Supporting Information –

Influence of the Lithium Substructure on the Diffusion Pathways and Transport Properties of the Thio-LISICON $Li_4Ge_{1-x}Sn_xS_4$

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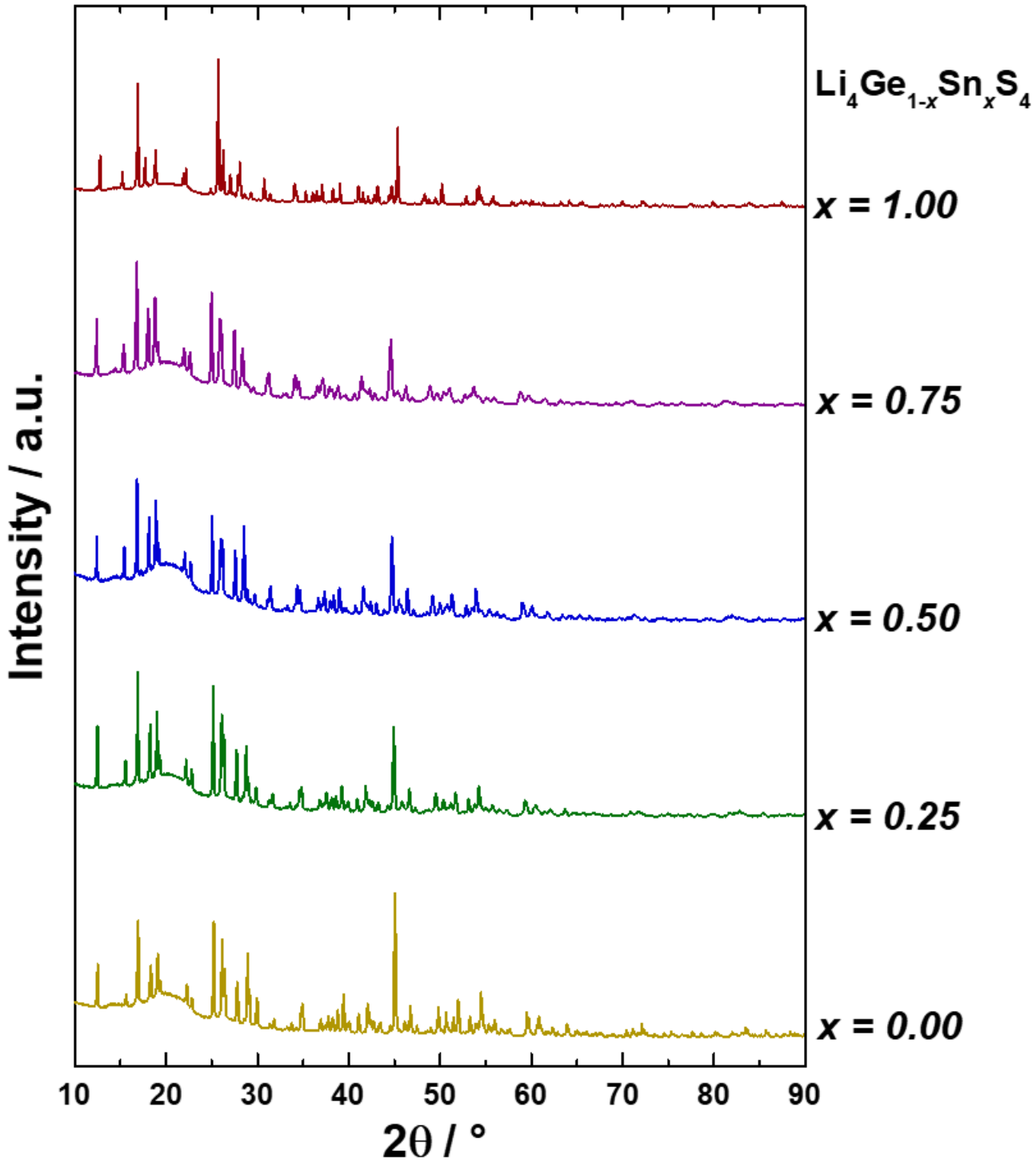

Figure S1: Laboratory X-ray powder diffractograms of $Li_4Ge_{1-x}Sn_xS_4$.

Table S1: Refined structural parameters for Li_4GeS_4.

Li_4GeS_4 structure from neutron powder diffraction data (space group *Pnma*). *a* = 14.0722(3) Å; *b* = 7.7501(1) Å; *c* = 6.1500(1) Å Fit residuals (R_{wp}, GoF): 4.97 %, 1.45						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	4*c*	0.4101(4)	0.75	0.3674(8)	1	2.28(7)
Li2	8*d*	0.1765(3)	-0.0002(4)	0.3074(7)	1	2.82(7)
Li3	8*d*	0.0070(6)	-0.020(1)	0.472(2)	0.5	1.7(1)
Ge	4*c*	0.41096(9)	0.25	0.3515(2)	1	1.32(2)
S1	8*d*	0.3431(2)	0.0153(3)	0.2206(4)	1	1.39(4)
S2	4*c*	0.0858(3)	0.75	0.2078(4)	1	1.25(5)
S3	4*c*	0.0603(2)	0.25	0.2678(5)	1	1.17(5)

Table S2: Refined structural parameters for $Li_4Ge_{0.75}Sn_{0.25}S_4$.

$Li_4Ge_{0.75}Sn_{0.25}S_4$ structure from neutron powder diffraction data (space group *Pnma*). *a* = 14.1272(4) Å; *b* = 7.7791(2) Å; *c* = 6.1940(2) Å Fit residuals (R_{wp}, GoF): 4.65 %, 1.37						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	4*c*	0.4091(5)	0.75	0.369(1)	1	2.5(1)
Li2	8*d*	0.1763(3)	-0.0027(5)	0.3128(7)	1	2.47(8)
Li3	8*d*	0.0034(8)	-0.015(1)	0.467(2)	0.5	1.8(2)
Ge	4*c*	0.4105(1)	0.25	0.3521(2)	0.72(1)	1.28(4)
Sn	4*c*	0.4105(1)	0.25	0.3521(2)	0.28(1)	1.28(4)
S1	8*d*	0.3428(2)	0.0125(3)	0.2207(4)	1	1.35(5)
S2	4*c*	0.0855(3)	0.75	0.2128(5)	1	1.35(6)
S3	4*c*	0.0614(2)	0.25	0.2672(6)	1	1.58(8)

Table S3: Refined structural parameters for $Li_4Ge_{0.5}Sn_{0.5}S_4$.

$Li_4Ge_{0.5}Sn_{0.5}S_4$ structure from neutron powder diffraction data (space group *Pnma*). *a* = 14.1768(9) Å; *b* = 7.8108(5) Å; *c* = 6.2399(4) Å Fit residuals (R_{wp}, GoF): 4.49 %, 1.33						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	4c	0.4067(6)	0.75	0.370(1)	1	2.7(1)
Li2	8d	0.1766(3)	-0.0021(5)	0.3194(8)	1	2.3(1)
Li3	8d	0.0035(8)	-0.022(1)	0.473(2)	0.5	1.5(2)
Ge	4c	0.4097(1)	0.25	0.3544(2)	0.50(1)	1.19(5)
Sn	4c	0.4097(1)	0.25	0.3544(2)	0.50(1)	1.19(5)
S1	8d	0.3411(2)	0.0082(3)	0.2187(5)	1	1.40(6)
S2	4c	0.0842(3)	0.75	0.2195(5)	1	1.32(7)
S3	4c	0.0630(2)	0.25	0.2653(6)	1	1.09(8)

Table S4: Refined structural parameters for $Li_4Ge_{0.25}Sn_{0.75}S_4$.

$Li_4Ge_{0.25}Sn_{0.75}S_4$ structure from neutron powder diffraction data (space group *Pnma*). *a* = 14.226(2) Å; *b* = 7.8437(9) Å; *c* = 6.2833(8) Å Fit residuals (R_{wp}, GoF): 5.12 %, 1.34						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	4*c*	0.4070(6)	0.75	0.373(1)	1	2.7(1)
Li2	8*d*	0.1773(4)	-0.0041(6)	0.3200(8)	1	2.3(1)
Li3	8*d*	0.002(1)	-0.018(2)	0.468(2)	0.5	1.9(2)
Ge	4*c*	0.4088(1)	0.25	0.3557(3)	0.23(1)	1.22(5)
Sn	4*c*	0.4088(1)	0.25	0.3557(3)	0.77(1)	1.22(5)
S1	8*d*	0.3400(2)	0.0049(4)	0.2167(5)	1	1.49(7)
S2	4*c*	0.0841(3)	0.75	0.2272(6)	1	1.40(8)
S3	4*c*	0.0647(3)	0.25	0.2658(7)	1	1.4(1)

Table S5: Refined structural parameters for Li_4SnS_4.

Li_4SnS_4 structure from neutron powder diffraction data (space group *Pnma*). *a* = 13.8227(6) Å; *b* = 7.9914(3) Å; *c* = 6.3913(2) Å Fit residuals (R_{wp}, GoF): 6.09 %, 1.68						
Atom	Wyckoff Site	x/*a*	y/*b*	z/*c*	Occ.	B_{eq} / Å^2
Li1	4c	0.437(1)	0.75	0.152(2)	1	6.1(3)
Li2	8d	0.1615(6)	-0.0066(9)	0.343(1)	1	3.1(1)
Li3	8d	-0.034(2)	-0.028(5)	0.477(6)	0.25(1)	4.8(8)
Li4	4c	0.794(2)	0.75	0.021(4)	0.50(2)	4.9(7)
Sn	4c	0.4125(2)	0.25	0.3635(4)	1	1.54(4)
S1	8d	0.3316(2)	0.0073(5)	0.2325(6)	1	1.98(6)
S2	4c	0.0931(6)	0.75	0.2306(7)	1	1.9(1)
S3	4c	0.0744(6)	0.25	0.2609(8)	1	2.0(1)

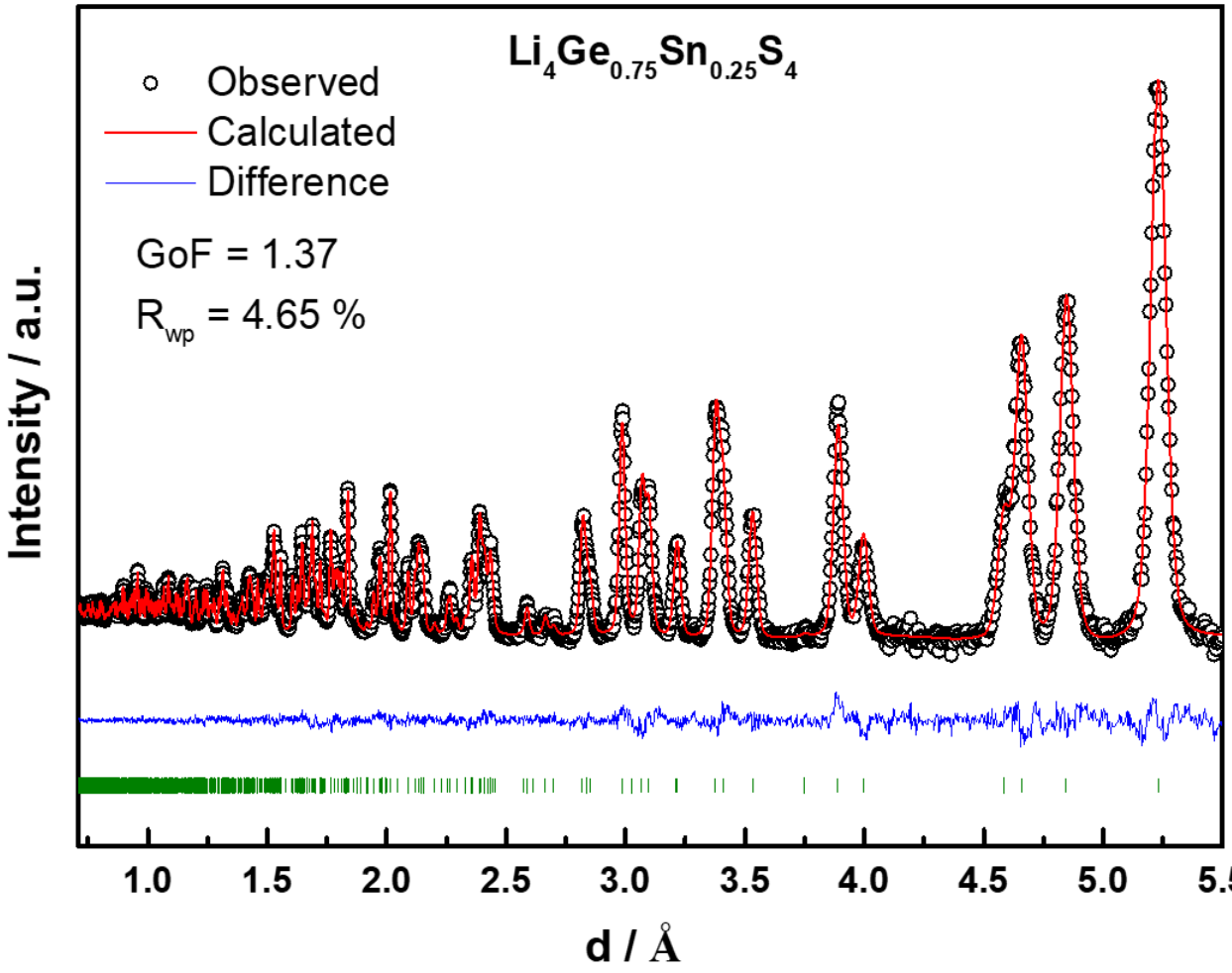

Figure S2: Neutron powder diffraction data for $Li_4Ge_{0.75}Sn_{0.25}S_4$ and corresponding Rietveld refinement. Experimental data are shown in black and the red line denotes the calculated pattern, while the difference profile is shown in blue. Calculated positions of the Bragg reflections are shown as green vertical ticks.

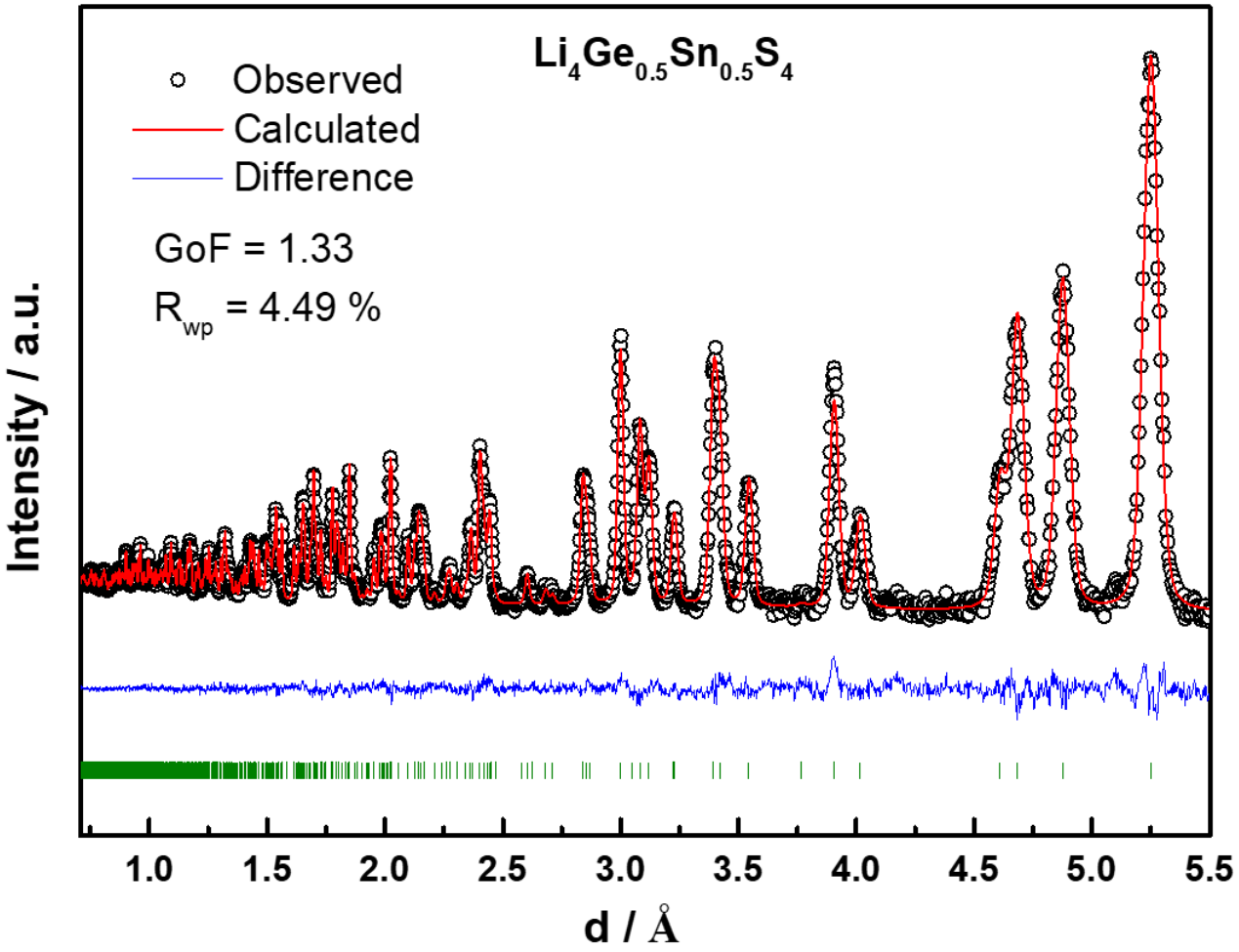

Figure S3: Neutron powder diffraction data for $Li_4Ge_{0.5}Sn_{0.5}S_4$ and corresponding Rietveld refinement. Experimental data are shown in black and the red line denotes the calculated pattern, while the difference profile is shown in blue. Calculated positions of the Bragg reflections are shown as green vertical ticks.

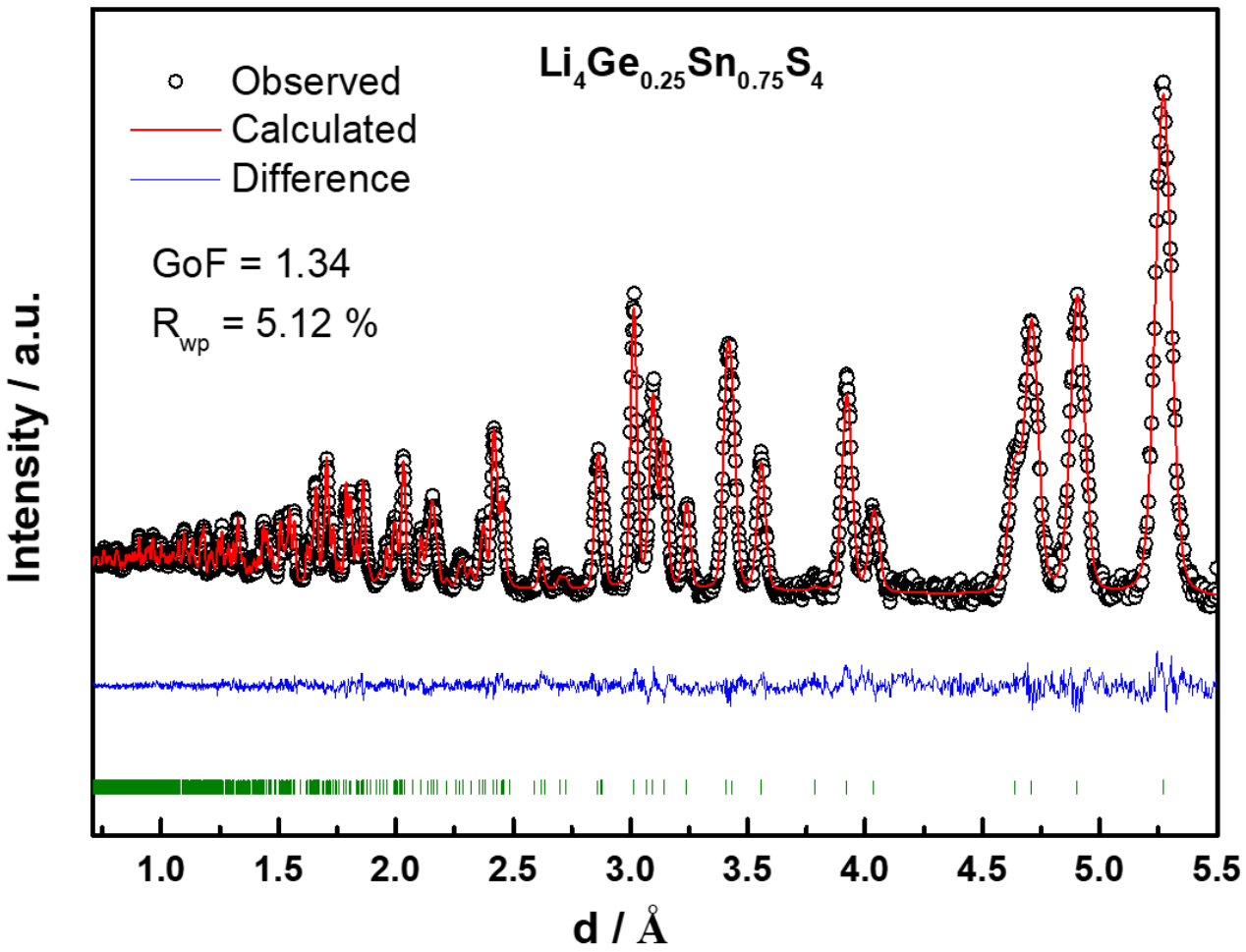

Figure S4: Neutron powder diffraction data for $Li_4Ge_{0.25}Sn_{0.75}S_4$ and corresponding Rietveld refinement. Experimental data are shown in black and the red line denotes the calculated pattern, while the difference profile is shown in blue. Calculated positions of the Bragg reflections are shown as green vertical ticks.

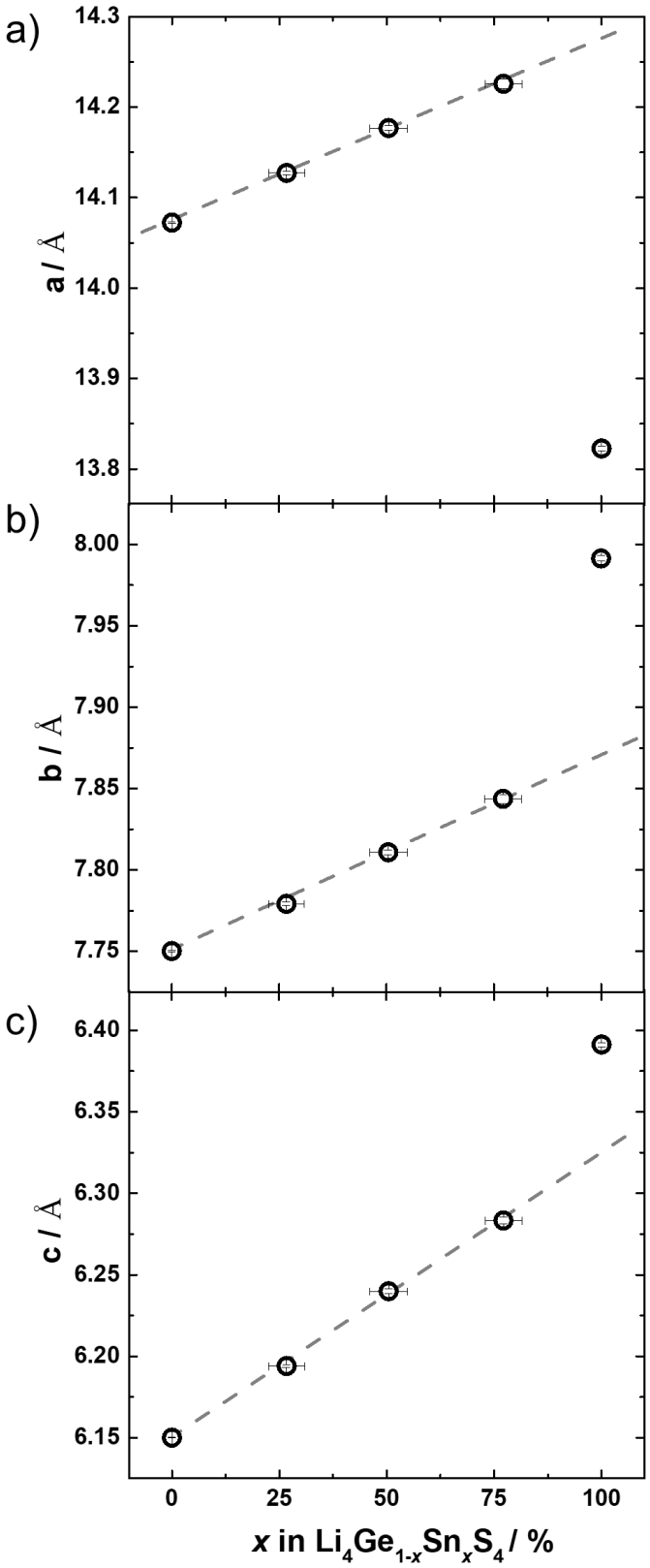

Figure S5: Lattice parameters of $Li_4Ge_{1-x}Sn_xS_4$ against the refined Sn occupancy extracted from Rietveld refinements against neutron diffraction data.