Fast Lithium Ion Conductivity in Li_2SnS_3: Synthesis, Physicochemical Characterization and Electronic Structure

Jacilynn A. Brant,[†] Danielle M. Massi,[†] N. A. W. Holzwarth,[‡] Joseph H. MacNeil,[ˈ] Alexios P. Douvalis,[⊥] Thomas Bakas,[⊥] Steve W. Martin,[∓] Michael D. Gross,[△] and Jennifer A. Aitken[†,*]

[†]Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh Pennsylvania 15282, USA
[‡]Department of Physics, Wake Forest University, Winston-Salem, North Carolina 27109, USA
[⊥]Department of Physics, University of Ioannina, Ioannina 45110, Greece
[∓]Department of Materials Science and Engineering, Iowa State University, Ames Iowa 50011 USA
[ˈ]Department of Chemistry, Chatham University, Pittsburgh, PA 15232, USA
[△]Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 27109, USA

Table S1. Results from single crystal X-ray diffraction. Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Li_2SnS_3.

Atom	x	y	z	U(eq)
Li(1)	0.2466(5)	0.0840(3)	0.9997(9)	9.7(9)
Li(2)	0	0.417(3)	0.2500	18(2)
Li(3)	0.2500	0.2500	0.5000	29(2)
Sn(1)	0	0.0833(1)	0.2500	8.2(1)
Sn(2)	0	0.7499(1)	0.2500	8.1(1)
S(1)	0.11158(9)	0.0831(4)	0.63122(4)	10.3(2)
S(2)	0.13553(9)	0.2418(4)	0.13117(5)	10.2(4)
S(3)	0.36516(9)	0.0920(4)	0.37087(5)	10.4(4)

Table S2. Results from single crystal X-ray diffraction. Li-S bond distances (Å) in the Li_2SnS_3 structure.

Li(1)-S(1)[1]	2.570(3)	Li(2)-S(1)[5]	2.6625(6)	Li(3)-S(3)[5]	2.566(3)
Li(1)-S(2)	2.576(5)	Li(2)-S(1)[6]	2.6625(6)	Li(3)-S(3)	2.566(3)
Li(1)-S(2)[2]	2.709(5)	Li(2)-S(2)	2.67(3)	Li(3)-S(1)[5]	2.711(3)
Li(1)-S(1)[3]	2.709(5)	Li(2)-S(2)[1]	2.67(3)	Li(3)-S(1)	2.711(3)
Li(1)-S(3)[3]	2.709(5)	Li(2)-S(3)[7]	2.68(3)	Li(3)-S(2)[9]	2.7133(6)
Li(1)-S(3)[4]	2.719(3)	Li(2)-S(3)[8]	2.68(3)	Li(3)-S(2)	2.7133(6)

Operators for generating equivalent atoms

1: (-x, y, -z+1/2) 2: (-x+1/2, -y+1/2, -z) 3: (x, -y, z-1/2) 4: (-x+1, y, -z+1/2)
5: (-x+1/2, -y+1/2, -z+1) 6: (x-1/2, -y+1/2, z-1/2) 7: (x-1/2, y+1/2, z) 8: (-x+1/2, y+1/2, -z+1/2)
9: (x+1/2, -y+1/2, z+1/2)

Table S3. Results from single crystal X-ray diffraction. Sn-S bond distances (Å) in the Li_2SnS_3 structure.

Sn(1)-S(1) × 2	2.539(3)	Sn(2)-S(1) × 2	2.543(3)
Sn(1)-S(2) × 2	2.540(3)	Sn(2)-S(2) × 2	2.5373(6)
Sn(1)-S(3) × 2	2.5520(7)	Sn(2)-S(3) × 2	2.549(3)

Table S4. Unit cell parameters, Crystallographic sites, labelling of atoms and site occupation factors (SOFs) in the Li_2SnS_3 structures determined from single crystal X-ray diffraction (SC-XRD) and synchrotron X-ray powder diffraction (SXRPD).

	SC-XRD (this work)		**SC-XRD(Ref. 1)**		**SXRPD (this work)**	
a (Å)	6.3964(5)		6.3961(7)		6.40048(4)	
b (Å)	11.0864(9)		11.089(1)		11.08547(7)	
c (Å)	12.405(1)		12.416(1)		12.42226(4)	
β	99.867(5)		99.860(2)		99.8833(3)	
Site*	**Atom**	**SOF**	**Atom**	**SOF**	**Atom**	**SOF**
8f	Li(1)	1.0	Li(1)	1.0	Li(1)/Sn(4)	0.69(1) / 0.31(1)
4e	Li(2)	1.0	Li(2)/Sn(3)	0.920(6) / 0.08(6)	Li(2)/Sn(3)	0.136(5) / 0.864(5)
4d	Li(3)	1.0	Li(3)	1.0	Li(3)/Sn(5)	0.960(2) / 0.04(2)
4e	Sn(1)	1.0	Li(4)/Sn(1)	0.047(4) / 0.953(4)	Li(4)/Sn(1)	0.489(3) / 0.511(3)
4e	Sn(2)	1.0	Li(5)/Sn(2)	0.034(4) / 0.966(4)	Li(5)/Sn(2)	0.502(3) / 0.498(3)

*Wyckoff letter and multiplicity

Table S5. Refinement statistics of the Li_2SnS_3 structure refinements obtained from single crystal X-ray diffraction.

	This work	**Kuhn et al.**[1]
R1 (I>2σ(I))	0.0131	0.0503
wR2 (I>2σ(I))	0.0286	0.1594
R1 (all data)	0.0174	0.0540
wR2 (all data)	0.0302	0.1619

Table S6. Calculated lattice parameters and lattice parameters obtained via single crystal X-ray diffraction for Li_2SnS_3 (this work) and Li_2SnO_3 (Kreuzburg et al)[2].

	a (Å)	**b (Å)**	**c (Å)**	**β (°)**
Li_2SnS_3 (calculated)	6.28	10.87	12.08	99.82
Li_2SnS_3 (experimental)	6.3964(5)	11.0864(9)	12.405(1)	99.867(5)
Li_2SnO_3 (calculated)	5.21	9.03	9.73	100.27
Li_2SnO_3 (experimental)	5.295	9.184	10.032	100.13

Table S7. Computed fractional atomic coordinates for Li_2SnS_3.

Atom	x	y	z
Li(1)	0.245	0.085	0.000
Li(2)	0.000	0.417	0.250
Li(3)	0.250	0.250	0.500
Sn(1)	0.000	0.083	0.250
Sn(2)	0.000	0.749	0.250
S(1)	0.115	0.083	0.627
S(2)	0.132	0.245	0.128
S(3)	0.368	0.089	0.374

Table S8. Computed fractional atomic coordinates for Li_2SnO_3.

Atom	x	y	z
Li(1)	0.232	0.077	-0.001
Li(2)	0.000	0.085	0.250
Li(3)	0.250	0.250	0.500
Sn(1)	0.000	0.417	0.250
Sn(2)	0.000	0.749	0.250
O(1)	0.133	0.257	0.130
O(2)	0.115	0.583	0.130
O(3)	0.132	0.910	0.128

Table S9. Fractional atomic coordinates from single crystal X-ray diffraction for Li_2SnO_3 reported by Kreuzburg et al.[2]

Atom	x	y	z
Li(1)	0.239(3)	0.078(2)	-0.001(2)
Li(2)	0.000	0.083	0.25
Li(3)	0.25	0.25	0.5
Sn(1)	0.000	0.4165(1)	0.25
Sn(2)	0.000	0.7508(1)	0.25
S(1)	0.1337(8)	0.260(2)	0.1333(4)
S(2)	0.1102(9)	0.0584(2)	0.1342(5)
S(3)	0.1346(8)	0.909(2)	0.1329(4)

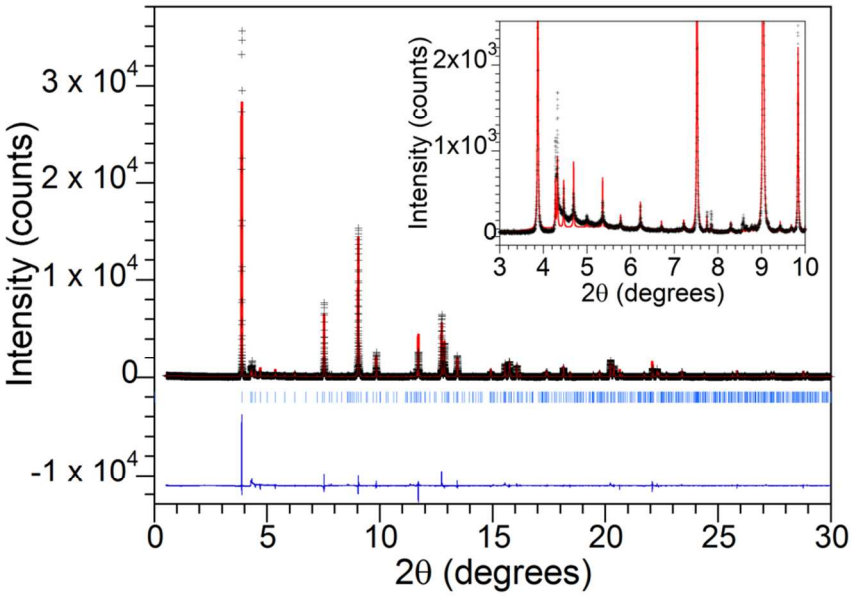

Figure S1. Results of Rietveld refinement for Li_2SnS_3. The collected SXRPD data are plotted with plus signs (+), overlapped by the calculated pattern using the model (line). Expected Bragg reflections for the Li_2SnS_3 are displayed with tick marks (|). The difference between the collected data and the calculated pattern is shown at the bottom of the plot.

Data were collected to 50° 2θ and all data were used in the refinement, but not shown here due to minimal diffraction peaks between 30-50°. The inset shows the non-uniform peak broadening that may indicate the presence of stacking faults. Agreement factors are: $\chi^2 = 3.301$, $R_p = 0.1359$, and $wR_p = 0.1696$.

Air-stability of Li_2SnS_3

It is noteworthy that preliminary results indicate that impedance measurements were reproducible on a pellet of Li_2SnS_3 that was exposed to ambient conditions for two months. X-ray powder diffraction (XRPD) data were collected on a freshly prepared sample of Li_2SnS_3 in a back-filled sample holder, and compared to data that were collected on a sample of Li_2SnS_3 that was exposed to ambient conditions (~20 °C, ~60% humidity) for one week. XRPD was performed using a Panalytical X'Pert Pro MPD powder X-ray diffractometer using copper K_α radiation (λ = 1.541871 Å) and a tube power of 45 kV and 40 mA. Data were collected from 10° to 80° 2θ with a step size of 0.001° and scan rate of 0.0105771°/s. A 0.02 rad soller slit, a divergent slit of 1/4° and an anti-scatter slit of 1/2° comprised the incident beam optics, while the diffracted beam optics consist of a 0.02 rad soller slit and a 1/4° anti-scatter slit.

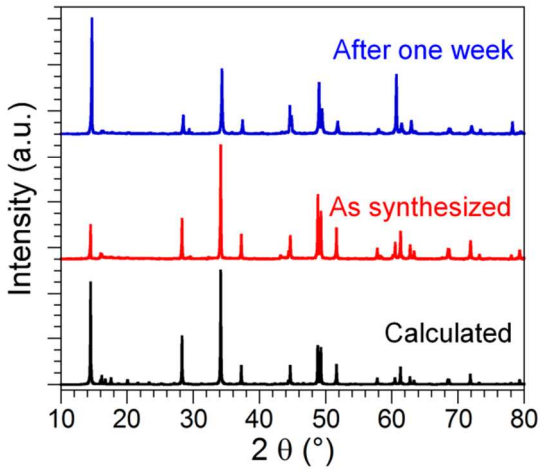

Figure S2. X-ray powder diffraction data of Li_2SnS_3. The XRPD pattern was calculated (bottom, black line) using the model that contains Li/Sn site disorder, which was obtained via Rietveld refinement using synchrotron X-ray powder diffraction. Data that were collected on an as-synthesized sample of Li_2SnS_3 are shown with a red line (middle). Data that were collected on the same sample after exposure to ambient conditions for one week are shown with a blue line (top).

According to X-ray powder diffraction data, the Li_2SnS_3 sample is air-stable under ambient conditions for at least one week. While some variations in peak height are observed, the overall pattern remains consistent. The peak positions remain the same, revealing that the structure does not change. Also, no crystalline decomposition products are expected to exist, additional peaks are not observed.

REFERENCES

1. Kuhn, A.; Holzmann, T.; Nuss, J.; Lotsch, B. V., *J. Mater. Chem. A* **2014,** *2*, 6100-6106.
2. Kreuzburg, G.; Stewner, F.; Hoppe, R., *Z. Anorg. Allg. Chem.* **1971,** *379*, 242-254.