Computational Study of $Li_{(2+x)}SnO_3$ and $Li_{(2+x)}SnS_3$*

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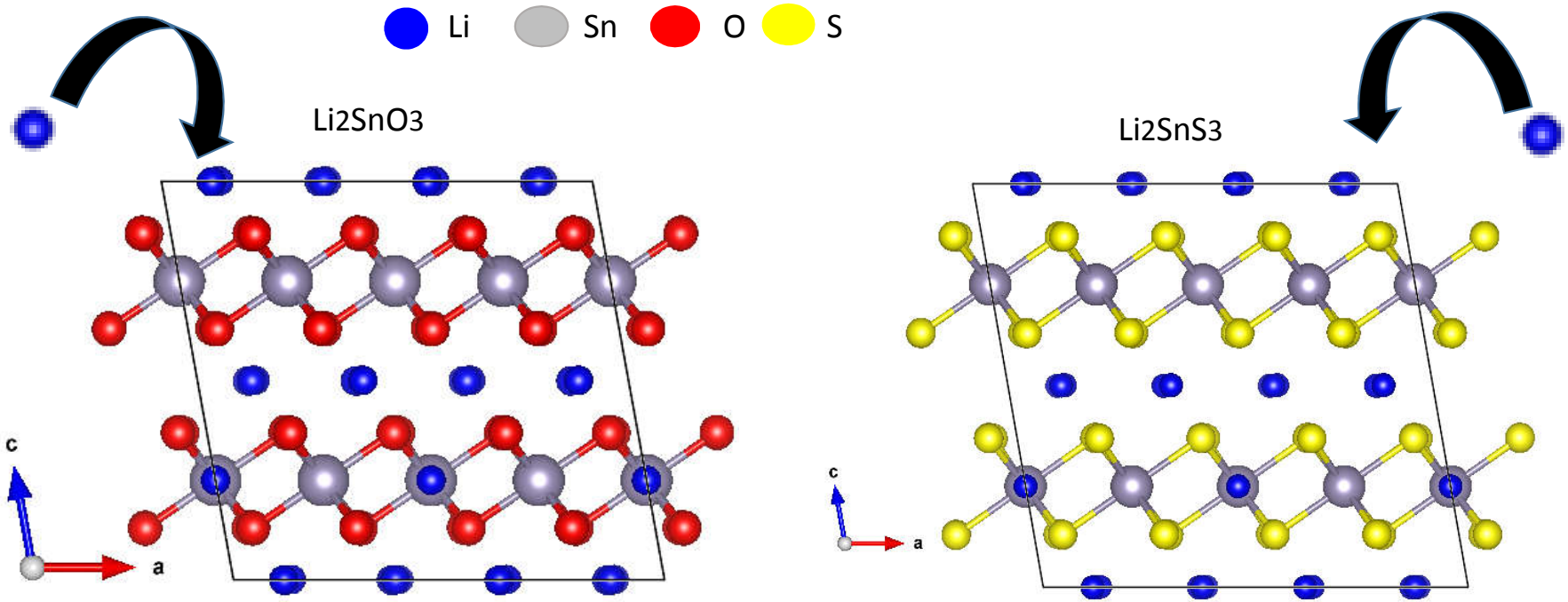


*Supported by NSF grants DMR-1105485 and 1507942 and WFU's Deac computer facility

Background of Li_2SnS_3 and Li_2SnO_3

- Close packed layered Space group 15 C2/c
- Li_2SnS_3 characterized as fast ionic conductor $\sim 10^{-3}\,\frac{S}{cm}$

  pure material insulating (Brant et al., CM **27**, 189 (2014))

- Li_2SnO_3 studied as electrode material under complex mechanism

  poor ionic conductor $\sim 10^{-8}\,\frac{S}{cm}$

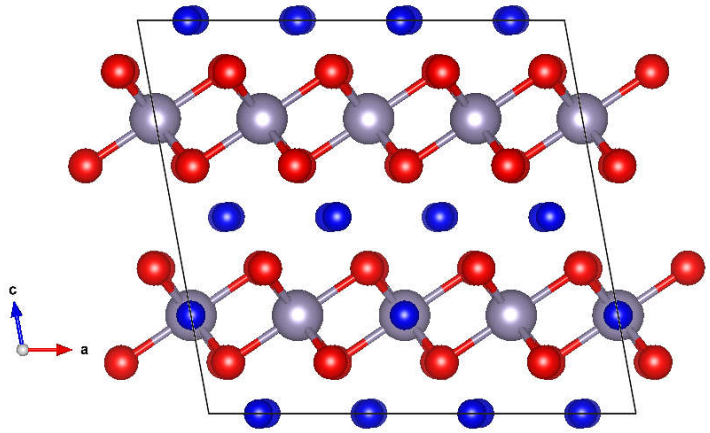
  pure material insulating

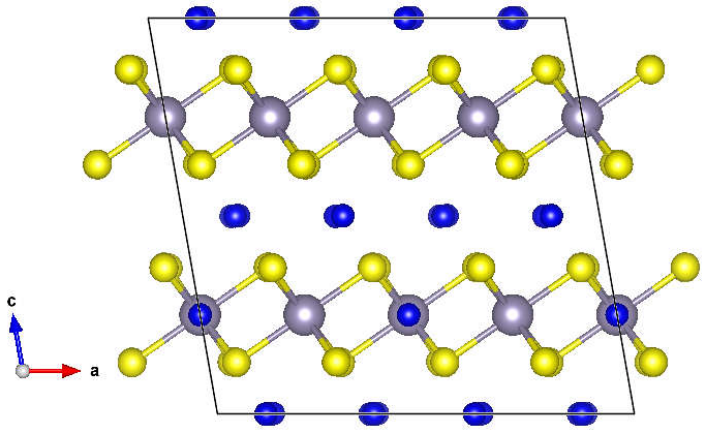
$$Li_2SnO_3 + 4Li \rightarrow 3Li_2O + Sn$$

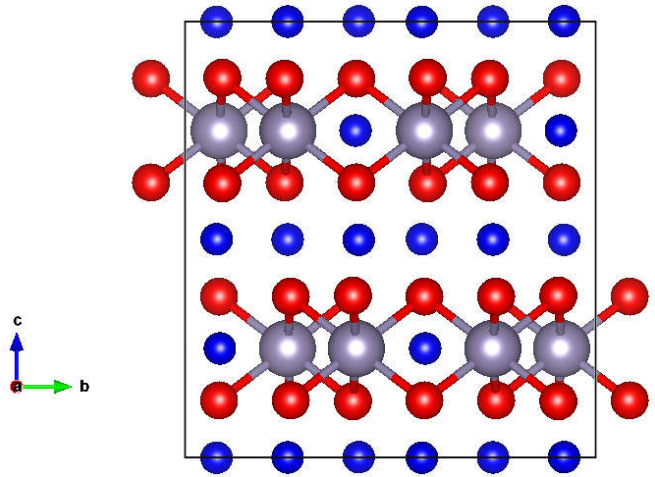
$$3 * Li_2O + Sn + 4.4Li \leftrightarrow 3Li_2O + Li_{4.4}Sn$$

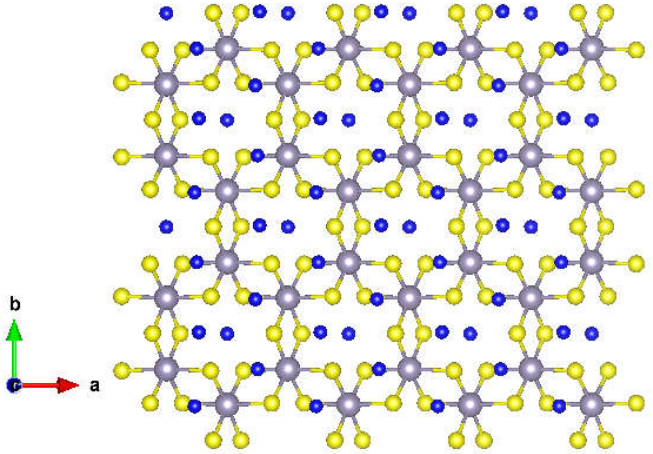
Courtney & Dahn, JES **144**, 2943 (1997)
Zhang et al., J. Alloy Compd. **415**, 229 (2006)
Wang et al., Surf. Interface Anal. **45**, 1297 (2013)
L.P.Teo, et al. Ionics 18:655-665 (2012)

Layered monoclinic structure









Motivation for modeling Lithiation process

- For Li_2SnO_3 wanted to understand the Lithiation process in context of experimental work

  What is the Lithiation process?

  When and how does the material start to decompose?

- For Li_2SnS_3 wanted to compare and contrast with Li_2SnO_3

  Can Li_2SnS_3 function as an electrode?

  Is the structure stable upon Li intercalation.

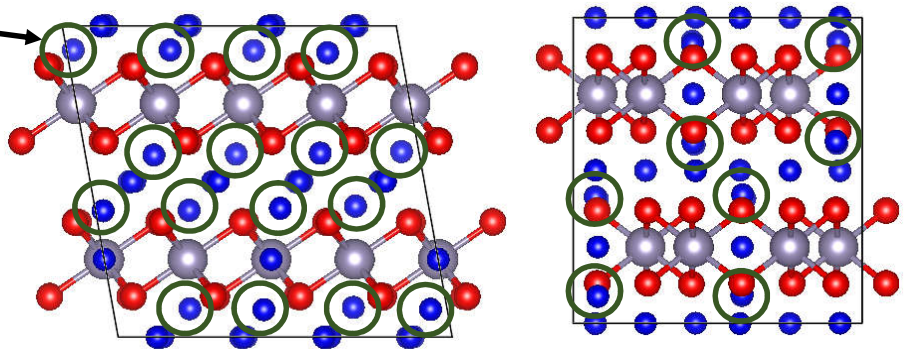
Computational methods

- Density functional theory with LDA
- PAW formalism using datasets generated with ***ATOMPAW*** code (Holzwarth et al. *CPC* **135**, 329 (2001)) http://pwpaw.wfu.edu
- Electronic structure calculations performed using ***QUANTUM ESPRESSO .*** (Giannozzi et al. *JPCM* **21,** 394402 (2009); http://www.quantum-espresso.org, Gonze et al., *CPC* **180***,* 2582 (2009)); http://www.abinit.org
- Plane wave expansion for wave functions with $|k+G|^2 \leq 64$ Ry
- Brillouin zone integration mesh of 0.003 $bohr^{-3}$
- Visualization software: ***Xcrysden, VESTA***
- Plotting **xmgrace, gnuplot**

Modeling the Lithiation process

- Where are the interstitials?

2X1X1 supercells



- The Lithiation model was of intercalation type, with Li-ions “migrating” onto a lattice of interstitial sites

- 8 equivalent interstitial sites found per 1X1X1 unit cell giving

$$Li_2Sn(O/S)_3 + x * Li \rightarrow Li_{(2+x)}Sn(O/S)_3 \quad \text{with} \quad 0 \leq x \leq 1$$

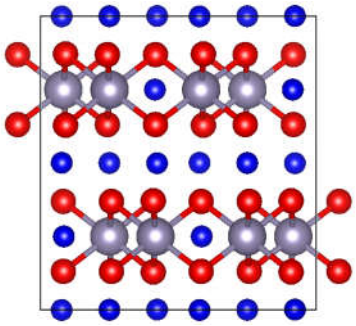
theoretical limits of intercalation

- Initially a random sampling of configurations done on 2X1X1 supercells

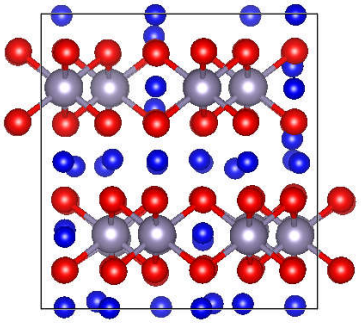
  results warranted more runs for Li_2SnO_3 at low concentration

Variable-Cell optimizations for $Li_{(2+x)}SnO_3$

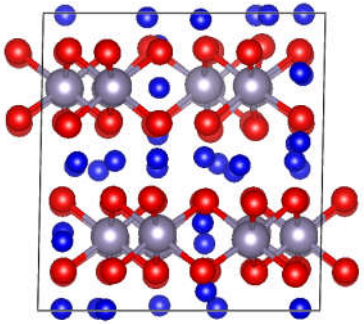
x=0



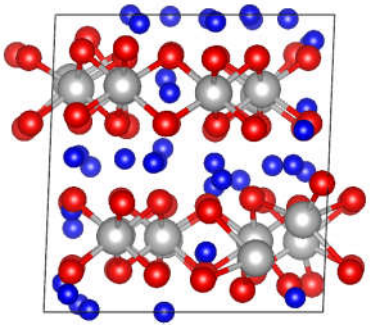
x = 0.125



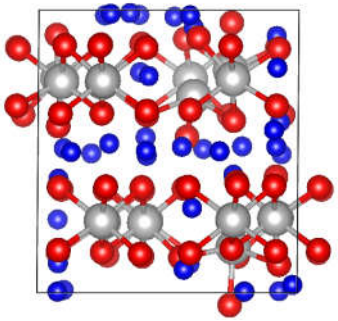
x = 0.25



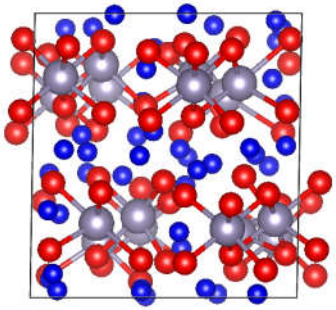
x = 0.375



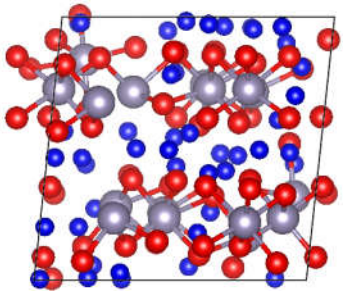
x = 0.5



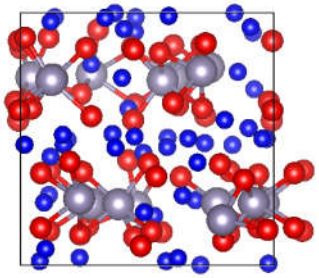
x = 0.75



x = 0.875



x=1

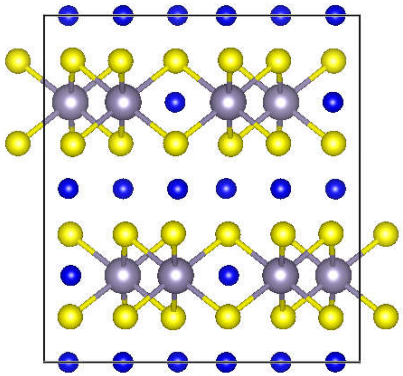


Experiment shows loss of diffraction peaks in range $0.75 \lesssim x \lesssim 5$

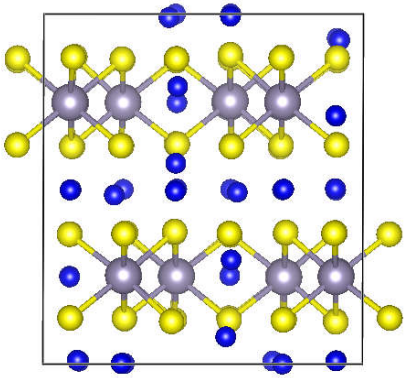
Zhang et al., J. Alloy Compd. **415**, 229 (2006)

Variable cell optimizations for $Li_{(2+x)}SnS_3$

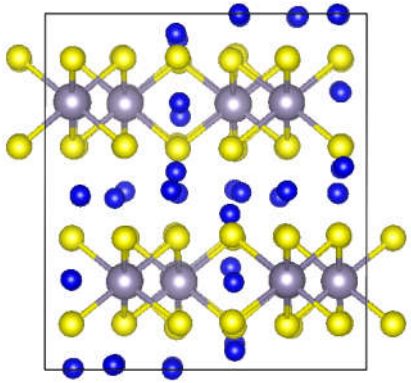
x = 0



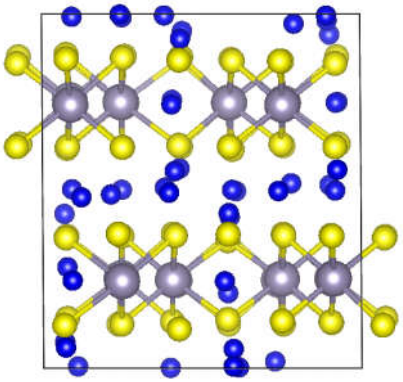
x = 0.25



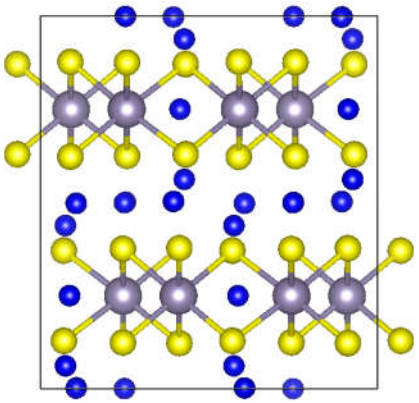
x=0.5



x = 0.75



x = 1



Voltage Calculation from $\Delta E_{reaction}$

- For intercalation processes Aydinol et al introduced
  (Aydinol et al, Phys. Rev B. vol 56 no. 3 1997)

$$V_{average} = \frac{-\Delta G}{x*Z} = -\frac{\Delta E_r - T\Delta S_r + P\Delta V_r}{x*Z} \approx \frac{-\Delta E_{reaction}}{x*Z}$$ with $Z = \frac{charges}{charge\ carrier} = 1$ for Li

as an approximation for the average open cell voltage over an intercalation range x

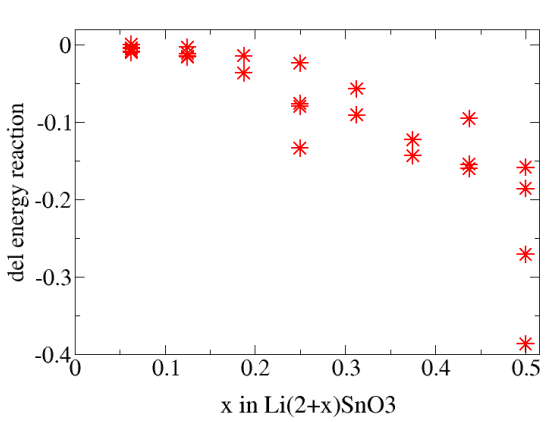
For $Li_{(2+x)}Sn(O/S)_3$

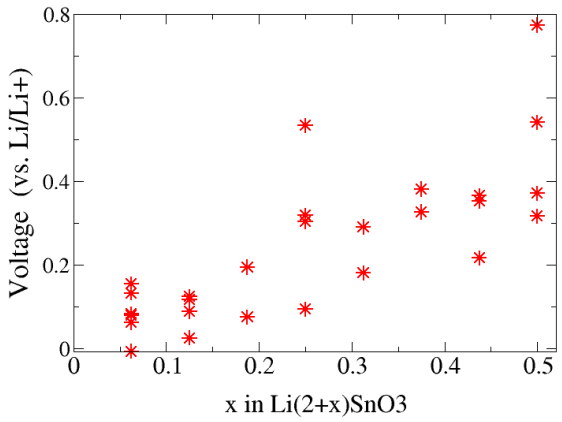
$$\Delta E_{reaction} = E\{Li_{(2+x)}Sn(O/S)_3\} - E\{Li_2Sn(O/S)_3\} - x * E\{bcc\ Li\}$$

$\Delta E_{reaction}\,(x)$

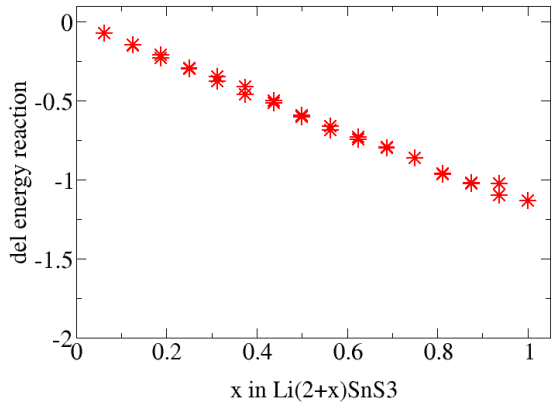
$V_{average}\,(x)$

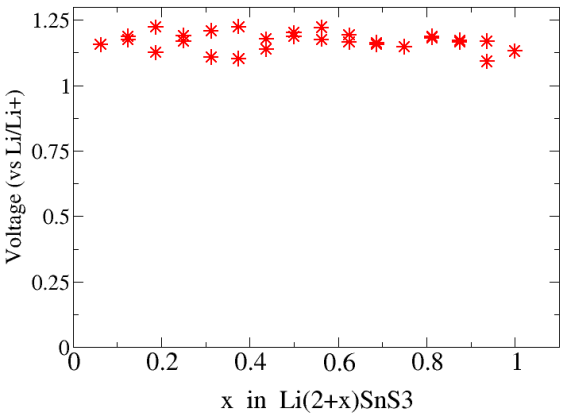
Li_2SnO_3





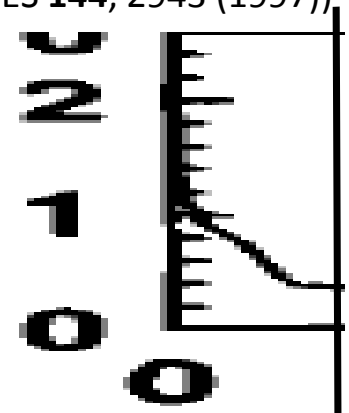
Li_2SnS_3



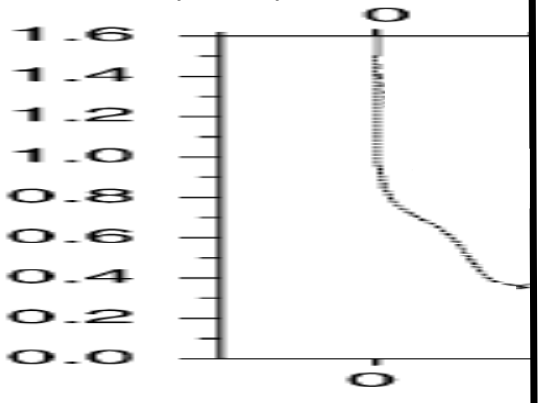


Comparison with experiment, Li_2SnO_3

(Courtney & Dahn, JES **144**, 2943 (1997))



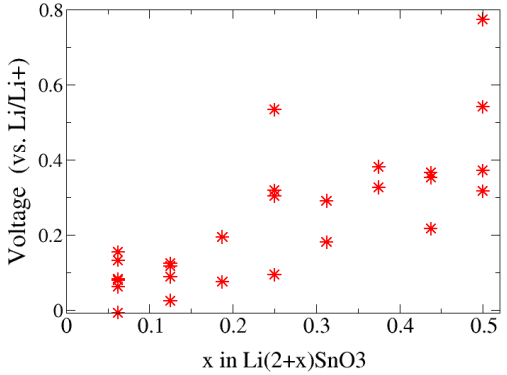
(Zhang et al., J. Alloy Compd. **415**, 229 (2006))



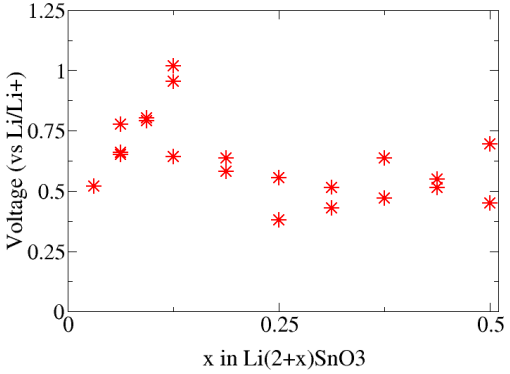
Voltage

$x \approx 0.5$

pristine material



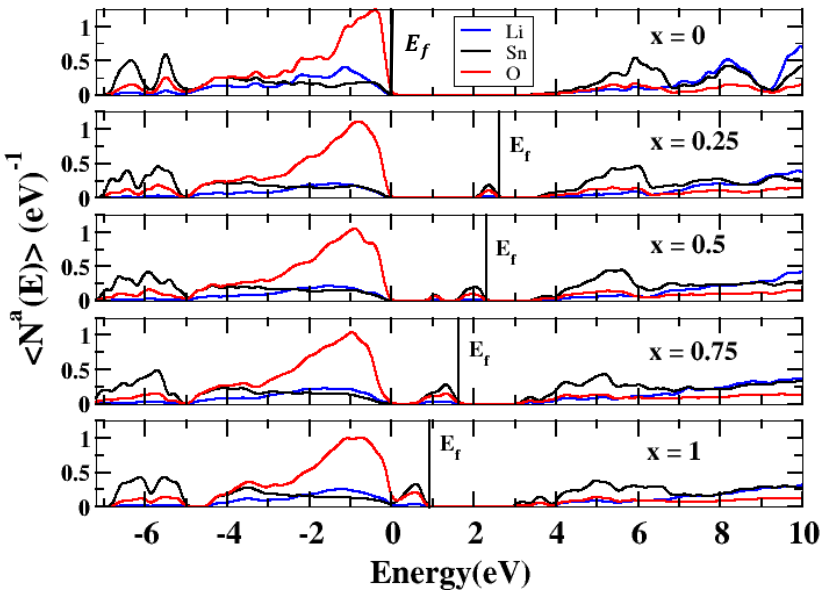
Sn/Li anti-site defect at concentration 0.0625 per formula unit



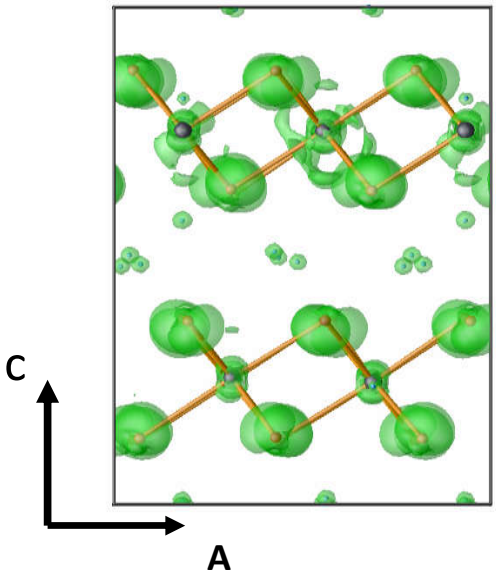
Sn/Li site sharing mentioned in

Tarakina et al.
Z. Kristallogr. Suppl. **30** (2009) 375-380

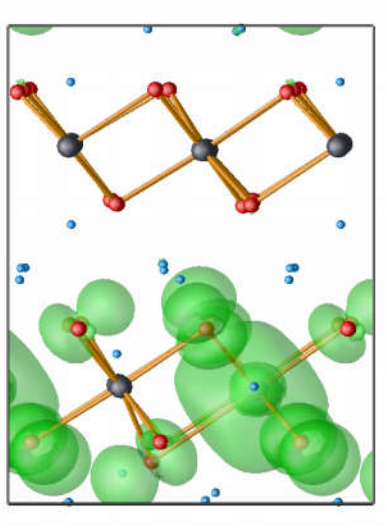
Density of States and charge density plots for $Li_{(2+x)}SnO_3$



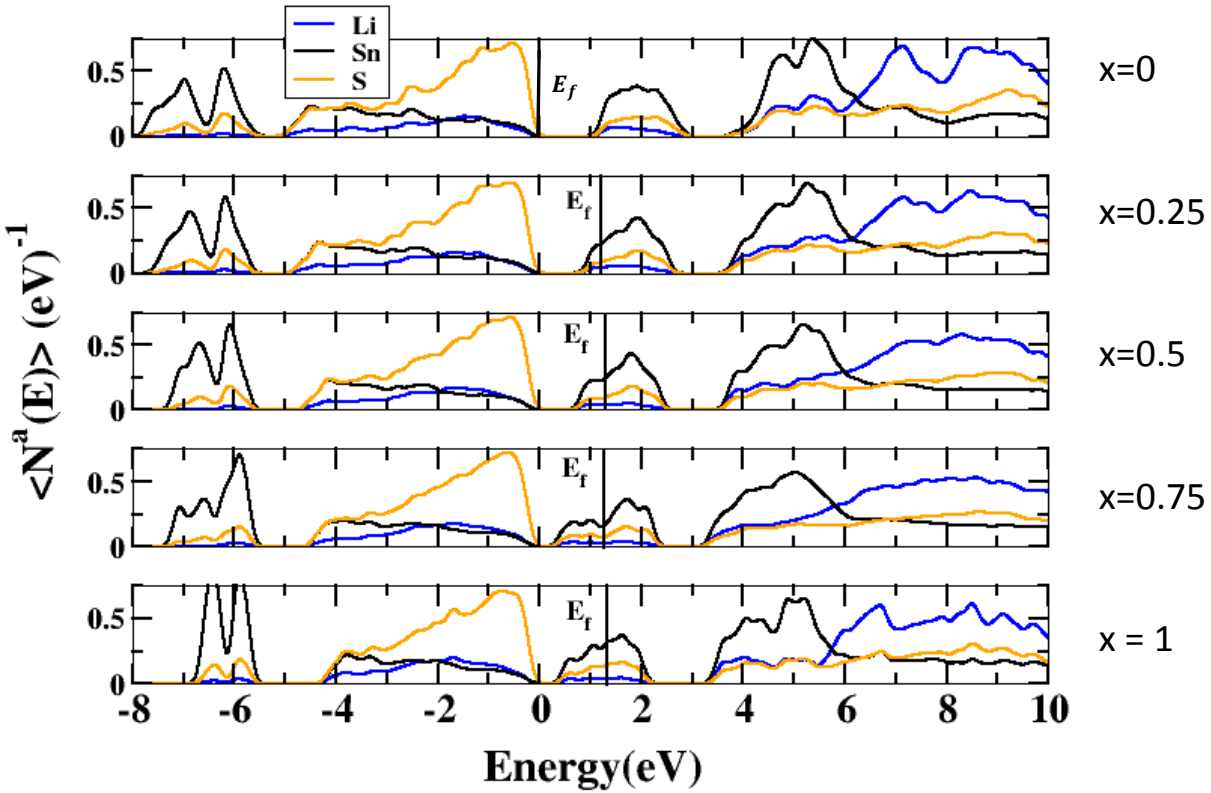
x= 0.125 iso level 0.007 $\frac{e}{Å^3}$



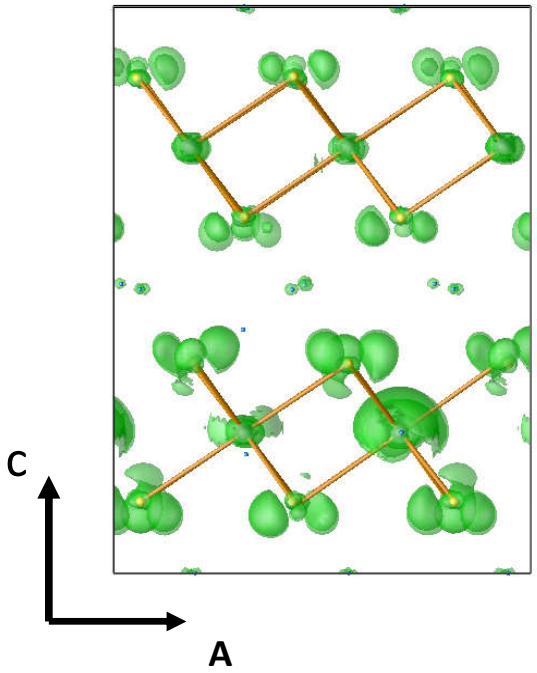
x = 0.25 iso level 0.015 $\frac{e}{Å^3}$



Density of States and charge density plot for $Li_{(2+x)}SnS_3$



x = 0.125 iso level 0.006 $\frac{e}{Å^3}$



Conclusions

- Simulations show $Li_{(2+x)}SnO_3$ qualitatively shows amorphous transition occurring in range consistent with experiment $x \gtrsim 0.75$
- Voltage profile for pristine $Li_{(2+x)}SnO_3$ is inconsistent with experiment, introducing an Li/Sn antisite defect better approximates experimental data
- $Li_{(2+x)}SnS_3$ is theoretically stable up to x = 1
- $Li_{(2+x)}SnS_3$ Density of States is consistent with properties of an electrode

References

- I.A.Courtney, et al. "*Electrochemical and Situ X-Ray Diffraction studies of Reaction of Lithium with Tin Oxide composites*". J. Electrochem. Soc, Vol. 144, No.6, June 1997

- J. A. Brant, et al. "*Fast Lihtium Ion Conduction in Li2SnS3 : Synthesis, Physicochemical Characterization, and Electronic Structure*". ACSJCa| JCA10.0.1465/W

- L.P.Teo, et al. "*Conductivity and dielectric studies of Li2SnO3*". Ionics (2012) 18:655-665

- D.W.Zhang, et al. "*Li2SnO3 derived secondary Li-Sn alloy electrode for lithium-ion batteries*" . Journal of Alloys and Compounds 415 (2006)229-233

- Q.Wang , et al. "*Preparation of Li2SnO3 and its application in lithium-ion batteries*". Surf. Interface Anal, 2013, 45, 1297-1303

- M.K. Aydinol, K. Cho, et al. "*Ab initio* study of lithium intercalation in metal oxides and metal dichalcogenides**".** Phys, Rev B. vol 56, no. 3 july 15 1997

- Tarakina et al. "*Investigation of stacking disorder in Li2SnO3*" Z. Kristallogr. Suppl. **30** (2009) 375-380

Interpretation in language of cluster expansion

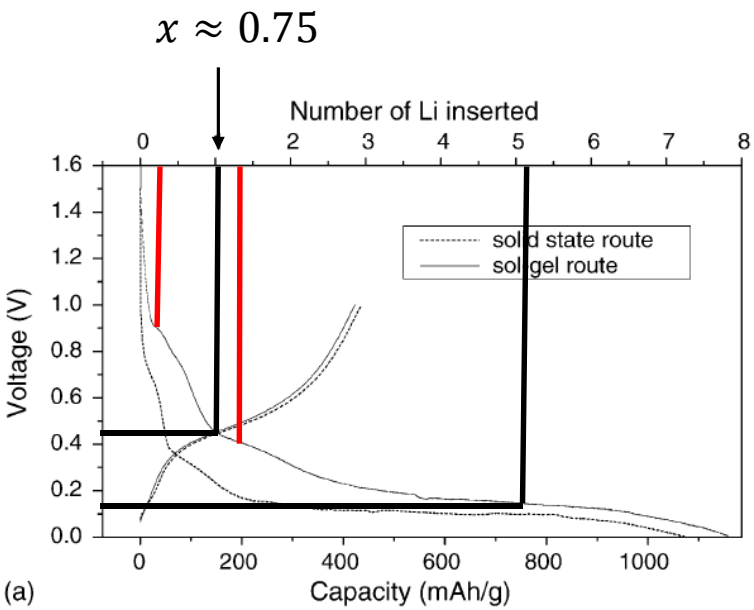
- A cluster expansion allows one to write the energy in terms of expansion occupation variables (Meng and Dompablo, Enrgy & Env. Sci. DOI: 10.1039/b901825e, 2009)

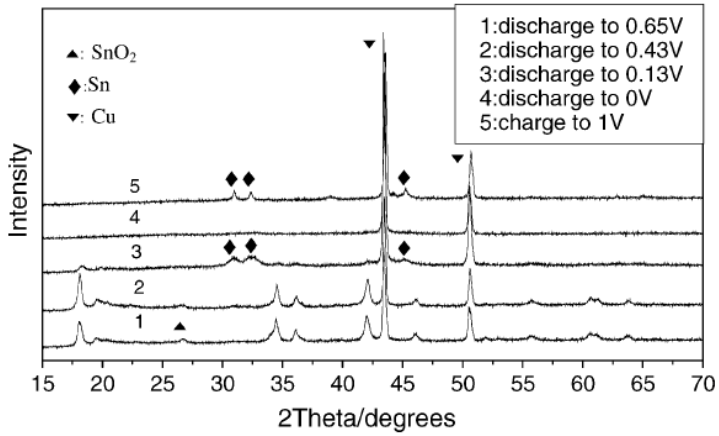
$$E = \quad Eo \; + \sum_{i} V_i * \sigma_i + \sum_{i,j} V_{i,j} * \sigma_i * \sigma_j + \sum_{i,j,k} V_{i,j,k} * \sigma_i * \sigma_j * \sigma_k + \; \ldots \ldots$$

- The V terms are effective cluster interactions, σ are the occupation variables

- Results for Li_2SnS_3 suggest the onsite interaction term is dominant and independent of concentration

- Results for Li_2SnO_3 suggest contributions from higher order terms and concentration dependence





At discharge to V = 0.43 diffraction peaks still present

This is $\approx x = 0.75 \;\; in \;\; Li_2SnO_3 \;\; + \;\; x * Li \;\; \rightarrow Li_{(2+x)}SnO_3$

At V = 0.13 diffraction peaks mostly gone