Comment on “Structure Prediction of Li—Sn and Li—Sb Intermetallics for Lithium-Ion Batteries Anodes”

Raja Sen and Priya Johari

Department of Physics, School of Natural Sciences, Shiv Nadar University, Greater Noida, Gautam Buddha Nagar, UP 201 314, India.

E-mail: priya.johari@snu.edu.in, psony11@gmail.com
In a recently published article Mayo et al.\textsuperscript{1} presented the ground state crystal structures of various experimentally unknown Li-Sn intermetallic compounds at ambient pressure (~0 GPa) and 0 K temperature using ab-initio random structure searching method (AIRSS) with high-throughput screening from the Inorganic Crystal Structure Database (ICSD).\textsuperscript{2} In their study,\textsuperscript{1} besides the experimentally known phases of Li-Sn such as, Li\textsubscript{2}Sn\textsubscript{5} (P4/mmb), Li\textsubscript{7}Sn\textsubscript{3} (P2\textsubscript{1}/m), Li\textsubscript{5}Sn\textsubscript{2} (R\textbar3m), Li\textsubscript{13}Sn\textsubscript{5} (P\bar{3}1m), Li\textsubscript{17}Sn\textsubscript{4} (F\bar{4}3m), and Li\textsubscript{7}Sn\textsubscript{2} (Cmmm),\textsuperscript{3-13} Mayo et al. also reported two previously unknown stable phases for Li-Sn such as, Li\textsubscript{8}Sn\textsubscript{3}-R\bar{3}m and Li\textsubscript{7}Sn\textsubscript{2}-P\bar{1} along with several Li-Sn metastable phases (Li\textsubscript{1}Sn\textsubscript{1}, Li\textsubscript{2}Sn\textsubscript{3}, Li\textsubscript{7}Sn\textsubscript{9}, Li\textsubscript{3}Sn\textsubscript{2}, Li\textsubscript{5}Sn\textsubscript{3}, Li\textsubscript{2}Sn\textsubscript{1}, Li\textsubscript{3}Sn\textsubscript{1}, Li\textsubscript{4}Sn\textsubscript{1}, Li\textsubscript{5}Sn\textsubscript{1}, and Li\textsubscript{7}Sn\textsubscript{1}) which lie within 20 meV/atom from the convex hull tie-line. However, while going through their article, we noticed a significant inconsistency and contradictions in their results. Moreover, a one-to-one comparison with our published results\textsuperscript{14} revealed a disagreement in the symmetry of Li\textsubscript{3}Sn\textsubscript{1}, Li\textsubscript{7}Sn\textsubscript{2}, Li\textsubscript{4}Sn\textsubscript{1}, Li\textsubscript{5}Sn\textsubscript{1}, and Li\textsubscript{7}Sn\textsubscript{1} discussed by Mayo et al.\textsuperscript{1}

Predicting the lowest energy ground state structures is always an important task, as that is what determines the properties of any material and specifically, in the context of Li-ion batteries this is particularly crucial, since the open circuit voltage, Li-diffusivity, and swelling upon lithiation, etc., depend critically on the crystal structure and its respective ground state energy. We, therefore, re-calculated the formation energy of the reported phases (given as CIF files in the “Supporting Information” by Mayo et al.\textsuperscript{1}) and our predicted phases, by considering higher and strict convergence criteria (see the “Methodology and Computational Details in SI”) and compared the results on an equal footing by calculating the formation enthalpy of each Li-Sn compound. Interestingly, current calculations reveal that Mayo et al.\textsuperscript{1} not only predicted completely wrong structures in few cases (much higher in energy than what we found, in some cases a difference of more than 100 meV/atom), but for many other cases it is not just that they published a wrong symmetry for the right structure but the structures themselves are often wrong, which can mislead the scientific community.
Figure 1: Convex hull for the Li-Sn system at ambient pressure (~ 0 GPa) and 0 K temperature. For $Li_7Sn_9$ ($x = 0.4375$), $Li_5Sn_3$ ($x = 0.625$), $Li_3Sn_1$ ($x = 0.75$) and $Li_5Sn_1$ ($x = 0.833$), current calculations predict the correct ground state structures and phase, whose formation enthalpies are lower than the respective phase of the compounds reported by Mayo et al.\textsuperscript{1} Here, red colored stars represent the compounds for which wrong CIF files are provided by Mayo et al.\textsuperscript{1} in their “Supporting Information”, while the points enclosed by rectangular box represent the stoichiometries ($Li_3Sn_2$ and $Li_7Sn_1$) for which our calculations have predicted different phase with comparable formation energy with respect to the phase of the respective compound, reported by Mayo et al.\textsuperscript{1}

Through this comment, we therefore not only highlight several disparities in reporting the correct crystal structure and describing the proper symmetry of several Li-Sn compounds by Mayo et al.\textsuperscript{1} but, also present the correct ground state structures of Li-Sn compounds at ambient pressure (~ 0 GPa) and 0 K temperature, which are extremely important to know, in order to establish an in-depth understanding of the charge-discharge process in Li-Sn batteries.
LOWEST ENERGY Li-Sn STRUCTURES

In search of accurate ground state structures of the stable and metastable Li-Sn compounds at ambient pressure and 0 K temperature, current calculations following strict convergence criterion reveal few new phases whose formation enthalpies are either comparable or lower than the respective phase of the compounds reported by Mayo et al.\textsuperscript{1} Also, on comparing our results with those of Mayo et al.,\textsuperscript{1} it has been noticed that in most of the cases, either they have wrongly identified the ground state structure (symmetry) or there have been involved contradictions in presenting the proper space group and corresponding crystal structure of the compounds in their article (Figure \textsuperscript{1} and Table \textsuperscript{1}). In order to present a concise comparison and inconsistencies within the results reported by Mayo et al.,\textsuperscript{1} we have tabulated the description of crystal symmetry of stable and metastable Li-Sn compounds in Table \textsuperscript{1}. The table displays the crystal symmetry reported by Mayo et al. in the “ABSTRACT”, “Table 1”, “RESULTS”, and “Supporting Information” of their article\textsuperscript{1}, together with the symmetry and their respective fitness (vertical distance from the convex hull tie line) obtained by present calculations for each composition. The contradicting results (within their paper and with respect to current work using better convergence criteria) are highlighted in red colored fonts in Table \textsuperscript{1}. The CIF files corresponding to the newly predicted structures from current work have also been supplied in the Supporting Information of this comment, while correction for the symmetry and structure of contradicting Li-Sn compounds (marked in red in Table \textsuperscript{1}) are given next.

Mayo et al. have described the symmetry of Li\textsubscript{2}Sn\textsubscript{3} to be triclinic with space group P\textbar{} everywhere in the article. But, in the “Supporting Information”, they have provided the CIF file for P4/mmm phase. Thus, the structural information described in the manuscript mislead the exact crystallographic symmetry. Present calculations, however, predict the correct ground state structure of Li\textsubscript{2}Sn\textsubscript{3} to be P4/mmm, which is shown in Figure \textsuperscript{2} (b). The atomic arrangement of Li\textsubscript{2}Sn\textsubscript{3} - P4/mmm is very similar to Li\textsubscript{1}Sn\textsubscript{2} -P4/mmm. The only difference is, instead of double layers of four-membered rings of Sn, single layers of four-
Table 1: A one-to-one comparison between the results presented by Mayo et al.\cite{Mayo} and this work (in which calculations are performed with higher convergence criterion). This table also highlights the inconsistency (in red fonts) in presenting the correct ground state symmetry and incorrect prediction of structures of several Li-Sn compounds, in the recent work of Mayo et al.\cite{Mayo} at ambient pressure and 0 K temperature.

| Stoichiometry | Results of Mayo et al.\cite{Mayo} | Results of this work |
|---------------|----------------------------------|----------------------|
|               | Crystal symmetry described for ambient pressure in | Crystal symmetry described for ambient pressure |
|               | ABSTRACT | Table 1 #/# | RESULTS & DISCUSSION | Supporting Information | for ambient pressure |
| Sn            | -        | I4₁/amd (0) | -                    | -                      | I4₁/amd (0) |
| Li₂Sn₅*      | -        | P4/nbm (0)  | -                    | -                      | P4/nbm(0)  |
| Li₁Sn₂       | P4/mmm   | P4/mmm (8)  | P4/mmm              | P4/mmm (10)            |
| Li₂Sn₃       | P1       | P1 (6)      | P1                  | P4/mmm (10)            |
| Li₇Sn₉       | P4/n    | P4/n (19)   | P4/n                | C222 (7)               |
| Li₄Sn₄*      | -        | P2/m (0)    | -                    | -                      | P2/m (0)   |
| Li₃Sn₂       | P2/m    | P2/m (12)   | P2/m                | P2/m (7)               |
| Li₅Sn₅*      | Cmcm    | Cmcm (1)    | Cmcm                | Cmcm (1)               |
| Li₂Sn₁       | Cmcm    | Cmcm (1)    | Cmcm                | Cmcm (1)               |
| Li₇Sn₃       | -        | P2/m (2)    | -                    | -                      | P2/m (1)   |
| Li₅Sn₂       | -        | R₃m (2)     | -                    | -                      | R₃m (2)    |
| Li₃Sn₄*      | -        | P3m1 (0)    | -                    | -                      | P3m1 (0)   |
| Li₈Sn₃*      | R₃m     | R₃m (0)     | R₃m                 | R₃m (0)                |
| Li₄Sn₁       | P3₂     | P3₂ (6)     | (Not discussed)      | P3m1                   |
| Li₇Sn₂       | P1      | P1 (0)      | P1                  | P3m1 #                 |
| Li₁₃Sn₄       | P1      | P1 (0)      | P1                  | P3m1 #                 |
| Li₄Sn₃       | P2₁     | P2₁ (13)    | Not discussed        | R₃m                    |
| Li₁₇Sn₄*     | -        | F₃m (0)     | -                    | R₃m (13)               |
| Li₁₂Sn₅      | -        | F₃m (11)    | -                    | F₃m (10)               |
| Li₅Sn₁       | P6/mmm  | P6/mmm (19) | Not discussed        | P6/mmm (10)            |
| Li₇Sn₁       | C2      | Fmrm (18)   | Not discussed        | P6/mmm (11)            |
| Li₇Sn₁       | C2      | Fmrm (18)   | Not discussed        | Fmrm (11)              |
| Li            | -        | Im₃m (0)    | -                    | Im₃m (0)               |

\* The stable compounds of Li-Sn at ambient pressure (~ 0 GPa) and 0 K temperature are represented by a star (*).

#* Provided format of CIF file is wrong.

### Fitness of Li-Sn compounds (vertical distance from the convex hull tie line) given in Table 1 in the results Mayo et al.\cite{Mayo} are put in parentheses.
Figure 2: Lowest energy structures of meta-stable Li-Sn compounds: (a) Li$_7$Sn$_2$ (P$_3$m$_1$), (b) Li$_2$Sn$_3$ (P4/mmm), (c) Li$_7$Sn$_9$ (P2/m), (d) Li$_3$Sn$_2$ (Cmcm), (e) Li$_5$Sn$_3$ (R32), and (f) Li$_5$Sn$_3$ (Fmm2). The formation energy of Li$_3$Sn$_2$ (Cmcm) is found comparable with the phase Li$_3$Sn$_2$ (P2$_1$/m), as reported by Mayo et al. $^1$ In case Li$_5$Sn$_3$, current calculations have found two polymorphs (R32 and Fmm2) with same formation energy at ambient pressure (~0GPa) and 0 K temperature. In the figure, green and purple spheres denote the Li and Sn atoms, respectively.

membered rings of Sn can also be found in the Li$_2$Sn$_3$ - P4/mmm structure in an alternative sequence, as shown in Figure 2 (b). The absence of imaginary phonon frequency in the whole Brillouin zone as shown in Figure S1 (a) in SI represents the dynamical stability of Li$_2$Sn$_3$ - P4/mmm at ambient pressure condition.

In their article, Mayo et al. have described Li$_7$Sn$_9$ to exhibit P4$_2$/n symmetry, with ground state formation enthalpy lying about 19 meV/atom above the convex hull tie-line. However, in the CIF file they have provided the structure for C222 symmetry. On the contrary, current calculations discovered a new structure having symmetry P2/m. This structure
has been found to be energetically much stable than C222 phase (with 159 meV/atom difference in formation energy). Additionally, this structure has been found just 7 meV/atom above the convex hull tie line (Figure 1). In this structure, 1D infinite atomic chains of pure Li and Sn, can be found to run along [010] direction (Figure 2 (c)). Phonon dispersion curve (See Figure S1 (b) in SI) represents Li\textsubscript{7}Sn\textsubscript{9} - P2/m is also dynamically stable.

In case of Li\textsubscript{3}Sn\textsubscript{2}, P\textsubscript{2}\textsubscript{1}/m symmetry is predicted by Mayo et al. While, our calculations predict the ground state structure of Li\textsubscript{3}Sn\textsubscript{2} to exhibit Cmcm phase. It is found that in a tight relaxation of Hellmann-Feynman forces, P\textsubscript{2}\textsubscript{1}/m symmetry transforms into Cmcm symmetry. In Li\textsubscript{3}Sn\textsubscript{2}-Cmcm structure, Li atoms can be seen to intercalate between 1D zigzag chains and 2D buckled layer of Sn ions (Figure 2 (d)). Absence of imaginary frequency in phonon dispersion curve revels the dynamical stability of Li\textsubscript{3}Sn\textsubscript{2}-Cmcm phase, shown in Figure S1 (c) in SI.

The described symmetry of Li\textsubscript{5}Sn\textsubscript{3} highly misleads the actual crystallographic informations of the structure. In the “ABSTRACT” and “Table 1” of their article, Mayo et al. have described the symmetry to be Im\textsubscript{3}m, while in “RESULTS” section, they discussed the P\textsubscript{4}3\textsubscript{m} symmetry of Li\textsubscript{5}Sn\textsubscript{3}, and have provided its CIF file. Interestingly, on relaxing the Li\textsubscript{5}Sn\textsubscript{3}-P\textsubscript{4}3\textsubscript{m} structure provided by Mayo et al., it has been found energetically unstable (Figure 1). On the other hand, current calculations predict a new phase having space group R32 within the rhombohedral symmetry. The formation enthalpy of this phase is found to be lower than both, Im\textsubscript{3}m and P\textsubscript{4}3\textsubscript{m} phase of Li\textsubscript{5}Sn\textsubscript{3} (Table 1). Other than this, one more polymorph of Li\textsubscript{5}Sn\textsubscript{3} having symmetry Fmm\textsubscript{2} is found, whose formation enthalpy is as comparable as R32 phase of Li\textsubscript{5}Sn\textsubscript{3}. In R32 phase, two different type of 1D atomic chains, one with pure Li another having an alternative sequence of Li and Sn atoms, can be seen to run along c-axis (shown in Figure 2 (e)). While, the crystal structure of Fmm\textsubscript{2} is very much unusual, where bent trimers of pure Sn stacked one after another along crystallographic a-axis, are surrounded by Li atoms (Figure 2 (f)). The phonon dispersion curves of both of these newly predicted phases (R32 and Fmm\textsubscript{2}) are provided in SI (Figure S1 (d) & (e)). It should also
be noted here that few years back, Courtney et al. revealed through experimental study that all known phases of Li-Sn do not always form in the electrochemical cell of Sn anode, operating at room temperature. Their investigation indicates that for $x > 2.5$ in $\text{Li}_x\text{Sn}$, one of the unknown phases of Li-Sn adopts cubic like structure. In predicting new stable and metastable Li-Sn compounds, Mayo et al. therefore suggest that this cubic like arrangement may arise due the formation of $\text{Li}_5\text{Sn}_3$, as they have showed that the ground state structure of $\text{Li}_5\text{Sn}_3$ would be $\text{Im}\overline{3}m$. But, in this comment, it has been showed that the ground state structure of $\text{Li}_5\text{Sn}_3$ is rhombohedral and not cubic. Moreover, in our recent work, we have showed that at ambient pressure and room temperature, $\text{Li}_3\text{Sn}_1$ forms a cubic phase ($\text{P2/m } ^{311K}\text{Fm}\overline{3}m$), which is also consistent with results of Thackeray et al. Therefore, it may be concluded in this comment that the formation of cubic like arrangements in electrochemical cell may appears due to the formation of $\text{Li}_3\text{Sn}_1$-$\text{Fm}\overline{3}m$ phase, where Li atoms form a bcc-like sub-lattice.

For $\text{Li}_3\text{Sn}_1$, we again notice a huge inconsistency in the results. Mayo et al. described the symmetry to be $\text{P3}_2$ in the “RESULTS” section and Table 1 of their manuscript, while provided the structure for $\text{P3m1}$ symmetry in the “Supporting Information” and haven’t discussed its structure at all. This structure, however, on relaxation is found unstable. In contrast, our search predicts $\text{P2/m}$ symmetry for $\text{Li}_3\text{Sn}_1$ to be much more energetically stable than $\text{P3m1}$ phase. The $\text{Li}_3\text{Sn}_1$-$\text{P2/m}$ structure is found to lie just 7 meV/atom above our convex hull tie line (Figure 1 and Table 1). The structure of $\text{Li}_3\text{Sn}_1$-$\text{P2/m}$ has been described in our recent work. A one-to-one comparison with $\text{Li}_3\text{Sn}_1$-$\text{P3}_2$ could not be made on the basis of formation enthalpy because of unavailability of its crystal structure. However, we are confident that the lowest energy structure will correspond only to the $\text{Li}_3\text{Sn}_1$-$\text{P2/m}$ symmetry,

In case of $\text{Li}_7\text{Sn}_2$, experimentally known phase is $\text{Cmmm}$, while we found $\text{P3m1}$ phase (Figure 2 (a)) to be more stable than $\text{Cmmm}$. Though the difference in the enthalpy for both phases is just 6 meV/atom, which is also in agreement with results of Geneser et
The structure is also shown to be dynamically stable in our recent article. On the contrary, Mayo et al. predicted Li$_7$Sn$_2$ to be stable under PT symmetry, which they also claim to be 6 meV/atom lower in formation energy than the experimentally reported Cmmm phase. However, it has been noticed that the format of the CIF file is completely wrong (it is in “SHELX” format). On analyzing the given format, it is found that the structure given in their CIF file is actually representing the P$\overline{3}$m1 phase. Therefore, the discussion about Li$_7$Sn$_2$ in the Ref. [1] remains irrelevant, as it is providing a misleading crystallographic information.

In case of Li$_4$Sn$_1$, Mayo et al. have mentioned the P2$_1$ symmetry in the Abstract and Table1 but provided the CIF file for the R3m phase, which is the lowest energy structure. Thus, their paper provide a wrong and contradicting information about the symmetry in the text.

The information provided for Li$_5$Sn$_1$, is again highly contradictory. In “Abstract” Mayo et al. have described the symmetry to be P6/mmm (19 meV/atom above the convex hull tie line) and have provided its CIF file as well. However, in “Table 1” of their article they presented the structure symmetry to be Pmna. In contrast, we found the symmetry of structures to be C2/m, which is found 11 meV/atom above from the convex-hull tie line. This clearly indicates C2/m phase to be energetically favorable, as compared to P6/mmm phase.

In case of Li$_7$Sn$_1$, Mayo et al. described the symmetry to be C2, while in “Table 1”, as well as in the CIF file, they represented the Fmmm phase for this compound. On the other hand, our calculation predicted C2/m phase for Li$_7$Sn$_1$. The formation enthalpy of our predicted structure (C2/m) is found to be as comparable as the Fmmm structure, reported by Mayo et al. The C2/m phase is also shown to be dynamically stable in our recent study.

It is also noteworthy to mention here that Mayo et al. described Li$_{15}$Sn$_4$ as a known phase in the Li-Sn binary phase diagram. But, to the best of our knowledge, we did not find any such compound for Li-Sn from our calculations. The same has not even be available in
the ICSD database, as well. However, in cross verification of the reference \( \text{Li}_{15}\text{Sn}_4 \)\(^{[5]} \) given by Mayo et al., it has been observed that the reference is actually describing the structure of \( \text{Na}_{15}\text{Sn}_4 \), rather than \( \text{Li}_{15}\text{Sn}_4 \).

**Conclusions**

In summary, crystal structure and symmetry of several Li-Sn compounds reported by Mayo et al.\(^{[1]} \) are not only contradicting within the article (e.g., \( \text{Li}_2\text{Sn}_3 \), \( \text{Li}_7\text{Sn}_9 \), \( \text{Li}_5\text{Sn}_3 \), \( \text{Li}_3\text{Sn}_1 \), \( \text{Li}_7\text{Sn}_2 \), \( \text{Li}_4\text{Sn}_1 \), \( \text{Li}_5\text{Sn}_1 \), and \( \text{Li}_7\text{Sn}_1 \)) but in many cases (e.g., \( \text{Li}_7\text{Sn}_9 \), \( \text{Li}_5\text{Sn}_3 \), \( \text{Li}_3\text{Sn}_1 \) and \( \text{Li}_5\text{Sn}_1 \)) they are wrong as well. Thus, their claim of understanding the lithiation mechanism in Sn anode is incorrect and the conclusions are questionable. We hope that this comment will be helpful for the community to identify the correct ground state structure and phase of various Li-Sn compounds that may appear during lithiation-delithiation of Sn anode.

**Acknowledgement**

P. J. acknowledges the support provided by Grant No. SR/FTP/PS-052/2012 from Department of Science and Technology (DST), Government of India. R.S. wants to thank Mr. Dwaipayan Chakroborty for critical reading of the manuscript. The high performance computing facility and workstations available at the School of Natural Sciences, Shiv Nadar University, were used to perform all calculations.

**Supporting Information Available**

The following files are available free of charge. Methodology and Computational Details, Phonon dispersion curves of Li-Sn compounds (pdf), CIF files of newly predicted structures (ZIP)
References

(1) Mayo, M.; Morris, A. J. Chem. Mater. 2017, 9, 16071–16080.

(2) Pickard, C. J.; Needs, R. J. J. Phys.: Condens. Matter 2011, 23, 053201.

(3) Robert, F.; Lippens, P.; Olivier-Fourcade, J.; Jumas, J.-C.; Gillot, F.; Morcrette, M.; Tarascon, J.-M. J. Solid State Chem. 2007, 180, 339–348.

(4) Dunlap, R.; Small, D.; MacNeil, D.; Obrovac, M.; Dahn, J. J. Alloys Compd. 1999, 289, 135–142.

(5) Hansen, D.; Chang, L. J. Acta Cryst. 1969, B25, 2392–2395.

(6) Müller, W.; Schäfer, H. Z. Naturforsch. 1973, 28b, 246–248.

(7) Blase, W.; Cordier, G. Zeitschrift für Kristallographie 1990, 193, 317–318.

(8) Müller, W. Z. Naturforsch. 1974, 29b, 304–307.

(9) Frank, U.; Müller, W.; Schäfer, H. Z. Naturforsch. 1975, 30b, 1–5.

(10) Frank, U.; Müller, W. Z. Naturforsch. 1975, 30b, 316–322.

(11) Frank, U.; Müller, W.; Schäfer, H. Z. Naturforsch. 1975, 30b, 6–9.

(12) Goward, G.; Taylor, N.; Souza, D.; Nazar, L. J. Alloys Compd. 2001, 329, 82–91.

(13) Lupu, C.; Mao, J.-G.; Rabalais, J.; Guloy, A.; Richardson, J. J. Inorg. Chem. 2003, 42, 3765–3771.

(14) Sen, R.; Johari, P. ACS Appl. Mater. Interfaces 2017, 9, 40197–40206.

(15) Courtney, I. A.; Tse, J. S.; Mao, O.; Hafner, J.; Dahn, J. R. Phys. Rev. B 1998, 58, 15583–15588.
(16) Thackeray, M.; Vaughey, J.; Johnson, C.; Kropf, A.; Benedek, R.; Fransson, L.; Edstrom, K. *J. Power Sources* **2003**, *113*, 124–130.

(17) Genser, O.; Hafner, J. *Phys. Rev. B* **2001**, *63*, 144204.

(18) Zintl, E.; Harder, A. *Z. physik. Chem.* **1936**, *34*, 238–254.