Infrared Nonlinear Optical Properties of Lithium-containing Diamond-Like Semiconductors $Li_2ZnGeSe_4$ and $Li_2ZnSnSe_4$

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Table S1. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Li_2ZnGeSe_4$ and $Li_2ZnSnSe_4$.

Atom	x	y	z	U(eq)
$Li_2ZnGeSe_4$				
Li(1)	0.950(3)	0.160(2)	0.110(3)	0.015(4)
Li(2)	0.460(3)	0.311(2)	0.886(2)	o.008(4)
Zn(1)	0.4747(2)	0.3202(2)	0.3575(2)	0.017(1)
Ge(1)	0.9749(2)	0.1773(1)	0.6106(1)	0.012(1)
Se(1)	0.3595(2)	0.6585(2)	0.3469(1)	0.017(1)
Se(2)	0.3543(2)	0.1478(2)	0.1173(2)	0.016(1)
Se(3)	0.3350(2)	0.1866(2)	0.6043(1)	0.017(1)
Se(4)	0.8487(2)	0.3198(2)	0.3707(1)	0.016(1)
$Li_2ZnSnSe_4$				
Li(1)	0.375(5)	0.1590(8)	0.3580(4)	0.027(3)
Li(2)	0.371(4)	0.6693(8)	0.092(3)	0.019(4)
Zn(1)	0.3666(2)	0.6751(1)	0.6100(1)	0.018(1)
Sn(1)	0.8664(2)	0.8267(1)	0.3589(1)	0.014(1)
Se(1)	0.4896(1)	0.8181(1)	0.3611(1)	0.016(1)
Se(2)	0.4893(1)	0.3430(1)	0.6107(1)	0.017(1)
Se(3)	0.4896(1)	0.8350(1)	0.8544(1)	0.016(1)
Se(4)	0.9970(1)	0.6710(1)	0.6087(1)	0.017(1)

Table S2. Important bond lengths (Å) and angles (°) for $Li_2ZnGeSe_4$ and $Li_2ZnSnSe_4$[a]

$Li_2ZnGeSe_4$			
Li(1)-Se(3) #1	2.492(17)	Li(1)-Se(4)	2.50(2)
Li(1)-Se(1) #2	2.57(2)	Li(1)-Se(2) #2	2.65(2)
Li(2)-Se(2) #4	2.319(18)	Li(2)-Se(3)	2.603(18)
Li(2)-Se(4) #5	2.638(14)	Li(2)-Se(1) #6	2.645(19)
Zn(1)-Se(3)	2.4118(16)	Zn(1)-Se(2)	2.4368(18)
Zn(1)-Se(1)	2.4419(17)	Zn(1)-Se(4)	2.4522(18)
Ge(1)-Se(4)	2.3548(14)	Ge(1)-Se(3)#3	2.3609(16)
Ge(1)-Se(2)#7	2.3662(14)	Ge(1)-Se(1)#6	2.3746(16)
Se(3)#1-Li(1)-Se(4)	110.8(8)	Se(3)#1-Li(1)-Se(1)#2	112.2(8)
Se(4)-Li(1)-Se(1)#2	116.8(7)	Se(3)#1-Li(1)-Se(2)#3	105.8(7)
Se(4)-Li(1)-Se(2)#3	105.1(7)	Se(1)#2-Li(1)-Se(2)#3	105.3(8)
Se(2)#4-Li(2)-Se(3)	118.8(7)	Se(2)#4-Li(2)-Se(4)#5	114.8(7)
Se(3)-Li(2)-Se(4)#5	100.7(6)	Se(2)#4-Li(2)-Se(1)#6	115.7(7)
Se(3)-Li(2)-Se(1)#6	103.2(6)	Se(4)#5-Li(2)-Se(1)#6	101.1(6)
Se(3)-Zn(1)-Se(2)	112.23(6)	Se(3)-Zn(1)-Se(1)	105.87(6)
Se(2)-Zn(1)-Se(1)	109.39(6)	Se(3)-Zn(1)-Se(4)	110.01(6)
Se(2)-Zn(1)-Se(4)	110.98(6)	Se(1)-Zn(1)-Se(4)	108.15(7)
Se(4)-Ge(1)-Se(3)#3	108.68(5)	Se(4)-Ge(1)-Se(2)#7	107.09(6)
Se(3)#3-Ge(1)-Se(2)#7	111.10(5)	Se(4)-Ge(1)-Se(1)#6	112.33(6)
Se(3)#3-Ge(1)-Se(1)#6	108.93(6)	Se(2)#7-Ge(1)-Se(1)#6	108.74(6)
$Li_2ZnSnSe_4$			
Li(1)-Se(1)#1	2.516(12)	Li(1)-Se(4)#2	2.53(3)
Li(1)-Se(3)#2	2.58(3)	Li(1)-Se(2)	2.58(3)
Li(2)-Se(3)#3	2.43(2)	Li(2)-Se(4)#2	2.541(10)
Li(2)-Se(2)#2	2.56(2)	Li(2)-Se(1)	2.60(2)
Zn(1)-Se(1)	2.4459(12)	Zn(1)-Se(3)	2.4645(13)
Zn(1)-Se(4)#4	2.4712(13)	Zn(1)-Se(2)	2.4745(6)

Sn(1)-Se(4)	2.5059(13)	Sn(1)-Se(3)#5	2.5172(6)
Sn(1)-Se(1)	2.5201(13)	Sn(1)-Se(2)#6	2.5233(13)
Se(1)#1-Li(1)-Se(4)#2	111.1(11)	Se(1)#1-Li(1)-Se(3)#2	108.6(8)
Se(4)#2-Li(1)-Se(3)#2	107.8(12)	Se(1)#1-Li(1)-Se(2)	112.3(12)
Se(4)#2-Li(1)-Se(2)	109.6(7)	Se(3)#2-Li(1)-Se(2)	107.2(10)
Se(3)#3-Li(2)-Se(4)#2	112.8(8)	Se(3)#3-Li(2)-Se(2)#2	113.1(9)
Se(4)#2-Li(2)-Se(2)#2	107.2(5)	Se(3)#3-Li(2)-Se(1)	114.2(6)
Se(4)#2-Li(2)-Se(1)	103.3(8)	Se(2)#2-Li(2)-Se(1)	105.4(8)
Se(1)-Zn(1)-Se(3)	113.56(3)	Se(1)-Zn(1)-Se(4)#4	109.74(5)
Se(3)-Zn(1)-Se(4)#4	109.97(5)	Se(1)-Zn(1)-Se(2)	106.16(5)
Se(3)-Zn(1)-Se(2)	108.55(5)	Se(4)#4-Zn(1)-Se(2)	108.69(3)
Se(4)-Sn(1)-Se(3)#5	108.14(5)	Se(4)-Sn(1)-Se(1)	109.33(4)
Se(3)#5-Sn(1)-Se(1)	110.46(4)	Se(4)-Sn(1)-Se(2)#6	111.06(3)
Se(3)#5-Sn(1)-Se(2)#6	109.14(5)	Se(1)-Sn(1)-Se(2)#6	108.71(5)

[a] Symmetry transformations used to generate equivalent atoms:

For $Li_2ZnGeSe_4$: #1 x, y-1, z; #2 x-1/2, -y+1, z-1/2; #3 x, y, z-1; #4 x-1, y, z; #5 x+1/2, -y+2, z-1/2; #6 x+1/2, -y+1, z-1/2.

For $Li_2ZnSnSe_4$: #1 x+1/2, -y+2, z-1/2; #2 x-1/2, -y+2, z-1/2; #3 x, y+1, z; #4 x+1/2, -y+1, z+1/2; #5 x-1/2, -y+1, z+1/2; #6 x, y, z+1; #7 x-1, y, z; #8 x-1/2, -y+1, z-1/2.

Table S3 The unit cell parameter of $Li_2ZnGeSe_4$ and $Li_2ZnSnSe_4$ from the Rietveld refinements of X-ray powder diffraction.

	$Li_2ZnGeSe_4$	$Li_2ZnSnSe_4$
Space group	*Pn*	*Pn*
a (Å)	6.5513(2)	6.68609(7)
b (Å)	6.8647(2)	7.04202(4)
c (Å)	8.2478(2)	8.33546(6)
β (deg)	90.196(2)	90.0681(8)
V (Å^3)	370.92(3)	392.463(6)

Table S4. State energies (eV) of the lowest conduction band (LCB) and the highest valence band (HVB) of the crystals of $Li_2ZnGeSe_4$ and $Li_2ZnSnSe_4$.

Formular	k-point	LCB	HVB
$Li_2ZnGeSe_4$	Z (0, 0, 0.5)	2.88427	-0.28484
	G (0, 0, 0)	2.2738	0
	Y (0, 0.5, 0)	2.21009	-0.17423
	A (-0.5, 0.5, 0)	2.2165	-0.47618
	B (-0.5, 0, 0)	2.24886	-0.22952
	D (-0.5, 0, 0.5)	2.63182	-0.27883
	E (-0.5, 0.5, 0.5)	2.62436	-0.40205
	C (0, 0.5, 0.5)	2.84404	-0.418
$Li_2ZnSnSe_4$	Z (0, 0, 0.5)	2.87701	-0.28165
	G (0, 0, 0)	2.12908	0
	Y (0, 0.5, 0)	2.38436	-0.24972
	A (-0.5, 0.5, 0)	2.45764	-0.59275
	B (-0.5, 0, 0)	2.46015	-0.28374
	D (-0.5, 0, 0.5)	2.84191	-0.45987
	E (-0.5, 0.5, 0.5)	2.83272	-0.57024
	C (0, 0.5, 0.5)	2.92425	-0.46788

Table S5. The calculated bond valence and bond order of $Li_2ZnGeSe_4$ and $Li_2ZnSnSe_4$.

Bond	Bond length	Bond valence	Bond order
$Li_2ZnGeSe_4$			
Li(1)-Se(1)	2.57(2)	0.25	-1.10
Li(1)-Se(2)	2.65(2)	0.21	-0.63
Li(1)-Se(3)	2.492(17)	0.32	-0.56
Li(1)-Se(4)	2.50(2)	0.31	-0.88
	ΣBV=	1.09	
Li(2)-Se(1)	2.645(19)	0.21	-0.56
Li(2)-Se(2)	2.319(18)	0.50	-0.96
Li(2)-Se(3)	2.603(18)	0.23	-0.64
Li(2)-Se(4)	2.638(14)	0.21	-0.93
	ΣBV=	1.15	
Zn(1)-Se(1)	2.4419(17)	0.50	1.48
Zn(1)-Se(2)	2.4368(18)	0.50	1.50
Zn(1)-Se(3)	2.4118(16)	0.54	1.26
Zn(1)-Se(4)	2.4522(18)	0.48	1.19
	ΣBV=	2.02	
Ge(1)-Se(1)	2.3746(16)	0.93	1.48
Ge(1)-Se(2)	2.3662(14)	0.95	1.52
Ge(1)-Se(3)	2.3609(16)	0.97	1.49
Ge(1)-Se(4)	2.3548(14)	0.98	1.31
	ΣBV=	3.83	
$Li_2ZnSnSe_4$			
Li(1)-Se(1)	2.516(12)	0.30	-0.54
Li(1)-Se(2)	2.58(3)	0.25	-1.07
Li(1)-Se(3)	2.58(3)	0.25	-1.05
Li(1)-Se(4)	2.53(3)	0.28	-0.87
	ΣBV=	1.08	

Li(2)-Se(1)	2.60(2)	0.23	-0.53
Li(2)-Se(2)	2.56(2)	0.26	-0.89
Li(2)-Se(3)	2.43(2)	0.37	-0.88
Li(2)-Se(4)	2.541(10)	0.28	-0.58
	ΣBV=	1.14	
Zn(1)-Se(1)	2.4459(12)	0.49	1.27
Zn(1)-Se(2)	2.4745(6)	0.46	1.34
Zn(1)-Se(3)	2.4645(13)	0.47	1.43
Zn(1)-Se(4)	2.4712(13)	0.46	1.20
	ΣBV=	1.88	
Sn(1)-Se(1)	2.5201(13)	1.01	1.16
Sn(1)-Se(2)	2.5233(13)	1.00	1.28
Sn(1)-Se(3)	2.5172(6)	1.02	1.30
Sn(1)-Se(4)	2.5059(13)	1.05	1.24
	ΣBV=	4.08	

The bond valence calculation is based on Brown I. D.'s reference in 1985.[1]

$$V = \Sigma v_i = \Sigma exp(\frac{r_0 - r}{0.37}) \qquad (1)$$

$$r_0 = r_c + Ar_a + P - D - F \qquad (2)$$

In equation (1), V is the valence of cations, v_i is the bond valence, r_0 is a bond-valence parameter for certain bond, and r is the bond length. In equation (2), r_c and r_a are radii of cation and anion which can find in the tables of this reference, P, D and F are corrections required when the cation contains non-bonding *p*, *d*, and *f* electrons, respectively.

Bond order data is calculated by CASTEP program, the structure used is without any volume or geometry optimization and the distance cut-off for Mulliken bond population analysis is set as 3.5 Å.

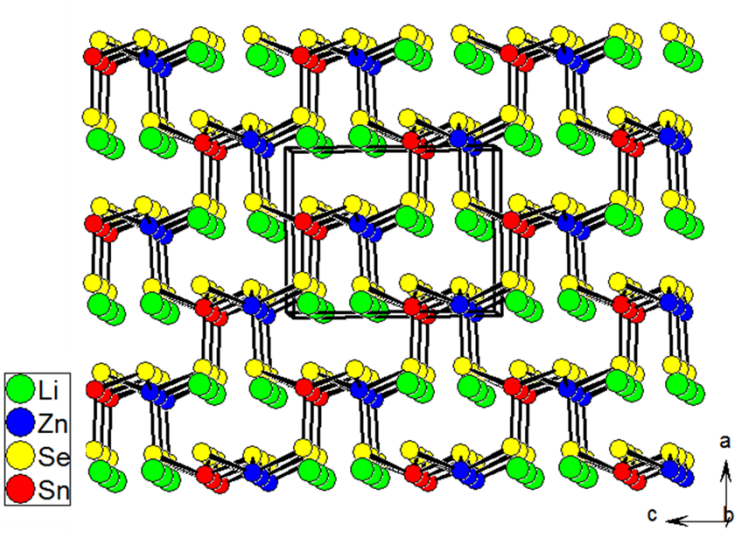


Figure S1, Honeycomb anionic structure of $[ZnSnS_4]^{2-}$ network with lithium cations balancing the charge.

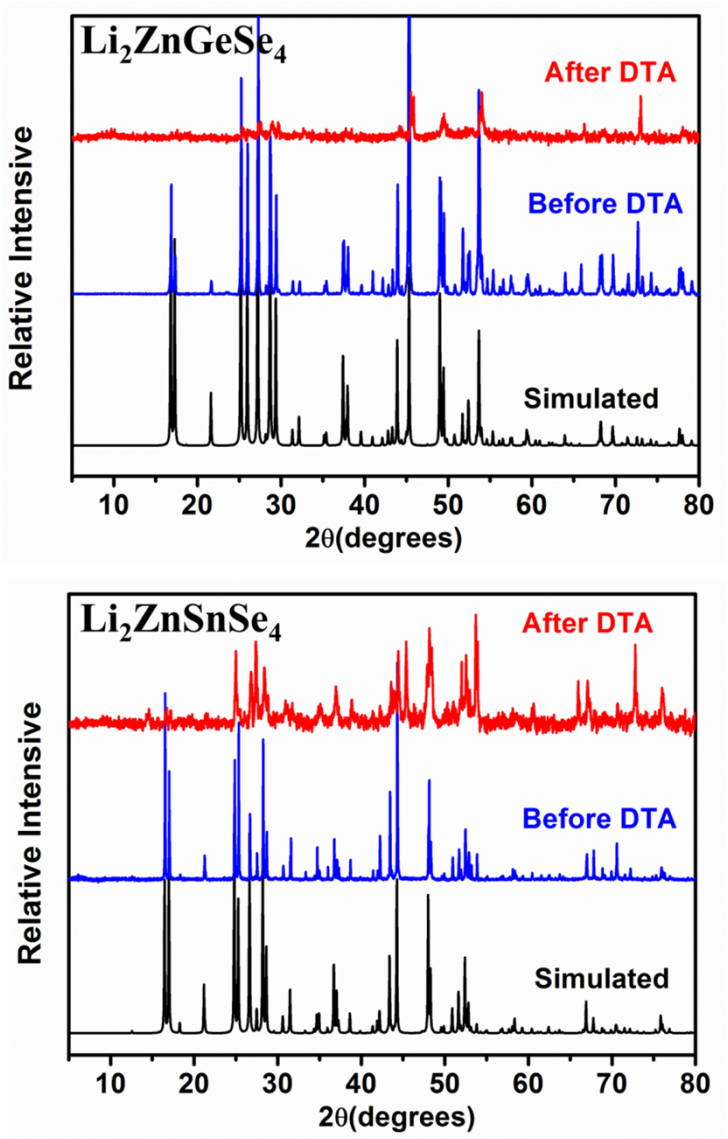
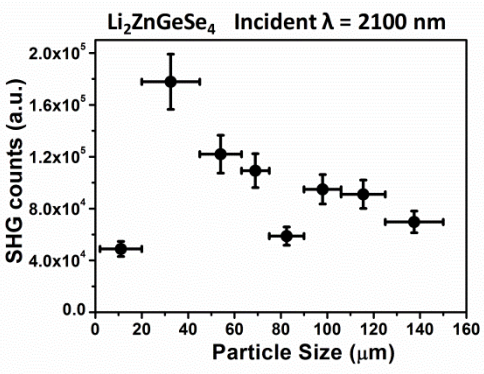
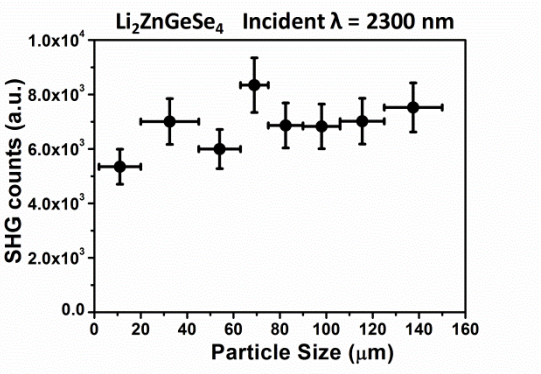
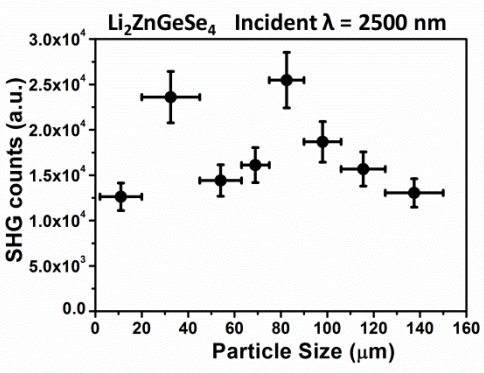
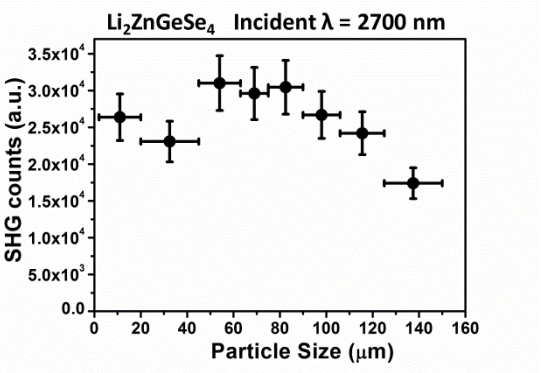


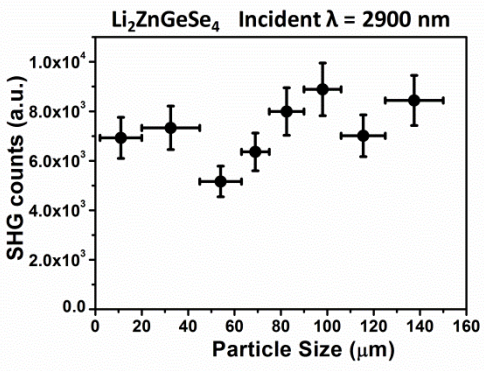
Figure S2. Simulated, as-synthesis, and after DTA heating's X-ray powder diffraction patterns for $Li_2ZnGeSe_4$ and $Li_2ZnSnSe_4$.

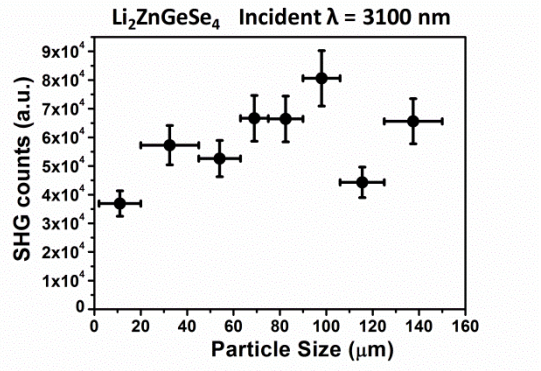

Li2ZnGeSe4 Incident λ = 2100 nm
SHG counts (a.u.)
Particle Size (μm)


Li2ZnGeSe4 Incident λ = 2300 nm
SHG counts (a.u.)
Particle Size (μm)


Li2ZnGeSe4 Incident λ = 2500 nm
SHG counts (a.u.)
Particle Size (μm)


Li2ZnGeSe4 Incident λ = 2700 nm
SHG counts (a.u.)
Particle Size (μm)


Li2ZnGeSe4 Incident λ = 2900 nm
SHG counts (a.u.)
Particle Size (μm)


Li2ZnGeSe4 Incident λ = 3100 nm
SHG counts (a.u.)
Particle Size (μm)

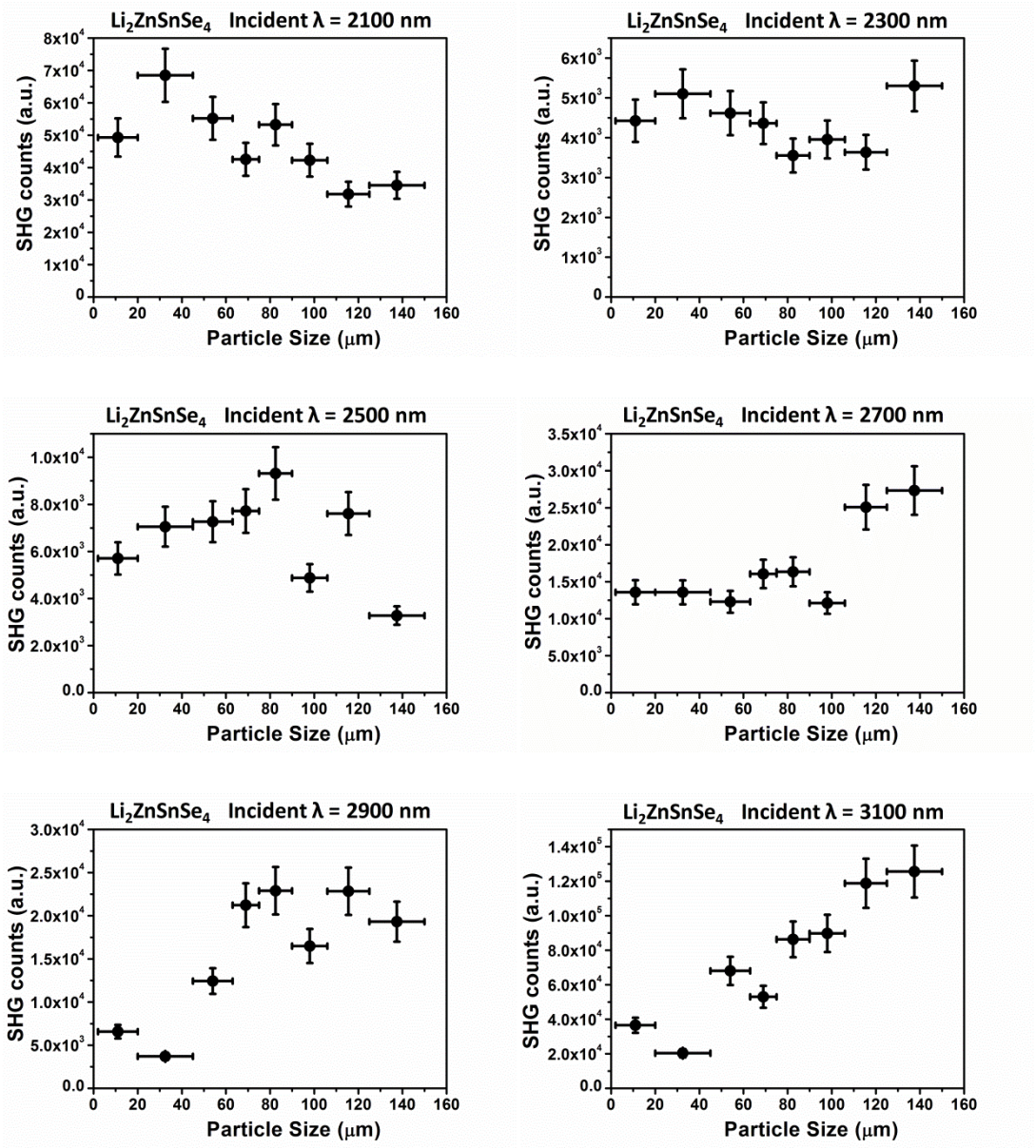


FIG. S3: SHG particle-size dependence of $Li_2ZnGeSe_4$ and $Li_2ZnSnSe_4$ at various wavelengths to determine the phase-matching onsets.

1 I. D. Brown, D. Altermatt, *Acta, Cryst.* 1985, **B41**, 244.