Computational (re)investigation of the structural and electrolyte properties of Li$_4$P$_2$S$_6$, Na$_4$P$_2$S$_6$, and Li$_2$Na$_2$P$_2$S$_6$

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Outline

- Motivations
- Computational methods
- Structures and stabilities of Na₄P₂S₆ and Li₄P₂S₆
- Structures and stabilities of predicted Li₂Na₂P₂S₆
- Comparison of electrolyte properties
- Summary and conclusions
Motivations

- Kuhn et al.\textsuperscript{1} observed that Na\textsubscript{4}P\textsubscript{2}S\textsubscript{6} crystallizes to form monoclinic space group C\textsubscript{2}/m (\#12)
- Computational results of Rush et al.\textsuperscript{2}: **Kuhn structure is meta-stable**
- Recent experimental results of Hood et al.\textsuperscript{3} also find the C\textsubscript{2}/m structure

- Using combined approach of NMR and X-ray, the new experimental analysis\textsuperscript{4} on Li\textsubscript{4}P\textsubscript{2}S\textsubscript{6} concludes the structure to be ordered with space group P\textsubscript{3}2\textsubscript{1} (\#150)
- Theoretically, Na\textsubscript{4}P\textsubscript{2}S\textsubscript{6} and Li\textsubscript{4}P\textsubscript{2}S\textsubscript{6} are chemically and structurally related

- Structure and stability of the mixed ion material Li\textsubscript{2}Na\textsubscript{2}P\textsubscript{2}S\textsubscript{6}

- Performance of Li\textsubscript{2}Na\textsubscript{2}P\textsubscript{2}S\textsubscript{6} in comparison with Na\textsubscript{4}P\textsubscript{2}S\textsubscript{6} as solid electrolytes

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\textsuperscript{3}Hood et al., Manuscript in preparation.
\textsuperscript{4}Neuberger et al., *Dalton Trans.* \textbf{47}, 11691-11695 (2018)
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  - Structures and stabilities of $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Li}_4\text{P}_2\text{S}_6$
  - Structures and stabilities of predicted $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$
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Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT) with the modified Perdew-Burke-Ernzerhof generalized gradient approximation (PBEsol GGA)  

*Previously reported results obtained using Local-density approximation (LDA)*

The projector augmented wave (PAW) formalism using ABINIT (https://www.abinit.org) & QUANTUM ESPRESSO (http://www.quantum-espresso.org)

Datasets generated by ATOMPAW code available at http://pwpaw.wfu.edu

Visualization software: XCrySDen, VESTA

Space-group analysis: FINDSYM

X-ray powder diffraction: Mercury

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The Helmholtz free energy:

\[ F(T) = F_{SL}(T) + F_{vib}(T) \approx U_{SL} + F_{vib}(T) \]

**Outputs of DFT and DFPT**

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**DFT**

At equilibrium: \( F_i = -\frac{\partial U(\{R_i\})}{\partial R_i} = 0 \)

- Optimized structural parameters
- Static lattice energy: \( U_{SL} = \min U(\{R_i\}) \)
- Kohn-Sham orbitals and energies
- Migration related energies

**DFPT**

Near equilibrium: \( M_\nu(\omega')^2 u_{\nu\alpha}(q) = \sum_{i\beta} C_{\nu\alpha}^{i\beta}(q) u_{i\beta}(q) \) and \( C_{\nu\alpha}^{i\beta}(q) \leftrightarrow C_{i\beta}^{\nu\alpha}(R) \)

- Phonon frequencies and eigenvectors at any wavevector
- Phonon dispersions: \( \omega' \sim q \)
- Phonon density of states (PDOS): \( g(\omega) = \frac{V}{(2\pi)^3} \int d^3q \sum_{\nu=1}^{3N} \delta(\omega - \omega'(q)) \)
- Thermodynamic properties such as the vibrational energy: \( F_{vib}(T) = k_B T \int_0^\infty d\omega \ln \left( 2 \sinh \left( \frac{h\omega}{2k_BT} \right) \right) g(\omega) \)

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**Stable and metastable structures**
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Structure analysis

Projection of the basic structure

\[
P_{\uparrow} = \pm Z_P \vec{c}
\]

\[
P_{\downarrow} = \pm \left( \frac{1}{2} - Z_P \right) \vec{c}
\]

Model structures considered

Hexagonal $P\overline{3}21$ (#150)$^1$
3 formula units / unit cell

Hexagonal $P\overline{3}1m$ (#162)$^3$
1 formula unit / primitive unit cell

Monoclinic $C2/m$ (#12)$^4$
1 formula unit / primitive unit cell

Subgroup of disordered Mercier$^2$
SG $P\overline{6}_3/mcm$

1$^{\frac{1}{3}}$ P↑ $^{\frac{2}{3}}$ P↓
100% P↑
100% P↑

$^1$Neuberger et al., *Dalton Trans.* 47, 11691-11695 (2018)
More about the P321 structure

Comparison of the fractional coordinates of Li$_4$P$_2$S$_6$ and Na$_4$P$_2$S$_6$ based on the Neuberger structure$^1$.

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x$</td>
<td>$y$</td>
</tr>
<tr>
<td>Li</td>
<td>6 $g$</td>
<td>0.666</td>
</tr>
<tr>
<td>Li</td>
<td>6 $h$</td>
<td>0.667</td>
</tr>
<tr>
<td>P</td>
<td>2 $c$</td>
<td>0.000</td>
</tr>
<tr>
<td>P</td>
<td>2 $d$</td>
<td>$\frac{1}{3}$</td>
</tr>
<tr>
<td>P</td>
<td>2 $d$</td>
<td>$\frac{1}{3}$</td>
</tr>
<tr>
<td>S</td>
<td>6 $i$</td>
<td>0.110</td>
</tr>
<tr>
<td>S</td>
<td>6 $i$</td>
<td>0.114</td>
</tr>
<tr>
<td>S</td>
<td>6 $i$</td>
<td>0.447</td>
</tr>
</tbody>
</table>


Comparing X-ray diffraction patterns at $\lambda = 1.54056$ Å

has an additional inversion center
# Static lattice results

**TABLE:** Summary of static lattice results calculated with PBEsol GGA formalism. Lattice constants for the primitive unit cells are listed in units of Å and angles in degrees. The static lattice energy differences $\Delta U_{SL}$ are listed as eV/(formula unit) referenced to the energy of the P$\overline{3}$m1 structure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$\alpha$ (deg)</th>
<th>$\beta$ (deg)</th>
<th>$\gamma$ (deg)</th>
<th>$\Delta U_{SL}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_4$P$_2$S$_6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P$\overline{3}$m1 (#162)</td>
<td>6.03</td>
<td>6.03</td>
<td>6.48</td>
<td>90.0</td>
<td>90.0</td>
<td>120.0</td>
<td>0.04</td>
</tr>
<tr>
<td>C2/m (#12)</td>
<td>6.08</td>
<td>6.08</td>
<td>6.89</td>
<td>97.9</td>
<td>97.9</td>
<td>119.1</td>
<td>0.31</td>
</tr>
<tr>
<td>P$\overline{3}$m1 (#164)$^a$</td>
<td>10.42</td>
<td>10.42</td>
<td>6.54</td>
<td>90.0</td>
<td>90.0</td>
<td>120.0</td>
<td>0.00</td>
</tr>
<tr>
<td>Na$_4$P$_2$S$_6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P$\overline{3}$m1 (#162)</td>
<td>6.45</td>
<td>6.45</td>
<td>7.13</td>
<td>90.0</td>
<td>90.0</td>
<td>120.0</td>
<td>0.09</td>
</tr>
<tr>
<td>C2/m (#12)$^b$</td>
<td>6.51</td>
<td>6.51</td>
<td>7.52</td>
<td>98.5</td>
<td>98.5</td>
<td>117.6</td>
<td>0.00</td>
</tr>
<tr>
<td>P$\overline{3}$m1 (#164)</td>
<td>11.10</td>
<td>11.10</td>
<td>7.25</td>
<td>90.0</td>
<td>90.0</td>
<td>120.0</td>
<td>0.00</td>
</tr>
</tbody>
</table>

$^a$ Corresponding experimental values quoted from Neuberger et al., *Dalton Trans.* 47, 11691-11695 (2018) are $a = b = 10.51$ Å, $c = 6.59$ Å.

$^b$ Corresponding experimental values deduced from Kuhn et al., *Z. Anorg. Allg. Chem.* 640, 689-692 (2014) are $a = b = 6.54$ Å, $c = 7.54$ Å, $\alpha = \beta = 98.7$ deg, $\gamma = 118.1$ deg.

LDA results suggest that C2/m structure is meta-stable.

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static and vibrational
Phonon spectrum

**Na₄P₂S₆** in the C2/m Structure (36 modes)

- Na⁺ 0~300 cm⁻¹
- (P₂S₆)⁴⁻ 300~600 cm⁻¹

**Li₄P₂S₆** in the P₃m₁ Structure (108 modes)

- Li⁺ 0~370 cm⁻¹
- (P₂S₆)⁴⁻ 370~600 cm⁻¹

PJDOS:

\[ g^2(\omega) = \frac{V}{(2\pi)^3} \int d^3q \sum_{\nu=1}^{3N} (\delta(\omega - \omega_\nu(q)))W_\nu W^{\nu*}(q) \]

Discontinuous branches at Γ: coupling between photon and photon²

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²Li et al., *J. Phys. Condens. Matter, accepted*
Stability analysis

Helmholtz free energy: \( F = U_{SL} + F_{vib} \)

\( U_{SL} \): \( P\bar{3}m1 = C2/m < P\bar{3}1m \)

\( F_{vib} \): \( C2/m < P\bar{3}m1 = P\bar{3}1m \)

\( F_{\text{lowest}} : C2/m \) (expt.\(^1\)\(^,\)\(^2\))

\( U_{SL} \): \( P\bar{3}m1 < P\bar{3}1m < C2/m \)

\( F_{vib} \): \( C2/m < P\bar{3}m1 = P\bar{3}1m \)

\( F_{\text{lowest}} : P\bar{3}m1 \) (expt.\(^3\))

Motivations

Computational methods

Structures and stabilities of Na$_4$P$_2$S$_6$ and Li$_4$P$_2$S$_6$

Structures and stabilities of predicted Li$_2$Na$_2$P$_2$S$_6$

Comparison of electrolyte properties

Summary and conclusions
Structures of the predicted material: Li$_2$Na$_2$P$_2$S$_6$

Replace the (a) $g$-type or (b) $h$-type Na ions in the monoclinic Na$_4$P$_2$S$_6$ with Li ions

TABLE: Comparison of the optimized lattice parameters for Li$_2$Na$_2$P$_2$S$_6$ in the $R^L_i$ and $R^L_h$ structures. Also listed is the static lattice energy differences $U_{SL}$ referenced to the energy of the $R^L_h$ structure in units of eV/formula unit.

<table>
<thead>
<tr>
<th></th>
<th>$R^L_i$</th>
<th>$R^L_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primitive cell:</td>
<td>$a = b$ (Å)</td>
<td>6.18</td>
</tr>
<tr>
<td></td>
<td>$c$ (Å)</td>
<td>7.50</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \theta$ (deg)</td>
<td>97.77</td>
</tr>
<tr>
<td></td>
<td>$\gamma$ (deg)</td>
<td>119.21</td>
</tr>
<tr>
<td>Conventional cell:</td>
<td>$a_c$ (Å)</td>
<td>6.26</td>
</tr>
<tr>
<td></td>
<td>$b_c$ (Å)</td>
<td>10.67</td>
</tr>
<tr>
<td></td>
<td>$c_c$ (Å)</td>
<td>7.50</td>
</tr>
<tr>
<td></td>
<td>$\theta_c$ (deg)</td>
<td>105.50</td>
</tr>
<tr>
<td>$\Delta U_{SL}$ (eV/FU)</td>
<td>-0.16</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Stability of the predicted material: Li$_2$Na$_2$P$_2$S$_6$

The possible reaction pathway:

\[ \text{Na}_4\text{P}_2\text{S}_6 + 2\text{Li} \rightarrow \text{Li}_2\text{Na}_2\text{P}_2\text{S}_6 + 2\text{Na} \]

\[ \Delta F(T) = \Delta U_{SL} + \Delta F_{vib}(T) + \Delta F_{\text{metal}}(T) \]

\[ \Delta = \Delta_{\text{Products}} - \Delta_{\text{Reactants}} \]

Energy changes at \( T = 300 \text{ K} \) in eV:

\[ \Delta U_{SL} = -0.29 \]

\[ \Delta F_{vib} = -0.06 \]

\[ \Delta F = -0.35 \]

Negative energies (net released energies) imply that the structure of Li$_2$Na$_2$P$_2$S$_6$ is stable with respect to the possible exothermic process.
Motivations

Computational methods

Structures and stabilities of $\text{Na}_4\text{P}_2\text{S}_6$ and $\text{Li}_4\text{P}_2\text{S}_6$

Structures and stabilities of predicted $\text{Li}_2\text{Na}_2\text{P}_2\text{S}_6$

Comparison of electrolyte properties

Summary and conclusions
Ion migration of vacancy mechanisms

**Activation energy:**

\[ E_{a}^{\text{cal}} = E_{m}^{\text{NEB}} + \frac{1}{2} E_{f} \]

**Conductivity:**

\[ \sigma \cdot T = K e^{-E_{a}^{\exp}/k_{B}T} \]

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Summary of vacancy diffusion results

<table>
<thead>
<tr>
<th>Material</th>
<th>Functional</th>
<th>Step</th>
<th>Distance</th>
<th>( E_{m}^{\text{cal}} )</th>
<th>( E_{f} )</th>
<th>( E_{a}^{\text{cal}} )</th>
<th>( E_{a}^{\exp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na}<em>{4}\text{P}</em>{2}\text{S}_{6} )</td>
<td>PBEsol GGA</td>
<td>( h_{1} \rightarrow h_{2} )</td>
<td>3.67</td>
<td>0.25</td>
<td>0.18</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>( h_{1} \rightarrow h_{2} )</td>
<td>3.59</td>
<td>0.30</td>
<td>0.24</td>
<td>0.42²</td>
<td></td>
</tr>
<tr>
<td>( \text{Li}<em>{2}\text{Na}</em>{2}\text{P}<em>{2}\text{S}</em>{6} )</td>
<td>PBEsol GGA</td>
<td>( h_{1} \rightarrow h_{2} )</td>
<td>3.44</td>
<td>0.16</td>
<td>0.13</td>
<td>0.23</td>
<td>--</td>
</tr>
</tbody>
</table>

The distance in units of Å, and all energies are given in eV units.

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Migration study using molecular dynamics simulations

- No $g \rightarrow h$ and $g \rightarrow g$ hopping
- All migrations occur within layer of $h$ sites
- Direct $h \rightarrow h$ vacancy migration is consistent with NEB analysis
- Indirect $h \rightarrow d \rightarrow h$ vacancy migration is prevalent
- No interstitial $d \rightarrow d$ migration
- Calculate $E_a$ from $D(T) = D_0 e^{-E_a/k_BT}$
  where $D = \frac{1}{6} \lim_{t \rightarrow \infty} \left( \frac{1}{t} \text{MSD}(t) \right)$

*$AIMD$ simulations were carried out using supercells composed of $2 \times 1 \times 2$ conventional units (96 atoms)

**$E_a$ was obtained from runs of 50-70 ps
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Structures and stabilities of predicted Li$_2$Na$_2$P$_2$S$_6$

Comparison of electrolyte properties

Summary and conclusions
Summary and conclusions

- According to PBEsol GGA results, Na$_4$P$_2$S$_6$ is to be stabilized in the C2/m structure and Li$_4$P$_2$S$_6$ is to be stabilized in the P$3$m1 structure.

- PBEsol GGA and LDA results of activation energy for Na ion migration reasonably agree with the experimental measurements which suggest a viable solid electrolyte.

- The predicted crystal Li$_2$Na$_2$P$_2$S$_6$ has a stable structure. Compared to Na$_4$P$_2$S$_6$, the mixed alkali electrolyte can substantially enhance Na ion conductivity.

- Both NEB and MD simulations reveal that the Na ion diffusions in both Na$_4$P$_2$S$_6$ and Li$_2$Na$_2$P$_2$S$_6$ are via vacancy mechanisms, and MD simulations provide more information on understanding the conductivity mechanisms.