Supporting Information

Li$_5$Sn, the most lithium-rich binary stannide: A combined experimental and computational study

Robert U. Stelzer,$^1$ Yuji Ikeda,$^2$ Prashanth Srinivasan,$^2$ Tanja S. Lehmann,$^1$ Blazej Grabowski,$^2$ and Rainer Niewa$^1$

$^1$Institute of Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany
$^2$Institute for Materials Science, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Appendix A: Displacement parameters of Li$_5$Sn in Cmcm (#7)

Table S1. Displacement parameters (Å$^2$) of Li$_5$Sn in Cmcm (#7) from experiments.

| Wyckoff | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---------|----------|----------|----------|----------|----------|----------|
| Li(1)   | 0.008(4) | 0.046(5) | 0.023(4) | 0        | 0        | 0        |
| Li(2)   | 0.028(3) | 0.033(2) | 0.028(2) | 0.0032(16) | 0.0008(18) | 0.005(2) |
| Sn      | 0.0189(2) | 0.0246(2) | 0.0173(2) | 0        | 0        | 0        |

Appendix B: Further computational details

B.1. Ab initio molecular dynamics (MD)

For the temperature-dependent Gibbs energy calculations (Section 3.4 in the main text), ab initio MD simulations were conducted for structures #7 and #23 to create both the reference effective harmonic potential and the MTP. We made 288-atom supercell models of the Li$_5$Sn structures. The ab initio MD runs were performed at 300 K (for the fitting of the effective harmonic potential) and 500 K (for the fitting of the MTP). The NVT-ensemble, where the temperature was controlled by a Langevin thermostat with a friction parameter of 0.01 fs$^{-1}$, was employed, and 1000 MD steps were run with the time step of 2 fs. The Fermi–Dirac distribution at the corresponding temperature of a given MD run was applied to include the impact of electronic excitations in the finite-temperature DFT extension by Mermin.$^{31}$ The exchange–correlation functional, the plane-wave cutoff energy, the mesh for the reciprocal-space sampling, and the orbitals treated as valence states were the same as those chosen for the 0 K structure optimization (setting A in Table 1 in the main text).

B.2. Effective harmonic potentials

The effective harmonic potentials for the structures #7 and #23 were first fitted to 300 K ab initio MD data (Appendix B.1) at four different volumes within the range 16–22 Å$^3$/atom using the implementation in the S/PHI/nX code.$^{32}$ Each effective force constant was then parametrized by a third-order polynomial in volume which served as the reference for each volume point in the TILD. From the volume-dependent effective force constants, effective phonon frequencies were calculated by constructing the dynamical matrix and solving the eigenproblem,$^{33,34}$ from which the contribution to the Helmholtz energy, i.e., the first term in eq 3 in the main text, was analytically calculated.

B.3. Moment tensor potentials (MTPs)

We fitted the MTPs to ab initio MD runs at seven different volumes within the range 16–22 Å$^3$/atom at 500 K (Appendix B.1) separately for the structures #7 and #23. We used 1058 basis functions with a maximum cut-off distance of 5 Å. Weights of 1, 0.01, and 0.001 were given to the energies, atomic forces, and stress tensors of configurations, respectively, during fitting. Root-mean-squared errors (RMSEs) in energy and forces of 0.3 meV/atom and 19 meV/Å and 0.2 meV/atom and 16 meV/Å were obtained for structures #7 and #23, respectively.

The fitted MTPs were utilized for the TILD (Section 3.4 in the main text) to compute the second and the third terms in eq 3 in the main text, as well as to investigate the temperature-dependent stability for structures #7 and #23 (Section 4.8 in the main text).
Appendix C: Structure #0: Comparison with Mayo and Morris\textsuperscript{85}

Structure #0 of Li\textsubscript{5}Sn with the space group \textit{P6/mmm} as determined in the present \textit{ab initio} simulations is essentially the same as the one reported by Mayo and Morris.\textsuperscript{85} Tables S2 and S3 show the lattice parameters and the fractional atomic coordinates, respectively, obtained in the present study and by Mayo and Morris,\textsuperscript{85} highlighting the good agreement with each other.

| Table S2. Lattice parameters of structure #0 with the space group \textit{P6/mmm}. |
|-----------------------------------|---------|---------|---------|-------|-------|-------|
| Reference                        | \(a\) (Å) | \(b\) (Å) | \(c\) (Å) | \(\alpha\) (deg.) | \(\beta\) (deg.) | \(\gamma\) (deg.) |
| Present \textit{ab initio}       | 4.691   | 4.691   | 5.741   | 90    | 90    | 120   |
| Mayo and Morris\textsuperscript{85} | 4.685   | 4.685   | 5.701   | 90    | 90    | 120   |

| Table S3. Fractional atomic coordinates of structure #0 with the space group \textit{P6/mmm}. |
|-----------------------------------|---------|---------|---------|---------|---------|---------|
| Wyckoff                           | Present \textit{ab initio} |        | Mayo and Morris\textsuperscript{85} |        |
|                                   | \(x\)   | \(y\)   | \(z\)   | \(x\)   | \(y\)   | \(z\)   |
| Li                                 | 1/3     | 2/3     | 0.77359 | 1/3     | 2/3     | 0.77460 |
| Li                                 | 0       | 0       | 1/2     | 0       | 0       | 1/2     |
| Sn                                 | 0       | 0       | 0       | 0       | 0       | 0       |

Appendix D: Structure #83: Comparison with Sen and Johari\textsuperscript{86}

Structure #83 of Li\textsubscript{5}Sn with the space group \textit{C2/m} as determined in the present \textit{ab initio} simulations is essentially the same as the one reported by Sen and Johari.\textsuperscript{86} Tables S4 and S5 show the lattice parameters and the fractional atomic coordinates, respectively, obtained in the present study and by Sen and Johari,\textsuperscript{86} highlighting the good agreement with each other. Note that the results of Sen and Johari\textsuperscript{86} correspond to 1 atm, while ours to zero pressure. For solid phases, however, such a small pressure difference will only marginally affect the results.

| Table S4. Lattice parameters of structure #83 with the space group \textit{C2/m}. |
|-----------------------------------|---------|---------|-------|-------|-------|-------|
| Reference                        | \(a\) (Å) | \(b\) (Å) | \(c\) (Å) | \(\alpha\) (deg.) | \(\beta\) (deg.) | \(\gamma\) (deg.) |
| Present \textit{ab initio}       | 15.897  | 5.745   | 12.023 | 90    | 128.81 | 90    |
| Sen and Johari\textsuperscript{86} | 15.918  | 5.738   | 12.043 | 90    | 128.86 | 90    |

| Table S5. Fractional atomic coordinates of structure #83 with the space group \textit{C2/m}. |
|-----------------------------------|---------|---------|---------|---------|---------|---------|
| Wyckoff                           | Present \textit{ab initio} |        | Sen and Johari\textsuperscript{86} |        |
|                                   | \(x\)   | \(y\)   | \(z\)   | \(x\)   | \(y\)   | \(z\)   |
| Li                                 | 0.02321 | 0.23895 | 0.12583 | 0.02329 | 0.23903 | 0.12587 |
| Li                                 | 0.35724 | 0.24208 | 0.12875 | 0.35730 | 0.24201 | 0.12869 |
| Li                                 | 0.23201 | 0.23806 | 0.37413 | 0.23212 | 0.23819 | 0.37423 |
| Li                                 | 0.40002 | 0.22446 | 0.37803 | 0.40011 | 0.22485 | 0.37799 |
| Li                                 | 0.05992 | 0      | 0.38638 | 0.05996 | 0      | 0.38658 |
| Li                                 | 0.30396 | 0      | 0.86362 | 0.30362 | 0      | 0.86329 |
| Sn                                 | 0.18374 | 0      | 0.11299 | 0.18370 | 0      | 0.11280 |
| Sn                                 | 0.57054 | 0      | 0.36794 | 0.57071 | 0      | 0.36776 |
Appendix E: Stability of structures #7 and #23 at finite temperatures

To determine the temperature up to which a stable TILD could be performed, the MTPs were first used to predict the stability of the corresponding phases during heating. The simulations were performed using LAMMPS on a 5148-atom system at a heating rate of 0.25 K/ps. Figure S1 shows the variation of the atomic volume while heating the systems from 500 K. A sudden jump in the curve indicates that the initial phase is no longer stable above that particular temperature as predicted by the MTPs. This temperature was found to be 675 K for structure #7 and 760 K for structure #23. Further calculations and analysis of the high temperature phases are beyond the scope of this work. Considering this as an over-heated value and choosing a conservative temperature, we decided to perform TILD up to 600 K.

Figure S1. Atomic volume as a function of temperature during heating of the #7 and #23 Li$_5$Sn structures using MTPs in a 5148-atom simulation cell.

Appendix F: Density of states: Li$_5$Sn in Cmcm (#7)

Figure S2 shows the ab initio computed densities of states (DOSs) for Cmcm Li$_5$Sn (#7) found in experiments using settings A (Li 2s and Sn 5s5p orbitals are treated as valence) and D (Li 1s2s and Sn 4d5s5p orbitals are treated as valence) from Table 1 in the main text. The DOSs clearly show a metallic trend. Further, the two computational settings show almost the same DOSs, indicating that not only the energetics (as demonstrated in Figure 8 in the main text) but also the electronic structures are robust against the choice of the PAW potentials considered in the present study.
**Figure S2.** *Ab initio* computed DOSs of *Cmcm* Li₅Sn (#7) found in experiments computed using settings A and D from Table 1 in the main text.

---

[S1] N. D. Mermin, Thermal properties of the inhomogeneous electron gas, *Phys. Rev.* 137, A1441 (1965).
[S2] S. Boeck, C. Freysoldt, A. Dick, L. Ismer, and J. Neugebauer, The object-oriented DFT program library S/PHI/nX, *Comput. Phys. Commun.* 182, 543 (2011).
[S3] D. C. Wallace, *Thermodynamics of Crystals* (Dover Publications, New York, 1998).
[S4] M. T. Dove, *Introduction to Lattice Dynamics* (Cambridge University Press, Cambridge, 1993).
[S5] M. Mayo and A. J. Morris, Structure prediction of Li–Sn and Li–Sb intermetallics for lithium-ion batteries anodes, *Chem. Mater.* 29, 5787 (2017); M. Mayo, J. P. Darby, M. L. Evans, J. R. Nelson, and A. J. Morris, Correction to structure prediction of Li–Sn and Li–Sb intermetallics for lithium-ion batteries anodes, *Chem. Mater.* 30, 5516 (2018).
[S6] R. Sen and P. Johari, Understanding the lithiation of the Sn anode for high-performance Li-ion batteries with exploration of novel Li–Sn compounds at ambient and moderately high pressure, *ACS Mater. Inter.* 9, 40197 (2017).
[S7] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *J. Comput. Phys.* 117, 1 (1995).