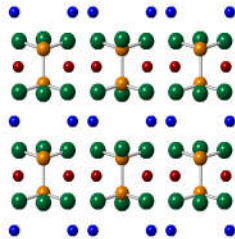


First principles investigation of the structural and electrochemical properties of $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Li}_4\text{P}_2\text{S}_6$

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Outline

I. Rationale

II. Methodology

III. Results

IV. Conclusions

Underlying Questions to Answer

I. What is the structure of $\text{Na}_4\text{P}_2\text{S}_6$ compared to $\text{Li}_4\text{P}_2\text{S}_6$?

II. Kuhn structure vs. Mercier structure

III. Is $\text{Na}_4\text{P}_2\text{S}_6$ a good solid electrolyte for Na-ion batteries?



First principles investigation of the structural and electrochemical properties of $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Li}_4\text{P}_2\text{S}_6$

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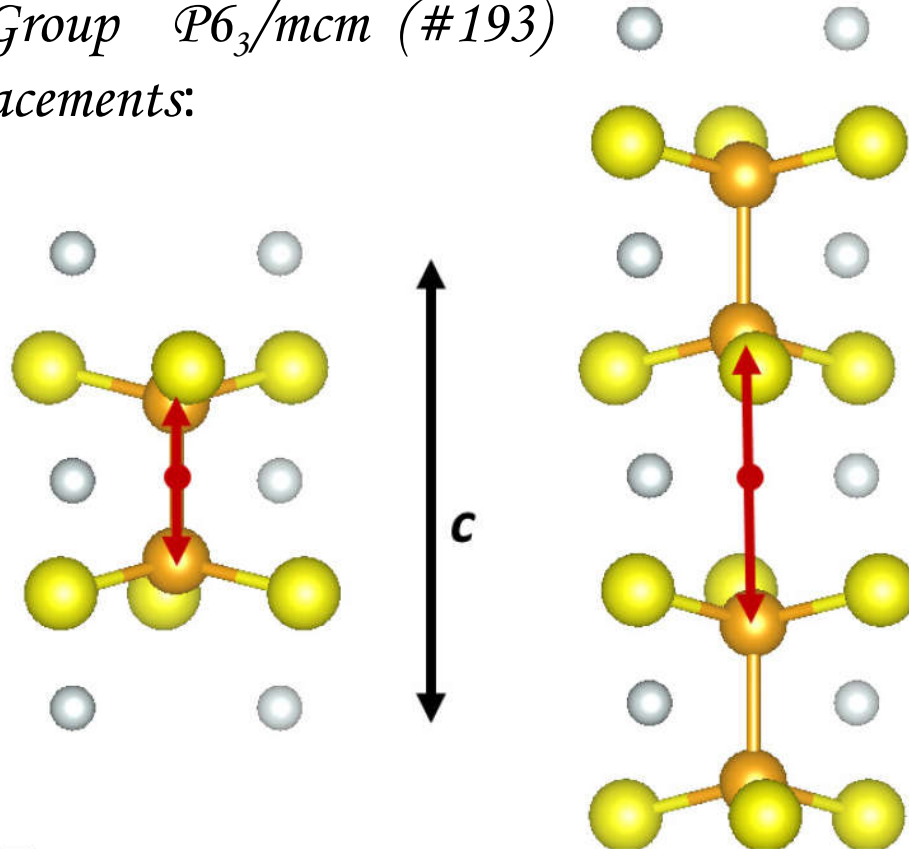
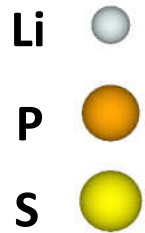
Rationale

- *Interest in Na-ion conductors (abundant, inexpensive, and air-stable)*
- *Stability of $\text{Li}_4\text{P}_2\text{S}_6$ compared to Li_3PS_4 (Solid State Ionics, Vol. 284(2016), pgs. 61-70)*
- *Mercier analyzed structure for $\text{Li}_4\text{P}_2\text{S}_6$ (Journal of Solid-State Chem., Vol.43(1982), pgs.151-162)*
- *Kuhn analyzed structure for $\text{Na}_4\text{P}_2\text{S}_6$ (ZAAC, Vol.640 (2014), pgs.689-692)*
- *Solve structural puzzle*

Methodology

- *Density Functional Theory with Local-density Approximation (LDA)*
- *Projector Augmented-Wave (PAW) Formalism (Phys. Rev. B, Vol. 50(1994), pgs.17953-17979)*
- *Datasets generated with ATOMPAW code (<http://www.pwpaw.wfu.edu>)*
- *Electronic Structure calculations performed using Quantum Espresso (<http://www.quantum-espresso.org>)*
- *Plane Wave Expansion for wave functions with $|\mathbf{k}+\mathbf{G}|^2 \leq 64 \text{ Ry}$*

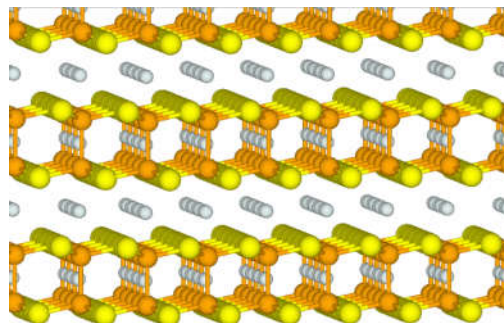
Mercier structure: Space Group $P6_3/mcm$ (#193)
Disorder in P-P placements:



$$P_{\uparrow} \equiv \pm z_P c \quad P_{\downarrow} \equiv \pm \left(\frac{1}{2} - z_P \right) c$$

Examples:

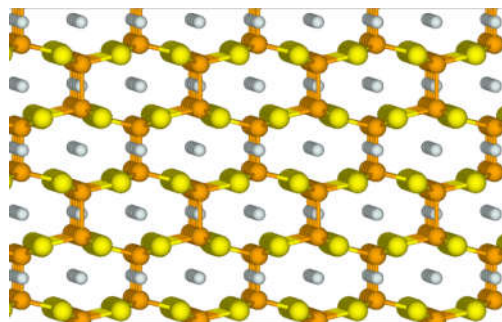
$P\bar{3}1m$



$$\Delta E = 0.03 \text{ eV}$$

100% P↑

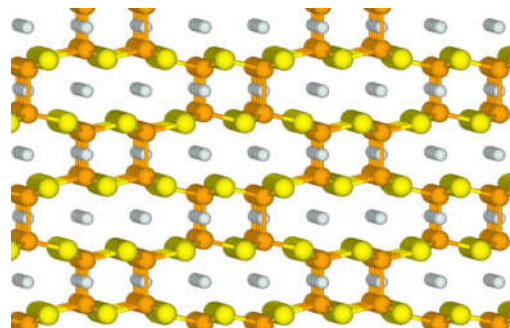
$Pn\bar{3}m$



$$\Delta E = 0$$

50% P↑
50% P↓

$Pnma$



$$\Delta E = 0$$

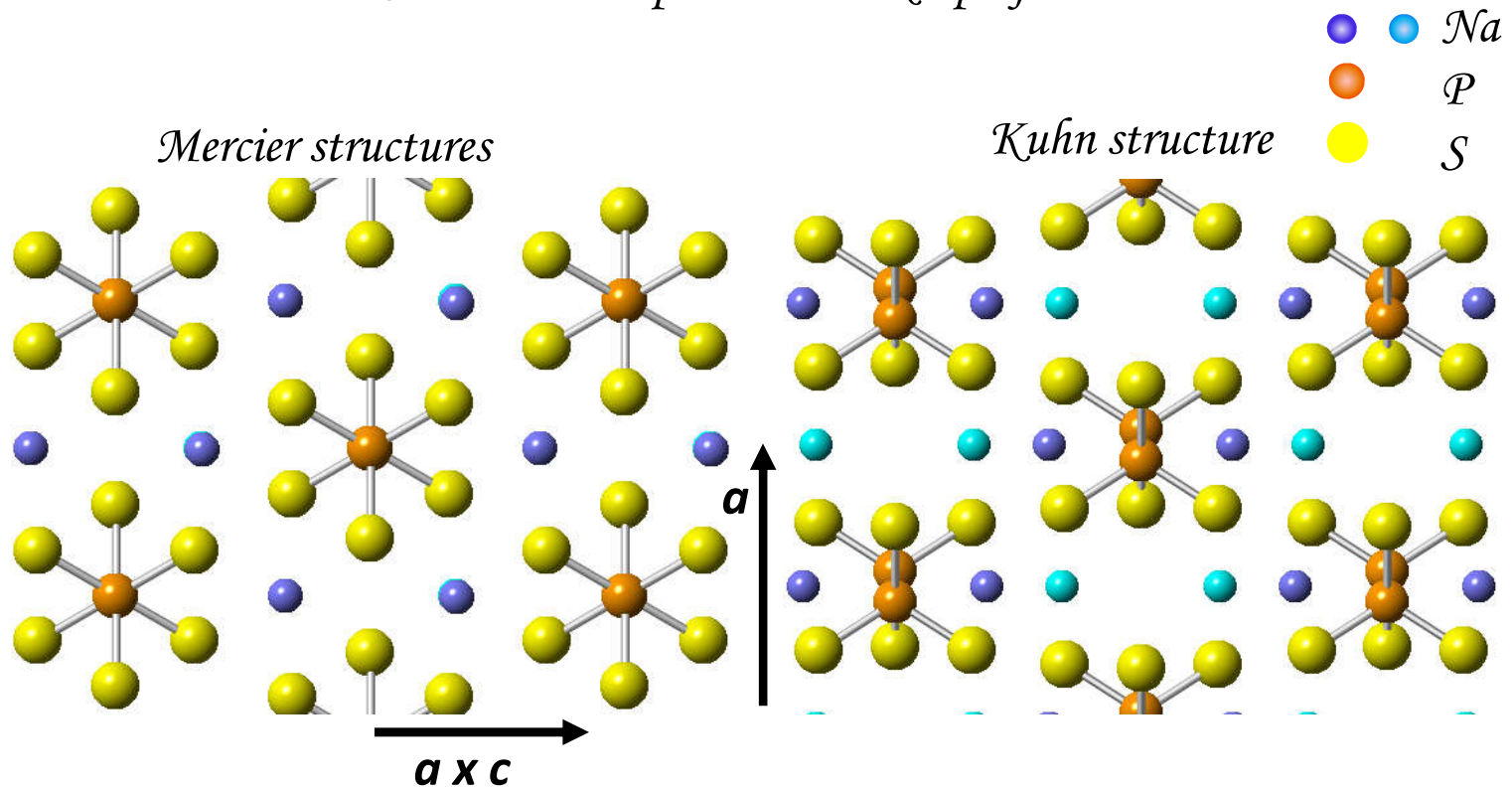
50% P↑
50% P↓



Two model configurations of disordered ground state structure

Results

Structural comparison – *c*-axis projection

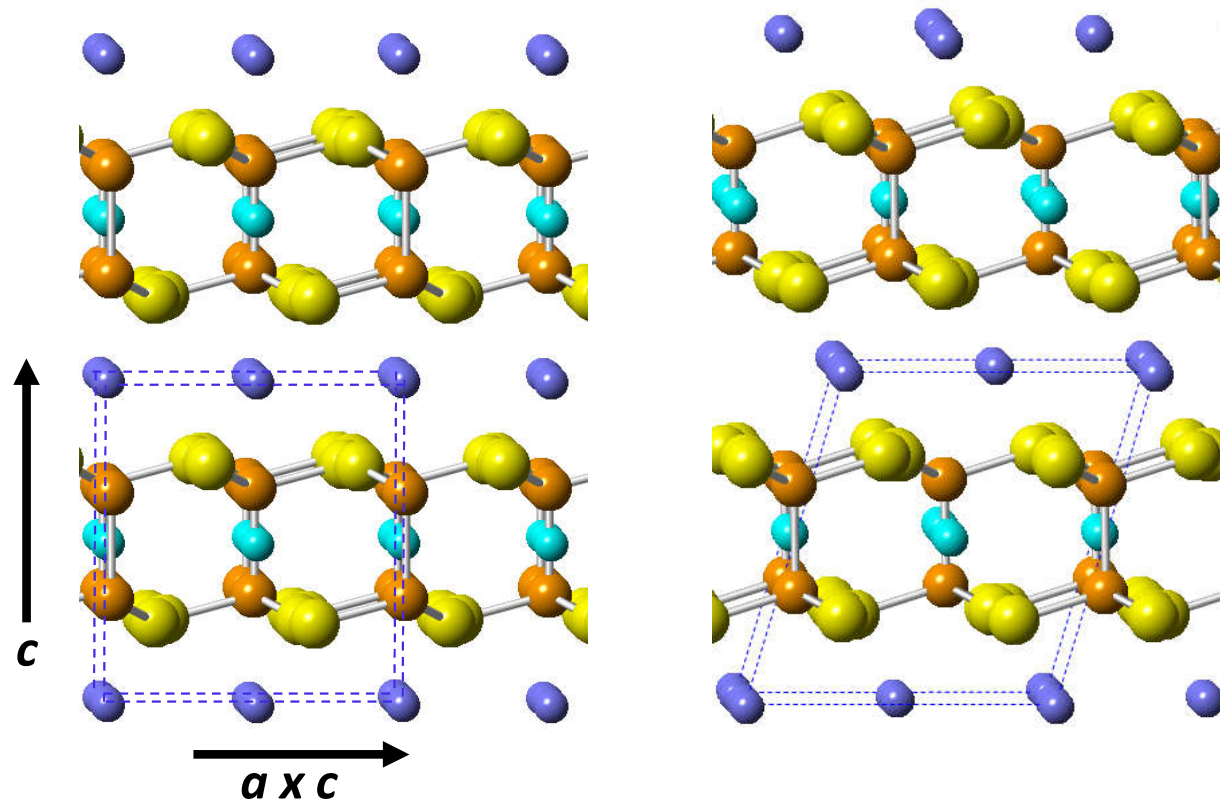
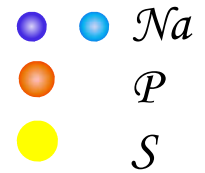




Structural comparison – view including *c*-axis

Mercier ($P\bar{3}1m$)

Kuhn ($C2/m$)



Results for $\text{Na}_4\text{P}_2\text{S}_6$:

Calculated heats of formation (eV per formula unit)
for $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Li}_4\text{P}_2\text{S}_6$ in 4 structural models

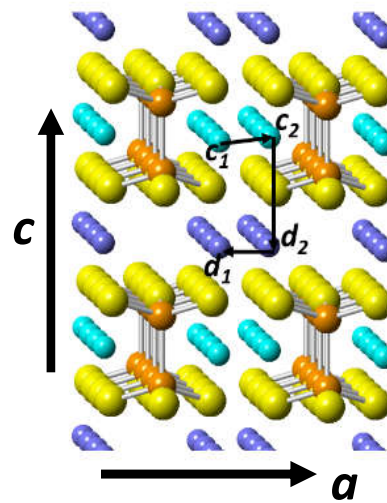
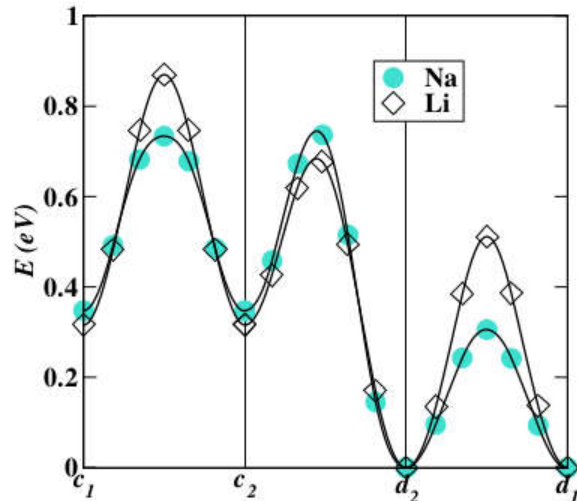
| | $\text{Na}_4\text{P}_2\text{S}_6$ | $\text{Li}_4\text{P}_2\text{S}_6$ |
|-----------------------|-----------------------------------|-----------------------------------|
| <i>Kuhn structure</i> | -11.47 eV | -12.07 eV |
| $P\bar{3}1m$ | -11.47 eV | -12.42 eV |
| <i>Pnmm</i> | -11.56 eV | -12.46 eV |
| <i>Pnma</i> | -11.56 eV | -12.46 eV |

Models of
Mercier
structure

- The calculations indicate the most stable structure for both $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Li}_4\text{P}_2\text{S}_6$ to be the disordered Mercier structure, which suggests that the Kuhn structure is meta-stable.

Comparison of vacancy migration of $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Li}_4\text{P}_2\text{S}_6$

Mercier ($P\bar{3}1m$)

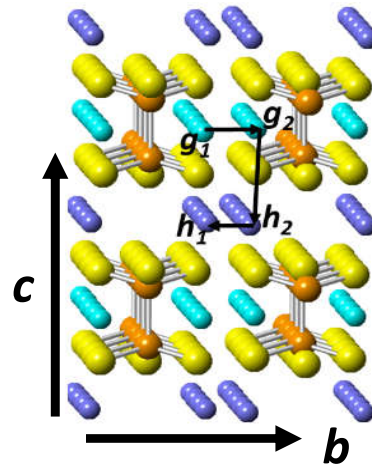
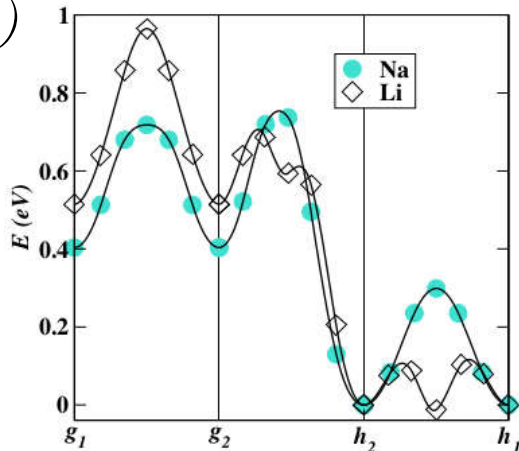


● Na
● P
● S

$$\sigma = \frac{C}{T} e^{-E_A/kT}$$

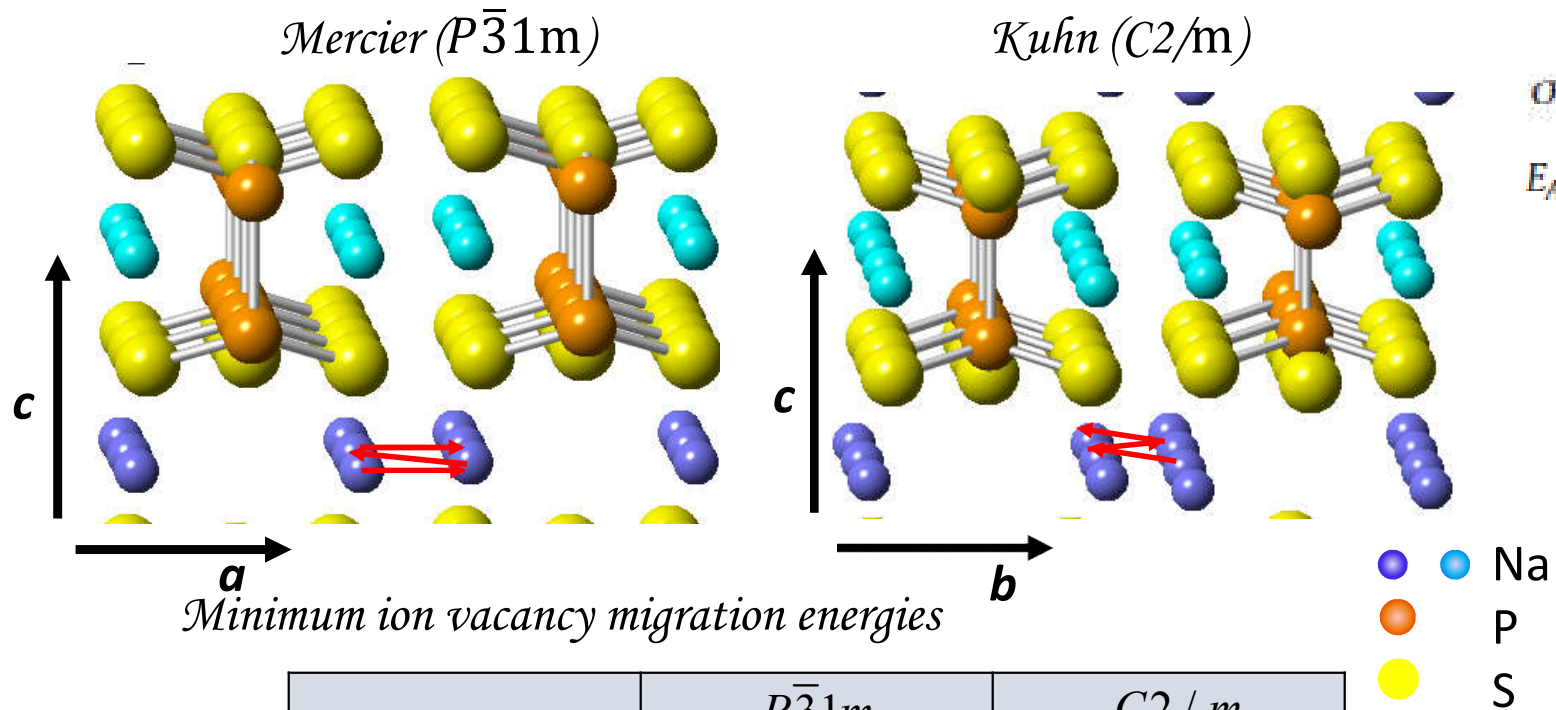
$$E_A = E_m + \frac{1}{2}E_f$$

Kuhn ($C2/m$)



“Nudged Elastic Band Method”

G. Henkleman, B.P. Uberuaga, H. Jónsson
J. Chem. Phys 113, pgs. 9901-9904 (2000)



| | $P\bar{3}1m$ | $C2/m$ |
|--------------|--------------|--------|
| $Na_4P_2S_6$ | 0.3 eV | 0.3 eV |
| $Li_4P_2S_6$ | 0.5 eV | 0.1 eV |

Conclusions

- *Kuhn structure is meta-stable*
- *Kuhn structure might have favorable conductivity ($E_f \approx 0.2\text{eV}$ & $E_a \approx 0.4\text{eV}$)*
- *Mercier structure is the ground-state structure for $\text{Na}_4\text{P}_2\text{S}_6$ & $\text{Li}_4\text{P}_2\text{S}_6$*

Questions?

“In questions of science, the authority of a thousand is not worth the humble reasoning of a single individual”

- Galileo Galilei



**Cartoon made by
Maxwell Turner*