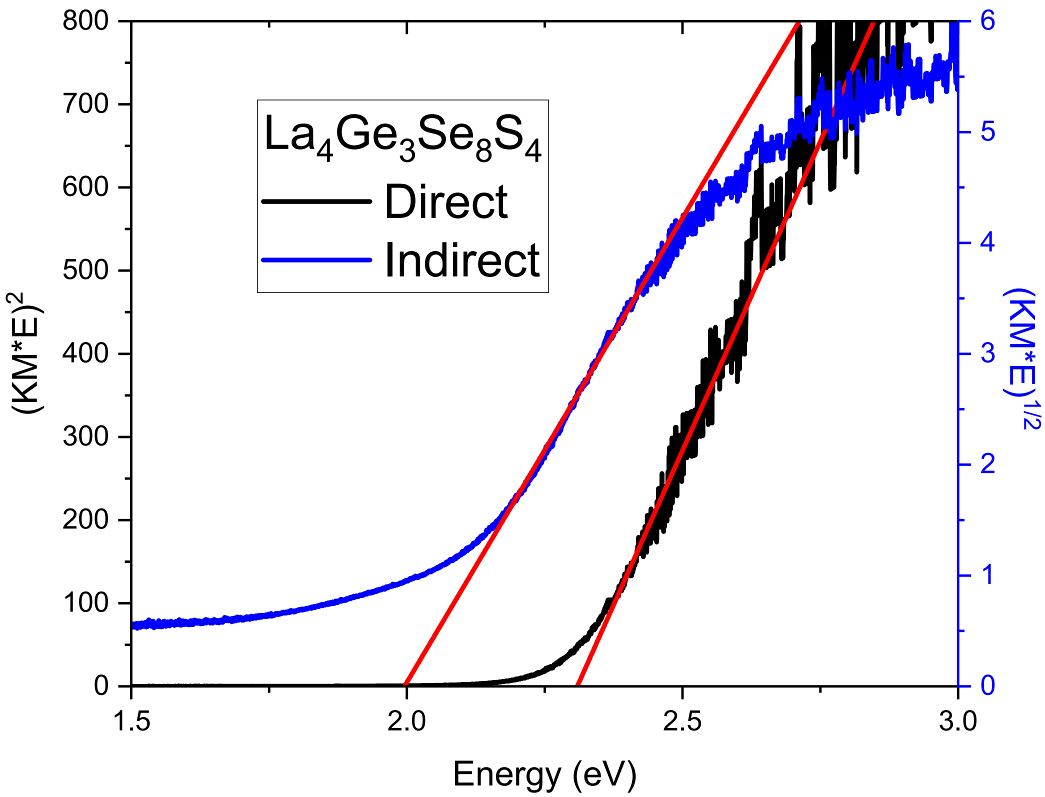


Figure S12. Tauc plots for allowed direct and indirect transitions of $La_4Ge_3Se_8S_4$.

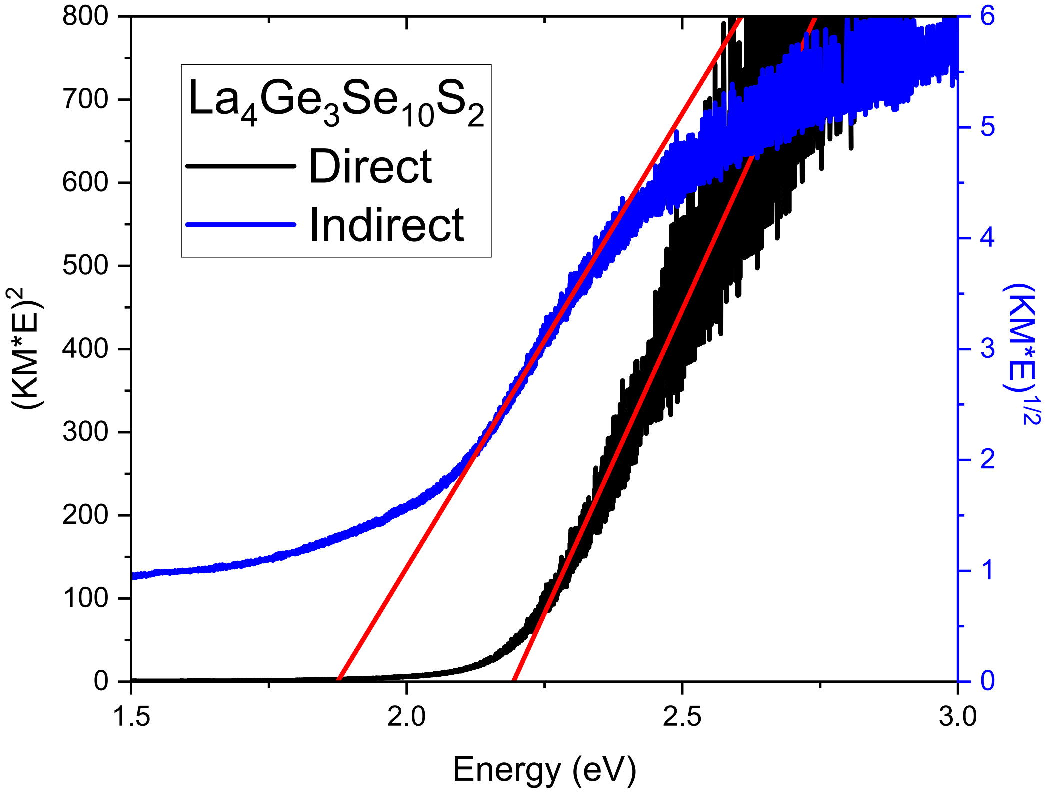


Figure S13. Tauc plots for allowed direct and indirect transitions of $La_4Ge_3Se_{10}S_2$.

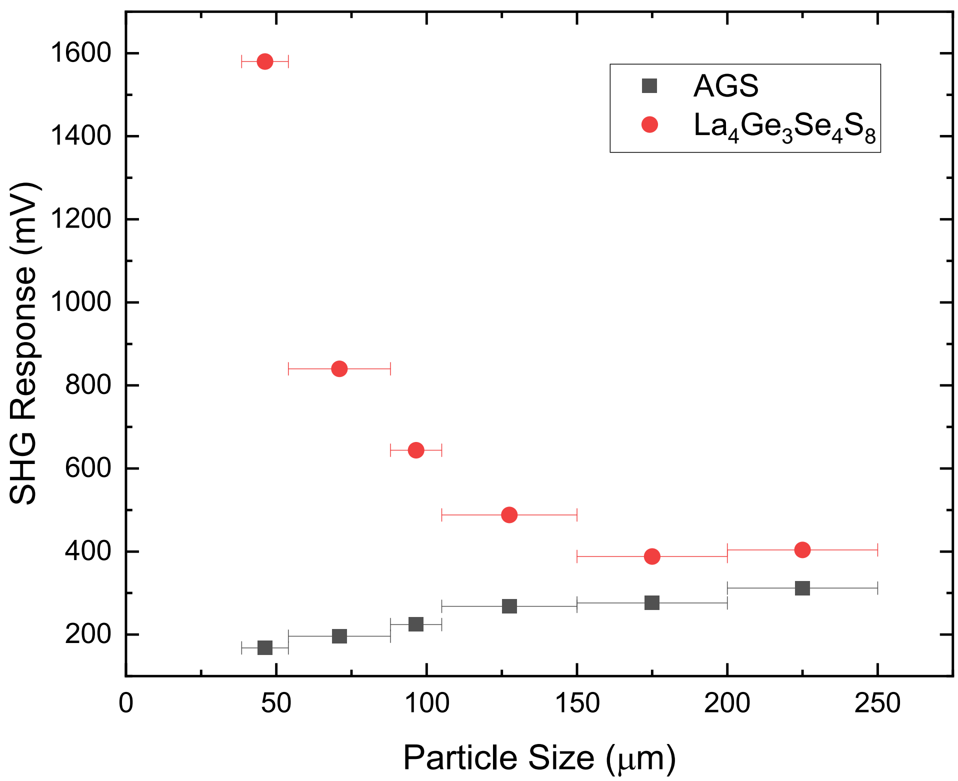


Figure S14. SHG intensities of $La_4Ge_3Se_4S_8$ and $AgGaS_2$ @2.09 μm measured at variable particle size samples.

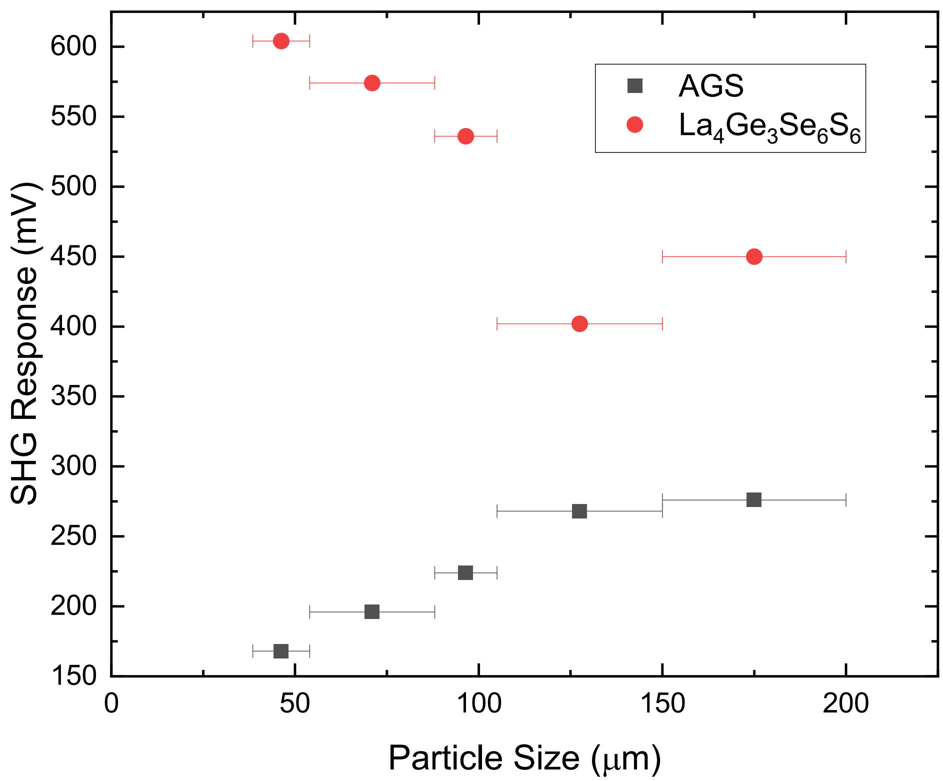


Figure S15. SHG intensities of $La_4Ge_3Se_6S_6$ and AgGaS2 @2.09 μm measured at variable particle size samples.

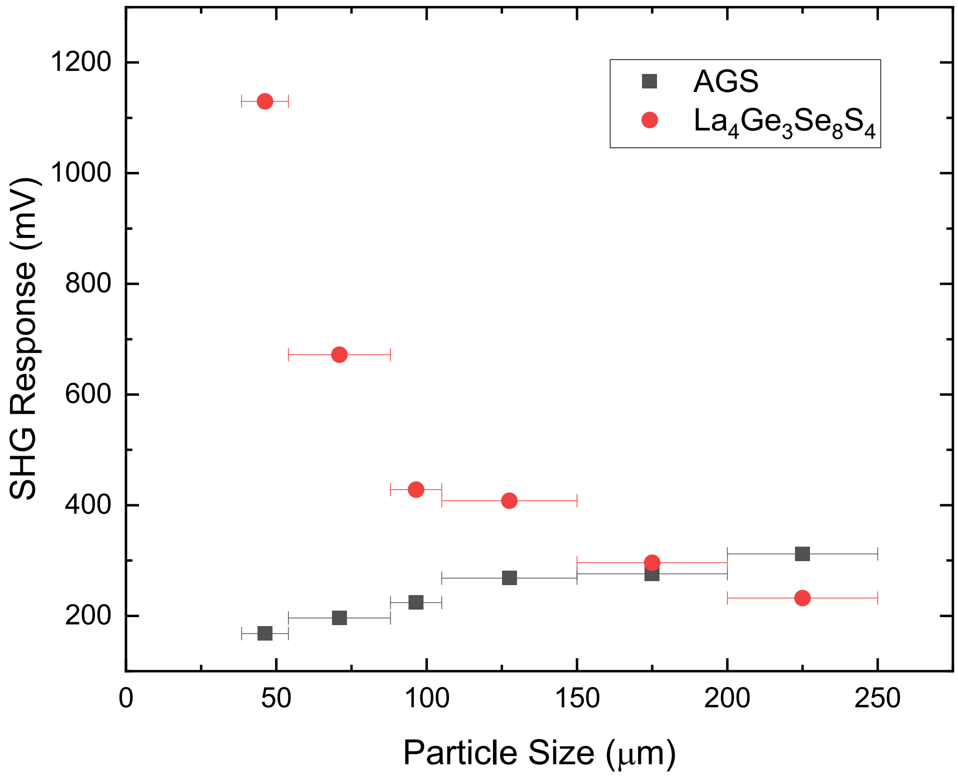


Figure S16. SHG intensities of $La_4Ge_3Se_8S_4$ and $AgGaS_2$ @2.09 μm measured at variable particle size samples.

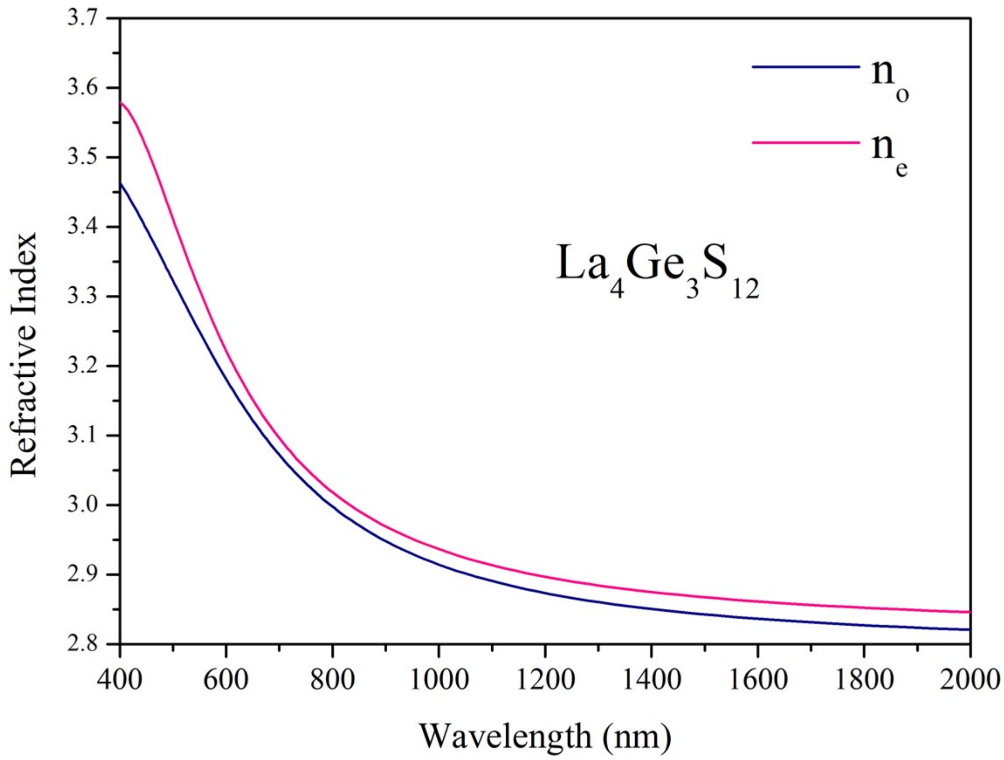


Figure S17. Calculated birefringence of $La_4Ge_3S_{12}$ versus wavelength of the fundamental light.

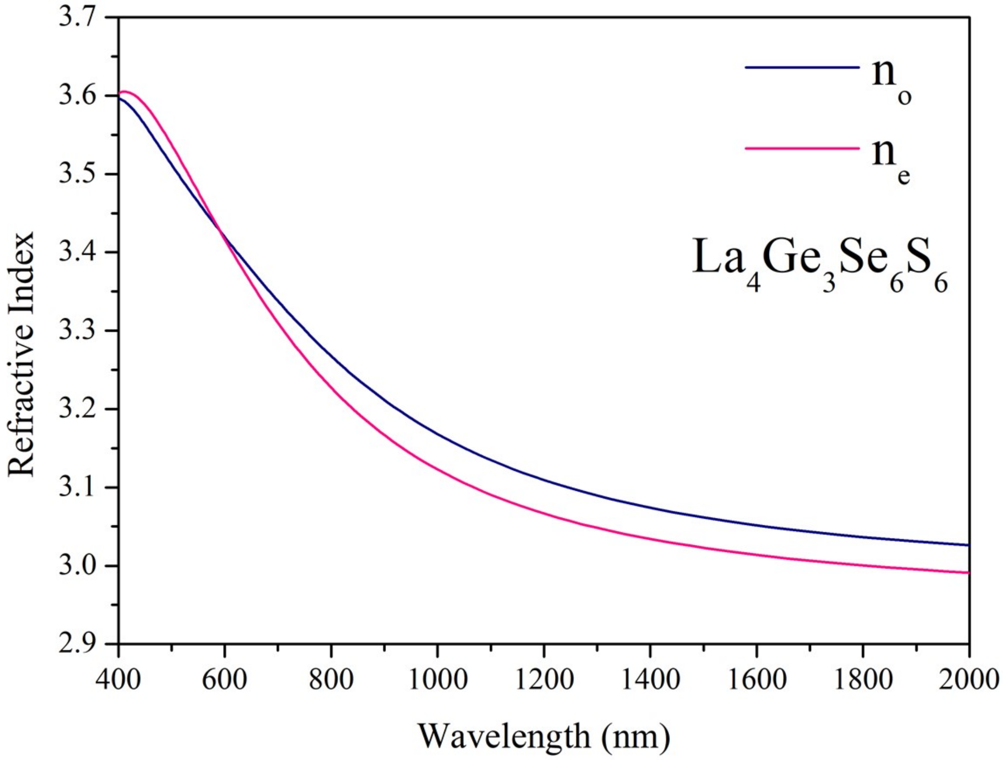
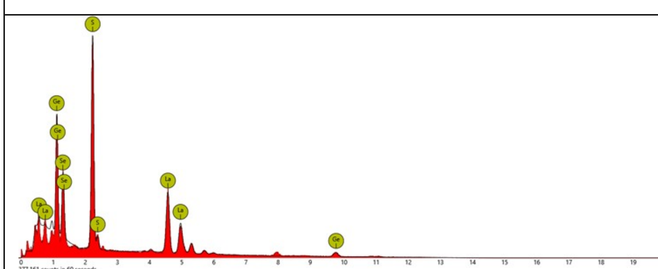
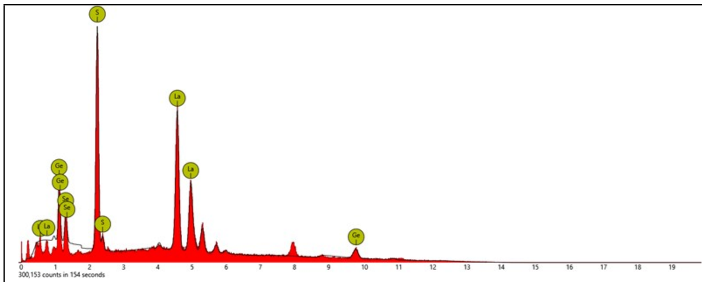
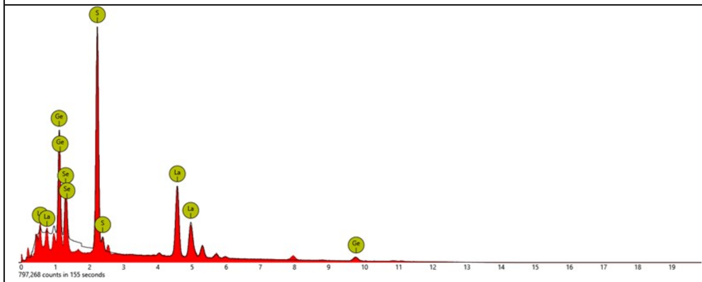
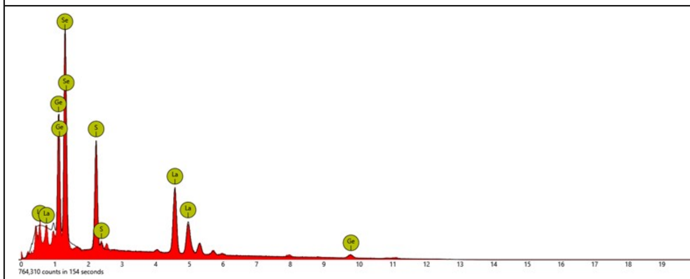
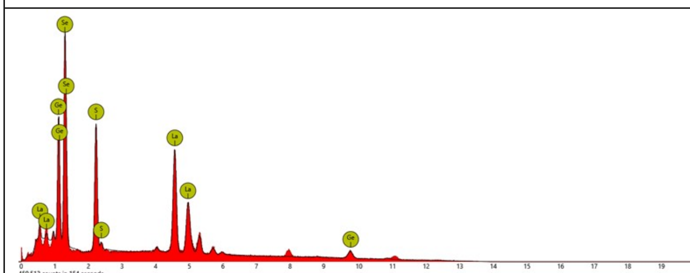
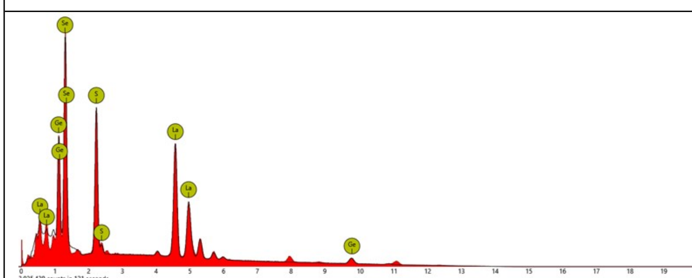
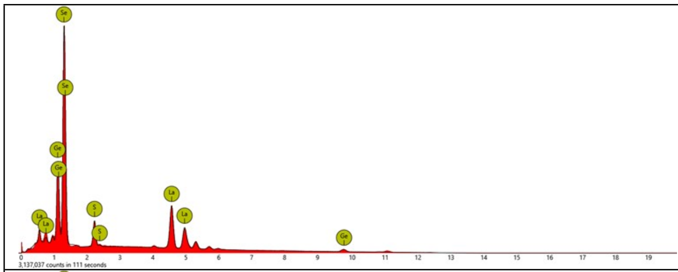
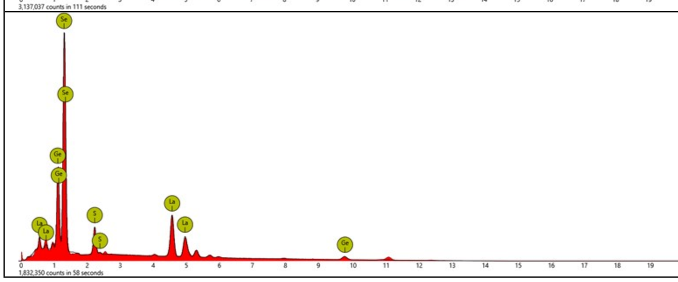


Figure S18. Calculated birefringence of $La_4Ge_3Se_6S_6$ versus wavelength of the fundamental light.

Table S4. Results of EDX analyses of selected crystals of $La_4Ge_3Se_2S_{10}$, $La_4Ge_3Se_6S_6$, and $La_4Ge_3Se_{10}S_2$.

Spectrum	Normalized Composition
	$La_{4.1}Ge_3Se_{2.2}S_{9.6}$

	$La_{4.0}Ge_3Se_{2.0}S_{9.1}$
	$La_{3.9}Ge_3Se_{2.1}S_{8.7}$
Average:	$\mathbf{La_{4.0(1)}Ge_3Se_{2.1(1)}S_{9.1(1)}}$
	$La_{3.6}Ge_3Se_{6.2}S_{5.7}$
	$La_{3.8}Ge_3Se_{5.6}S_{4.9}$
	$La_{4.3}Ge_3Se_{6.1}S_{5.8}$
Average:	$\mathbf{La_{3.9(1)}Ge_3Se_{5.9(1)}S_{5.5(1)}}$

	$La_{4.6}Ge_3Se_{10.4}S_{1.6}$
	$La_{4.2}Ge_3Se_{10.1}S_{1.6}$