First principles computer simulations of Li$_{10}$GeP$_2$S$_{12}$ and related lithium superionic conductors*

N. A. W. Holzwarth
Wake Forest University, Winston-Salem, NC, USA, 27109

- Motivation and background information
- Structural optimization and energetic results
- Preliminary results on Li$^+$ migration mechanisms

*Supported by NSF Grants DMR-0705239 and DMR-1105485.
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*preliminary results*

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![Graph showing thermal evolution of ionic conductivity](image)

**Figure 3** | Thermal evolution of ionic conductivity of the new Li$_{10}$GeP$_2$S$_{12}$ phase, together with those of other lithium solid electrolytes, organic liquid electrolytes, polymer electrolytes, ionic liquids and gel electrolytes$^{3-8,13-16,20,22}$. The new Li$_{10}$GeP$_2$S$_{12}$ exhibits the highest lithium ionic conductivity (12 mS cm$^{-1}$ at 27 °C) of the solid lithium conducting membranes of inorganic, polymer or composite systems. Because organic electrolytes usually have transport numbers below 0.5, inorganic lithium electrolytes have extremely high conductivities.
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![Figure 3](image)

**Figure 3** | Thermal evolution of ionic conductivity of the new \( \text{Li}_{10}\text{GeP}_2\text{S}_{12} \) phase, together with those of other lithium solid electrolytes, organic liquid electrolytes, polymer electrolytes, ionic liquids and gel electrolytes\(^{3,8,13,16,20,22} \). The new \( \text{Li}_{10}\text{GeP}_2\text{S}_{12} \) exhibits the highest lithium ionic conductivity (12 m S cm\(^{-1}\) at 27 °C) of the solid lithium conducting membranes of inorganic, polymer or composite systems. Because organic electrolytes usually have transport numbers below 0.5, inorganic lithium electrolytes have extremely high conductivities.
Other simulation studies on this material:
Work by MIT group published in Dec. 2011

First Principles Study of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ Lithium Super Ionic Conductor Material

Yifei Mo, Shyue Ping Ong, and Gerbrand Ceder*

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information

**KEYWORDS:** lithium ionic conductor, solid electrolyte, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, ab initio, molecular dynamics, phase diagrams

dx.doi.org/10.1021/cm203303y | Chem. Mater. 2012, 24, 15–17
Ionic Conductivity of Lithium Orthosilicate—Lithium Phosphate Solid Solutions

Y-W. Hu, I. D. Raistrick, and R. A. Huggins*

Center for Materials Research, Stanford University, Stanford, California 94305

\[ \sigma \cdot T = K e^{-E_A/kT} \]

\[ \frac{1}{2} \text{Li}_4\text{SiO}_4 + \frac{1}{2} \text{Li}_3\text{PO}_4 \]

0.9 eV

0.5 eV
Lithium Ionic Conductor Thio-LISICON

The Li₂S-GeS₂-P₂S₅ System

Ryoji Kanno* and Masahiro Murayama

Department of Chemistry, Faculty of Science, Kobe University, Hyogo 657-8501, Japan

\[ \frac{1}{4} \text{Li}_4 \text{GeS}_4 + \frac{3}{4} \text{Li}_3 \text{PS}_4 \]
Li_{10}GeP_{2}S_{12} \leftrightarrow \frac{1}{3}Li_{4}GeS_{4} + \frac{2}{3}Li_{3}PS_{4}

Li_{10}GeP_{2}S_{12} is a new material; not a solid solution of its constituents.
Goals of computer simulations

- Study structural and chemical stability
- Compare Li$_{10}$GeP$_2$S$_{12}$ and Li$_{10}$SiP$_2$S$_{12}$
- Investigate Li ion migration mechanisms

Calculational methods used in this study:

Calculations based on density functional theory with the local density approximation (LDA) using the Quantum Espresso and Abinit codes. USPP and PAW calculations compared

Li ion migration energies estimated using the Nudged Elastic Band (NEB) method (Hinkleman et al J. Chem. Phys. 113 9901 & 9978 (2000) using 2x2x1 supercell
Constituents of Li$_{10}$GeP$_2$S$_{12}$:

\[ \Delta H = -19.10 \text{ eV} \]

\[ \Delta H = -28.8 \text{ eV} \]

\[ \Delta H = -36.8 \text{ eV} \]

\[ \Delta H = -12.8 \text{ eV} \]

\[ \Delta H = -8.12 \text{ eV} \]

\[ \Delta H = -8.28 \text{ eV} \]

\[ \Delta H = -8.36 \text{ eV} \]

\[ \Delta H = -10.19 \text{ eV} \]

$\alpha^*$ - Li$_3$PS$_4$  
$\beta^*$ - Li$_3$PS$_4$  
$\gamma^*$ - Li$_3$PS$_4$

\[ Pbcn \]

\[ Pnma \]

\[ Pmn2_1 \]


Li$_{10}$GeP$_2$S$_{12}$
Space group P4$_2$/nmc (#137)
(from experiment)
Lattice parameters

<table>
<thead>
<tr>
<th></th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Li}_{10}\text{GeP}<em>2\text{S}</em>{12}) (exp*)</td>
<td>8.72</td>
<td>12.63</td>
</tr>
<tr>
<td>(\text{Li}_{10}\text{GeP}<em>2\text{S}</em>{12}) (Calc)</td>
<td>8.56</td>
<td>12.23</td>
</tr>
<tr>
<td>(\text{Li}_{10}\text{SiP}<em>2\text{S}</em>{12}) (Calc)</td>
<td>8.55</td>
<td>12.16</td>
</tr>
</tbody>
</table>


Experimentally determined symmetry (fractional occupancy):
Space group \(P4_2/nmc\) (#137)

Optimized structure with full occupancy:*
Space group \(P4_2mc\) (#105)

\((x, y, z) \rightarrow (y, x, -z)\)

*Determined using FINDSYM written by Stokes, Campbell, and Hatch at Brigham Young U. – http://stokes.byu.edu/iso/
### Experiment structure:
Space group $P4_2/nmc$ (#137)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$g$</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(1)</td>
<td>16h</td>
<td>0.69</td>
<td>0.26</td>
<td>0.27</td>
</tr>
<tr>
<td>Li(2)</td>
<td>4d</td>
<td>1.00</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>Li(3)</td>
<td>8f</td>
<td>0.64</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Ge(1)</td>
<td>4d</td>
<td>0.52</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>P(1)</td>
<td>4d</td>
<td>0.49</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>Ge(2)</td>
<td>2b</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>P(2)</td>
<td>2b</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>S(1)</td>
<td>8g</td>
<td>1.00</td>
<td>0.00</td>
<td>0.18</td>
</tr>
<tr>
<td>S(2)</td>
<td>8g</td>
<td>1.00</td>
<td>0.00</td>
<td>0.30</td>
</tr>
<tr>
<td>S(3)</td>
<td>8g</td>
<td>1.00</td>
<td>0.00</td>
<td>0.70</td>
</tr>
</tbody>
</table>

### Calculated structure:
Space group $P4_2/mc$ (#105)*

<table>
<thead>
<tr>
<th>Atom</th>
<th>$g$</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(1)</td>
<td>8f</td>
<td>1.00</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>Li(2)</td>
<td>2a/2b</td>
<td>1.00</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>Li(3)</td>
<td>8f</td>
<td>1.00</td>
<td>0.26</td>
<td>0.22</td>
</tr>
<tr>
<td>Ge(1)</td>
<td>2b</td>
<td>1.00</td>
<td>0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>P(1)</td>
<td>2a</td>
<td>1.00</td>
<td>0.00</td>
<td>0.50</td>
</tr>
<tr>
<td>P(2)</td>
<td>2c</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>S(1)</td>
<td>4d/4e</td>
<td>1.00</td>
<td>0.00</td>
<td>0.20</td>
</tr>
<tr>
<td>S(2)</td>
<td>4d/4e</td>
<td>1.00</td>
<td>0.00</td>
<td>0.30</td>
</tr>
<tr>
<td>S(3)</td>
<td>4d/4e</td>
<td>1.00</td>
<td>0.00</td>
<td>0.70</td>
</tr>
</tbody>
</table>

*Wyckoff symbols for #105, coordinates in #137 convention.
Decomposition reactions predicted on the basis of calculated enthalpies of formation (at zero temperature)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}_{10}\text{GeP}<em>2\text{S}</em>{12} \rightarrow 2\text{Li}_3\text{PS}_4 + \text{Li}_4\text{GeS}_4 )</td>
<td>0.77</td>
</tr>
<tr>
<td>( \text{Li}_{10}\text{SiP}<em>2\text{S}</em>{12} \rightarrow 2\text{Li}_3\text{PS}_4 + \text{Li}_4\text{SiS}_4 )</td>
<td>0.74</td>
</tr>
<tr>
<td>( \text{Li}_{13}\text{GeP}<em>3\text{S}</em>{16} \rightarrow 3\text{Li}_3\text{PS}_4 + \text{Li}_4\text{GeS}_4 )</td>
<td>0.55</td>
</tr>
<tr>
<td>( \text{Li}_{13}\text{SiP}<em>3\text{S}</em>{16} \rightarrow 3\text{Li}_3\text{PS}_4 + \text{Li}_4\text{SiS}_4 )</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Preliminary results for formation enthalpies from zero-temperature simulations predict all of the compounds to be unstable with respect to their constituents.
Possible Li ion vacancy migrations in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$
Possible Li ion vacancy migrations in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$
Possible Li ion vacancy migrations in Li$_{10}$GeP$_2$S$_{12}$

Vacancy site energies (eV)
1  0.0
2  0.5
3  0.1
Possible Li ion vacancy migrations in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ & $\text{Li}_{10}\text{SiP}_2\text{S}_{12}$

Preliminary NEB results for Li ion migration
Summary of preliminary results and conclusions
• Found (meta) stable structures for both Li_{10}GeP_{2}S_{12} and Li_{10}SiP_{2}S_{12}; ordered structure has space group P4_{2}mc instead of experimental structure with partial occupancies P4_{2}/nmc
• Both Li_{10}GeP_{2}S_{12} and Li_{10}SiP_{2}S_{12} are calculated to be unstable with respect to decomposition into constituents; implying that either there is a kinetic barrier favoring the new materials or there are other stabilizing mechanisms.
• Preliminary NEB results suggest $E_m = 0.5$ eV for both materials vacancy migrations along the c-axis. Migration along the a-axis is $\sim 0.2$ eV higher for Li_{10}SiP_{2}S_{12}.
• Further work need to verify these preliminary results and to consider interstitial sites.