Electronic Supplementary Material (ESI) for Dalton Transactions.

Lithium Selenometallates of Triel Elements, Li_5MSe_4 (M = Al and Ga), Aliovalent Doping and Their Ionic Conductivity

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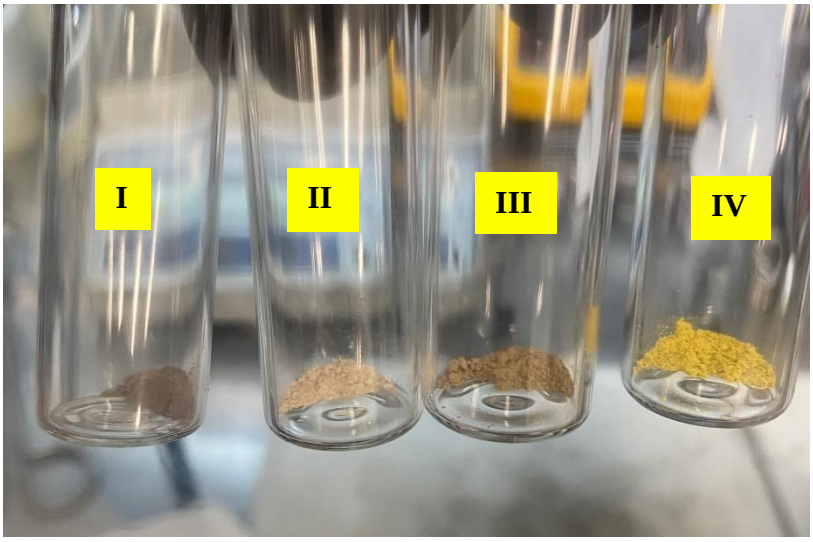

Figure S1. Photographs of hand-ground powder samples compounds, **I** – **IV**.

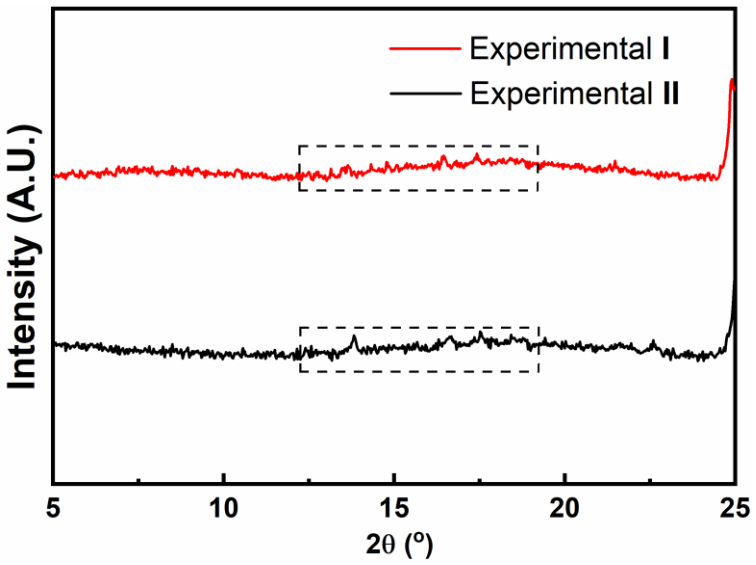

Figure S2. PXRD of zoomed in region of 2Θ = 5 to 25 of Li_5MSe_4 showing the presence of low angle lines.

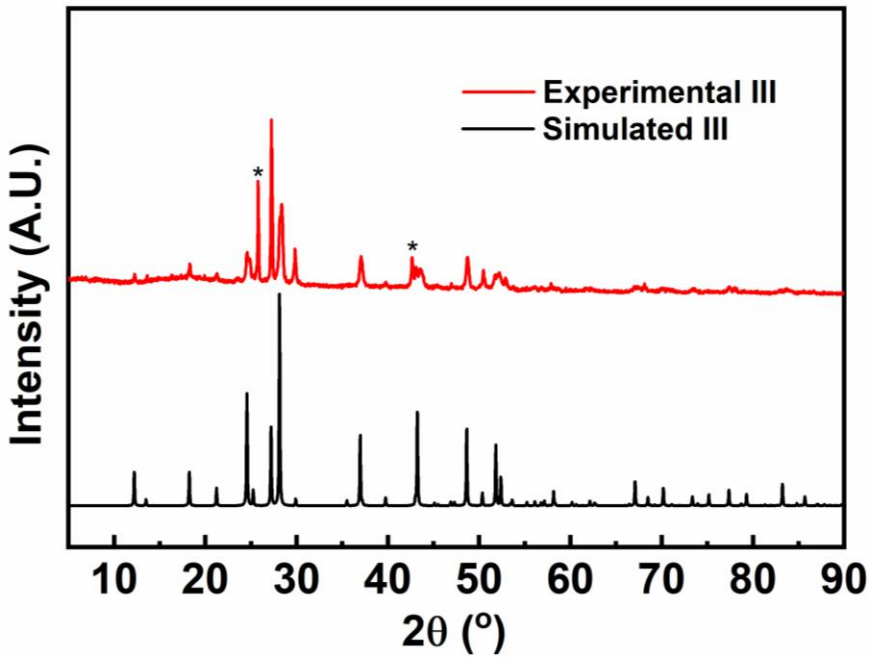

Figure S3. The experimental PXRD of $Li_{4.66}Al_{0.82}Sn_{0.22}Se_4$ (**III**) and its comparison with the simulated pattern. Asterisks indicate presence of some unknown impurity.

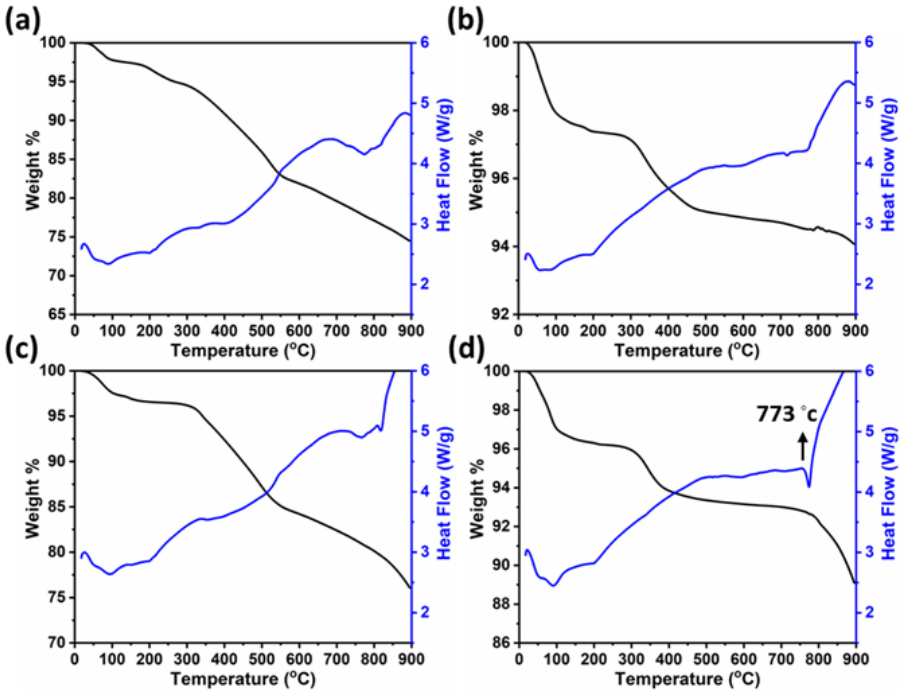

Figure S4. TGA-DSC curves of compound (a) **I**, (b) **II**, (c) **III**, and (d) **IV**.

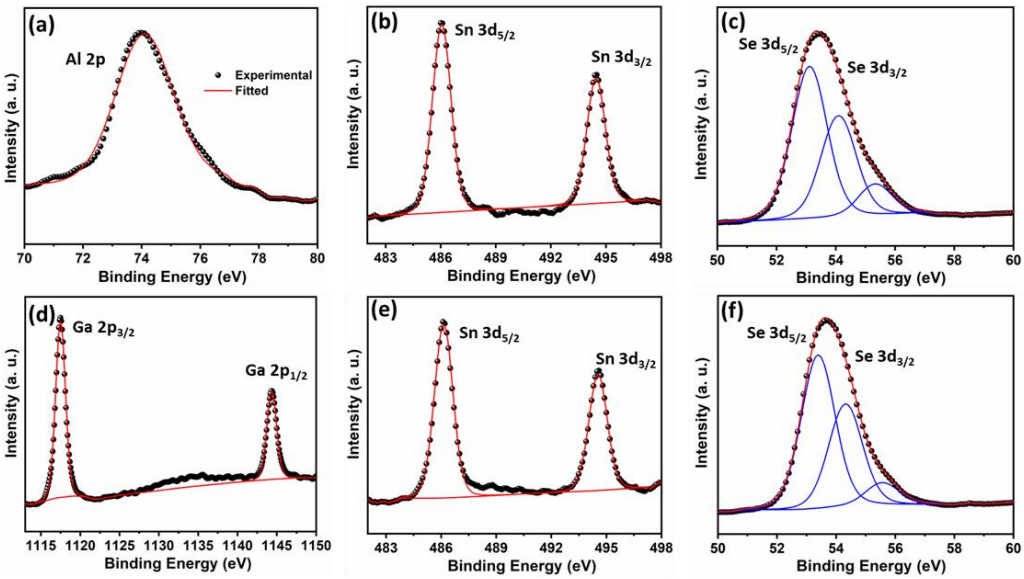

Figure S5. XPS spectra of compound **III** (a) Al 2p, (b) Sn 3d, (c) Se 3d and XPS spectra of compound **IV** (d) Ga 2p, (e) Sn 3d and (f) Se 3d.

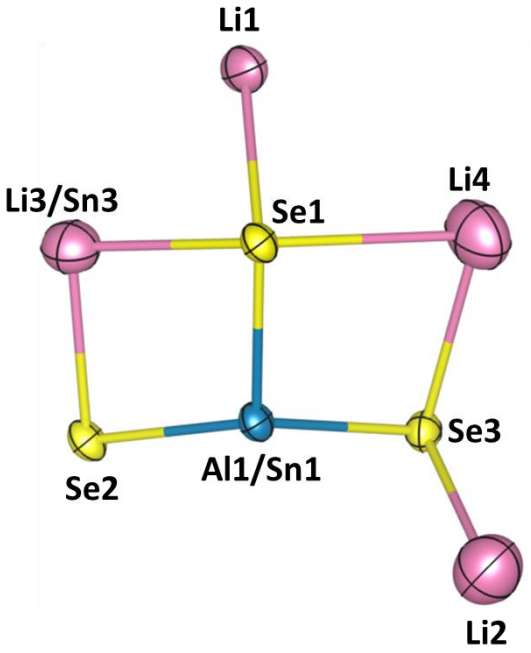

Figure S6. Asymmetric unit of $Li_{4.66}Al_{0.82}Sn_{0.22}Se_4$ (**III**).

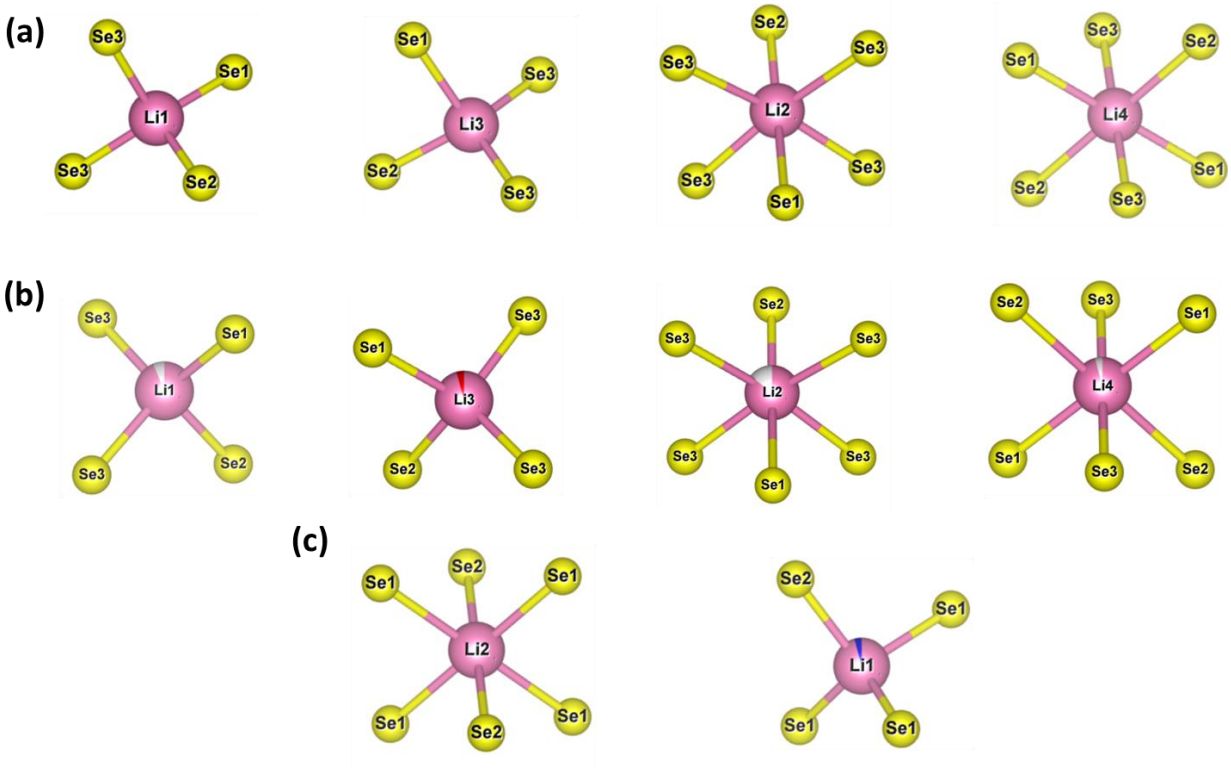

Figure S7. Li-ion coordination in **(a)** Li_5MSe_4 (**I** and **II**), **(b)** $Li_{4.66}Al_{0.82}Sn_{0.22}Se_4$ (**III**) showing vacancy creation (Li1, Li2, and Li4) and Sn^{4+} substitution (Li3 (red shade)) and **(c)** $Li_{4.37}Ga_{0.89}Sn_{0.24}Se_4$ (**IV**) showing Sn^{4+} substitution in Li1 site and no vacancy at Li2 site.

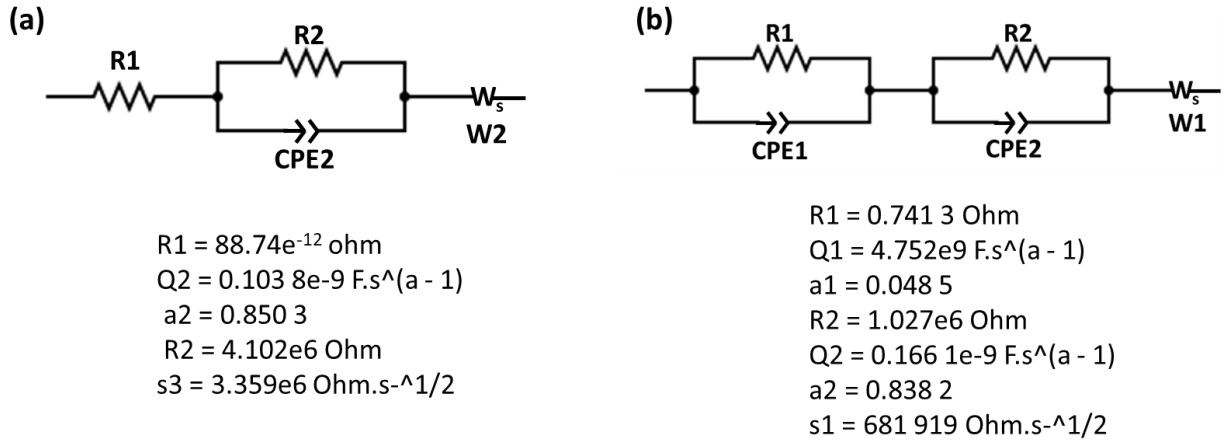

Figure S8. Equivalent circuit and fitting parameters for room temperature ionic conductivity of **(a)** Li_5MSe_4 (**I** and **II**) and **(b)** $Li_{4.66}Al_{0.82}Sn_{0.22}Se_4$ (**III**) and $Li_{4.37}Ga_{0.89}Sn_{0.24}Se_4$ (**IV**).

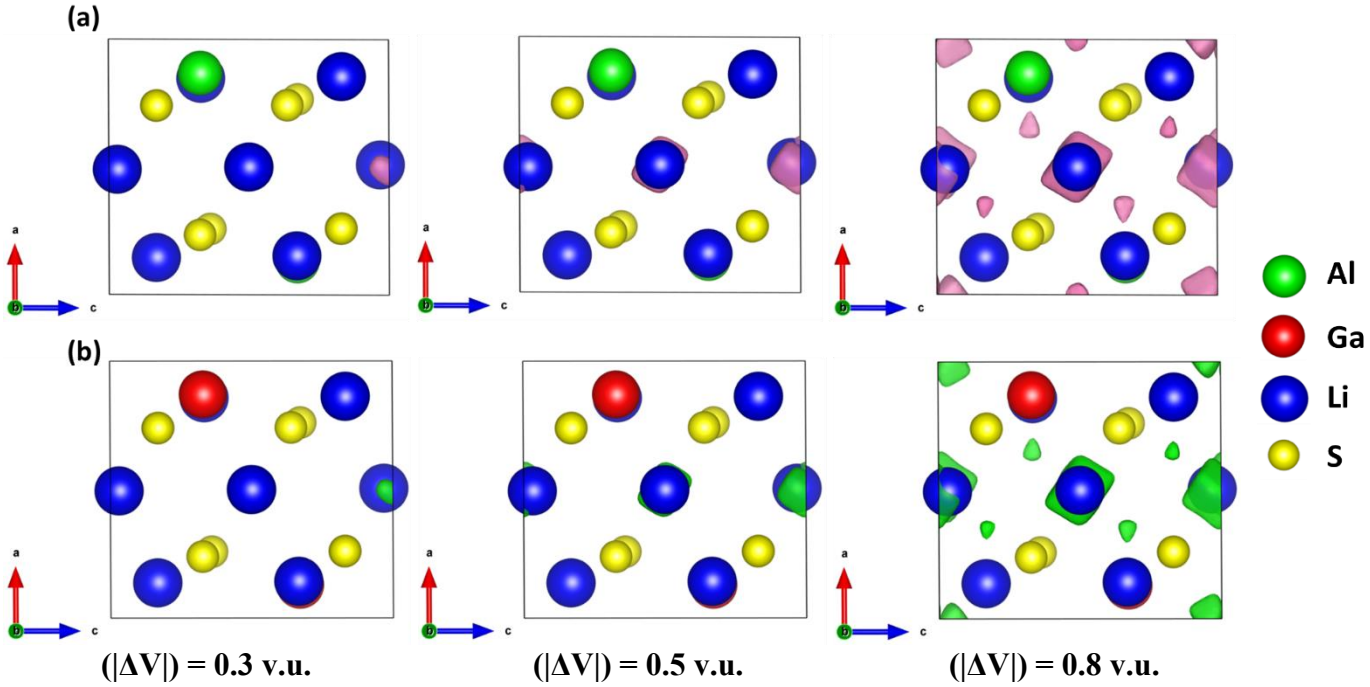

Figure S9. Bond valence sum maps at different |ΔV| of **(a)** Li_5AlSe_4 (**I**) and **(b)** Li_5GaSe_4 (**II**).

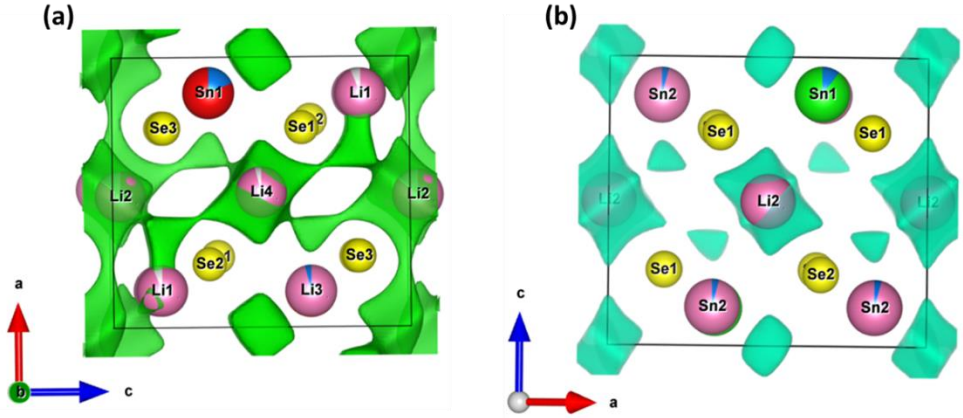

Figure S10. Bond valence sum ($|\Delta V|$ = 1.4 v.u.) maps of **(a)** $Li_{4.66}Al_{0.82}Sn_{0.22}Se_4$ (**III**) and $Li_{4.37}Ga_{0.89}Sn_{0.24}Se_4$ (**IV**).

Table S1. Atomic coordinates and equivalent isotropic displacement parameters of atoms for compound **I - IV.** U (eq) = 1/3 of the trace of the orthogonalized Ueq tensor.

Atomic Parameters						
Atom	Wyckoff	Occupancy	x/a	y/b	z/c	U (Å)
Li_5AlSe_4, I						
Al1	2e	1	0.1328(5)	0.2500	0.6721(5)	0.018(1)
Se1	2e	1	0.2572(2)	0.2500	0.3601(2)	0.016(1)
Se2	2e	1	-0.2340(2)	0.2500	0.6755(2)	0.015(1)
Se3	4f	1	0.2593(1)	0.4864(1)	0.8291(1)	0.016(1)
Li1	4f	1	0.1380(20)	0.4869(14)	0.1640(20)	0.016(3)
Li2	2e	1	0.5150(40)	0.2500	0.9770(30)	0.045(6)
Li3	2e	1	-0.1500(30)	0.2500	0.3280(30)	0.020(4)
Li4	2d	1	0.5000	0.5000	0.5000	0.037(6)
Li_5GaSe_4, II						
Ga1	2e	1	0.1294(1)	0.2500	0.6708(1)	0.006(1)
Se1	2e	1	0.2584(1)	0.2500	0.3594(1)	0.007(1)
Se2	2e	1	-0.2393(1)	0.2500	0.6742(1)	0.007(1)
Se3	4f	1	0.2602(1)	0.4868(1)	0.8300(1)	0.007(1)
Li1	4f	1	0.1375(15)	0.4880(10)	0.1666(13)	0.011(2)
Li2	2e	1	0.5050(20)	0.2500	0.9690(20)	0.033(3)
Li3	2e	1	-0.1426(17)	0.2500	0.3345(15)	0.005(2)
Li4	2d	1	0.5000	0.5000	0.5000	0.024(3)
$Li_{4.66}Al_{0.82}Sn_{0.22}Se_4$, III						
Al1	2e	0.82	0.1314(2)	0.2500	0.6717(2)	0.017(1)
Sn1	2e	0.18	0.1314(2)	0.2500	0.6717(2)	0.017(1)
Se1	2e	1	0.2608(1)	0.2500	0.3598(1)	0.018(1)
Se2	2e	1	-0.2345(1)	0.2500	0.6733(1)	0.019(1)
Se3	4f	1	0.2623(1)	0.4876(1)	0.8274(1)	0.019(1)
Li1	4f	0.94	0.1370(20)	0.4871(12)	0.1636(17)	0.030(3)
Li2	2e	0.86	0.5130(40)	0.2500	0.9710(30)	0.060(7)
Li3	2e	0.96	-0.1346(14)	0.2500	0.3325(12)	0.039(2)
Sn2	2e	0.04	-0.1346(14)	0.2500	0.3325(12)	0.039(2)
Li4	2d	0.96	0.5000	0.5000	0.5000	0.055(8)
$Li_{4.37}Ga_{0.89}Sn_{0.24}Se_4$, IV						
Ga1	2d	0.893	0.3333	0.6667	0.1275(2)	0.018(1)
Sn1	2d	0.107	0.3333	0.6667	0.1275(2)	0.018(1)
Se1	6i	1	0.6507(1)	0.8254(1)	0.2613(2)	0.023(1)
Se2	2d	1	0.3333	0.6667	0.7528(2)	0.020(1)
Li1	6i	0.956	0.3302(7)	0.1651(4)	0.1370(14)	0.043(2)
Sn2	6i	0.044	0.3302(7)	0.1651(4)	0.1370(14)	0.043(2)
Li2	3f	1	0.5000	0.0000	0.5000	0.066(8)

Table S2. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **I** - **IV**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Li_5AlSe_4, I						
Al1	10(2)	18(2)	26(2)	0	-1(1)	0
Se1	12(1)	17(1)	20(1)	0	2(1)	0
Se2	8(1)	18(1)	20(1)	0	0(1)	0
Se3	11(1)	17(1)	18(1)	-1(1)	-2(1)	-2(1)
Li1	11(7)	14(6)	23(7)	0(5)	0(6)	-4(5)
Li2	40(16)	45(16)	48(15)	0	-15(12)	0
Li3	29(11)	10(9)	20(10)	0	-4(8)	0
Li4	30(14)	44(15)	37(14)	6(9)	9(11)	-24(10)
Li_5GaSe_4, II						
Ga1	4(1)	13(1)	2(1)	0	-1(1)	0
Se1	6(1)	13(1)	2(1)	0	1(1)	0
Se2	1(1)	14(1)	5(1)	0	0(1)	0
Se3	5(1)	14(1)	3(1)	-1(1)	-1(1)	-2(1)
Li1	16(5)	8(4)	9(4)	0(3)	3(3)	-2(3)
Li2	14(7)	53(9)	31(7)	0	-9(5)	0
Li4	7(7)	34(8)	31(7)	-3(5)	6(5)	-10(5)
$Li_{4.66}Al_{0.82}Sn_{0.22}Se_4$, III						
Al1	13(1)	19(1)	19(1)	0	2(1)	0
Sn1	13(1)	19(1)	19(1)	0	2(1)	0
Se1	15(1)	18(1)	21(1)	0	3(1)	0
Se2	15(1)	19(1)	22(1)	0	5(1)	0
e3	16(1)	22(1)	19(1)	-2(1)	-1(1)	-2(1)
Li1	38(7)	23(5)	28(6)	1(4)	-3(5)	-7(4)
Li2	65(17)	57(15)	58(15)	0	-8(12)	0
Li3	42(5)	43(5)	33(4)	0	3(4)	0
Sn2	42(5)	43(5)	33(4)	0	3(4)	0
Li4	65(17)	44(13)	58(15)	-6(8)	6(12)	-13(9)
$Li_{4.37}Ga_{0.89}Sn_{0.24}Se_4$, IV						
Ga1	17(1)	17(1)	19(1)	0	0	9(1)
Sn1	17(1)	17(1)	19(1)	0	0	9(1)
Se1	23(1)	20(1)	25(1)	-1(1)	-2(1)	12(1)
Se2	19(1)	19(1)	21(1)	0	0	9(1)
Li1	40(4)	36(3)	54(5)	-2(2)	-3(3)	20(2)
Sn2	40(4)	36(3)	54(5)	-2(2)	-3(3)	20(2)
Li2	44(10)	45(12)	110(30)	-24(12)	-12(6)	22(6)

Table S3. Polyhedral distortion index of **I** and **III;** and **II** and **IV**.

Li_5AlSe_4 (I)		**$Li_{4.66}Al_{0.82}Sn_{0.22}Se_4$ (III)**	
Polyhedra	Distortion Index	Polyhedra	Distortion Index
$AlSe_4$	0.00168	(Al1/Sn1) $AlSe_4$	0.00273
(Li1) $LiSe_4$	0.01148	(Li1) $LiSe_4$	0.01096
(Li3) $LiSe_4$	0.01790	(Li3/Sn2) $LiSe_4$	0.00710
(Li2) $LiSe_6$	0.05150	(Li2) $LiSe_6$	0.05806
(Li4) $LiSe_6$	0.02443	(Li4) $LiSe_6$	0.02572
Li_5GaSe_4 (II)		**$Li_{4.37}Ga_{0.89}Sn_{0.24}Se_4$ (IV)**	
Polyhedra	Distortion Index	Polyhedra	Distortion Index
$GaSe_4$	0.00307	(Ga1/Sn1) $GaSe_4$	0.00002
(Li1) $LiSe_4$	0.01110	(Li1/Sn2) $LiSe_4$	0.00375
(Li3) $LiSe_4$	0.01104	(Li2) $LiSe_6$	0.01500
(Li2) $LiSe_6$	0.06637		
(Li4) $LiSe_6$	0.02048		