Pathways of Li$^+$ ion mobility in superionic perovskites by ab initio simulations

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LLTO family of Li\textsuperscript{+} ion conductors:
\[
\text{Li}_x\text{La}_{2/3-x/3}\text{O}_{1/3-2x/3}\text{TiO}_3
\]

- ABO\textsubscript{3} perovskite-type structure, with B=Ti \quad (a_p \approx 3.87 \text{ Å})
- A sites partly occupied by La, partly vacant
- Li \text{ disordered in part of the A-vacant cavities}

\[\downarrow\]
very high ionic conductivity at RT
\quad (10^{-3} \ \Omega^{-1}\text{cm}^{-1} \text{ for } x = 0.3)

- A variety of superlattice distortions according to \(x\) and \(T\)
How is the high Li\(^+\) ion mobility related to the structure?

- Nernst-Einstein equation:
  \[ \mu_+ = \frac{\sigma_+}{e n_+} = \frac{e}{kT} D \]

- Arrhenius law:
  \[ D = D_0 \exp(-E_a/kT) \]

\[ \rightarrow \text{lithium disorder} \]
  Arrhenius pre-exponential (probability) factor \(D_0\)

\[ \rightarrow \text{local crystal-chemical environment of lithium} \]
  Arrhenius activation energy \(E_a\)
• **Long-range structure** to be studied by elastic neutron scattering (but... experimental difficulties)

• **Local structure** extremely important to understand the mobility (NMR, Raman and inelastic neutron scattering: ....very few data)

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interest of computational modeling by accurate and reliable

quantum-mechanical methods
Crystallographic structure by neutron powder diffraction

- problems:
  - large neutron absorption cross section of natural lithium
  - significant incoherent scattering
  - small amount of Li per LLTO formula unit

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an accurate Rietveld refinement of Li occupancy and coordinates is often difficult

High-quality data are strictly required
Summary of experimental NPD results at RT

1. Doubling of $c$ ($c = 2a_p$), and partial La/Li ordering along the $z$ axis

2. Different superlattice in the (001) plane, and tilt of the TiO$_6$ octahedra, according to lithium content $x$ in Li$_x$La$_{2/3-x/3}$TiO$_3$

Varez et al., Chem. Mater. 15, 4637 (2003)
\[ \text{Li-rich (0.20 < x < 0.50) \rightarrow } a^0a^0c^- \text{ octahedral tilt} \]

tetragonal superstructure
\[ a = b = \sqrt{2} a_p \quad (Z=4) \]

\[ \text{Li-poor (0.12 < x < 0.20) \rightarrow } a^0b^0c^0 \text{ octahedral tilt} \]

orthorhombic superstructure
\[ a = 2a_p, \ b = 2a_p \quad (Z=8) \]
Disordered structures of $x=0.30$ and $0.16$ LLTO phases

$P4/nbm \quad \text{Li}_0.3\text{La}_{0.567}\text{TiO}_3$

$Cmmm \quad \text{Li}_{0.16}\text{La}_{0.62}\text{TiO}_3$

Li: located in square pyramidal coordination with $O_4$ windows separating adjacent A-type cavities
Summary of experimental results

- $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ and $2a_p \times 2a_p \times 2a_p$ superstructures in Li-rich ($P4/nbm$) and Li-poor ($Cmmm$) LLTO perovskites
- Anti-phase octahedral tilting along [001] ($P4/nbm$) and [010] ($Cmmm$)
- Partial ordering of La sites along [001] in both structures
- Li located in fourfold coordination close to bottlenecks between A site hollows, with extensive (001) two-dimensional disorder

Why theoretical analysis?

\[ \Downarrow \]

Ordered models for local structure + energetics of Li$^+$ ion jumping

\[ \Downarrow \]

Full understanding of ions transport processes in LLTO
Quantum-mechanical periodical calculations

- DFT Hamiltonian operator:
  B3LYP hybrid exchange-correlation potential

- Localized basis functions (Atomic Orbitals) with Gaussian-type radial part

- Basis sets:
  Ti: $8(s)6411(sp)31(d)G$; O: $8(s)411(sp)G$; Li: $6(s)1(sp)G$;
  La: Hay-Wadt ECP + 411(sp)21(d)G

- Least-energy structure optimization:
  conjugated gradients algorithm

- Computer code: CRYSTAL06
Starting ordered models for the LLTO local structure

Sequence of (001) perovskite layers, each with a given La-Li-\(\square\) distribution

→ **Li-poor phases:**

- \(x=1/8\) \(\text{Li}_{0.125}\text{La}_{0.625}\text{O}_{0.25}\text{TiO}_3\)
  - two layers
  - \(2a_p\times2a_p\times2a_p\) supercell (\(Z=8\))
  - 26 atoms in the asymmetric unit
  - Energy minimization:
  - 62 atomic coordinates relaxed within the \(Pm\) space group

Least-energy ordered models for Li$_{0.125}$La$_{0.625}$TiO$_3$

Model 1:  $P2\overline{2}mm$
4La / 1La+1Li+2$\square$

$a\cdot b^0c^0$  tilt

Model 2:  $Pm$
3La+1 / 2La+1Li+1$\square$

$a^0a^0c^-$  tilt

$E(\text{model 2}) - E(\text{model 1}) = 0.127$ eV/f.u.
<table>
<thead>
<tr>
<th>NPD Rietveld refinements</th>
<th>Models</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}<em>{0.16}\text{La}</em>{0.62}\text{TiO}_3 )</td>
<td>( \text{Li}<em>{0.18}\text{La}</em>{0.61}\text{TiO}_3 )</td>
</tr>
<tr>
<td>mod. 1</td>
<td>mod. 2</td>
</tr>
<tr>
<td>( \cdot \text{Occ.}(\text{La}) \ 1^\circ \text{layer} )</td>
<td>0.94</td>
</tr>
<tr>
<td>( \cdot \text{Occ.}(\text{La}) \ 2^\circ \text{layer} )</td>
<td>0.30</td>
</tr>
<tr>
<td>( \cdot \text{Tilt system} )</td>
<td>( a\cdot b^0c^0 )</td>
</tr>
</tbody>
</table>

\[ \Rightarrow \quad \text{Model 1 fits experimental results much better than model 2} \]

- Least-energy Li position:

  more similar to those of \( \text{Li}_{0.3}\text{La}_{0.567}\text{TiO}_3 \) and \( \text{Li}_{0.18}\text{La}_{0.61}\text{TiO}_3 \) than to that of \( \text{Li}_{0.16}\text{La}_{0.62}\text{TiO}_3 \)
\[ S(\text{configurational}) = R \ln \left( \frac{4!}{n_1(\text{La})!n_1(\text{Li})!n_1(\square)!} \frac{4!}{n_2(\text{La})!n_2(\text{Li})!n_2(\square)!} \right) \]

\[ F(\text{model 2}) - F(\text{model 1}) = \Delta E - T\Delta S = 12237 - 1.44T \text{ J mol}^{-1} \]

\[ \downarrow \]

Model 1 largely favoured over model 2

Boltzmann factor \[ \frac{\text{prob.}(\text{mod.2})}{\text{prob.}(\text{mod.1})} = \exp \left( - \frac{\Delta F}{RT} \right) = \]

\[ \begin{array}{c|c|c} \text{estimated occ.(La)} & 300 \text{ K} & 1300 \text{ K} \\ \hline \text{1° layer} & 0.998 & 0.905 \\ \text{2° layer} & 0.252 & 0.345 \end{array} \]

0.01 (300 K)

0.38 (1300 K)
Simulated pathways of Li\(^+\) ion diffusion in Li\(_{1/8}\)La\(_{5/8}\)TiO\(_3\)

‘frozen ion’ method:

- either \(x\) (1D pathway) or the \(x,y\) pair (2D) of Li coordinates are fixed
- all the other atomic coordinates are relaxed to minimize the energy
- the energy \(E\) of the non-equilibrium configuration is obtained
- the procedure is repeated for other \(x\) or \(x,y\) values, and \(E\) is plotted vs. \(x\) (1D) or vs. \(x,y\) (2D)
Mobility paths confined to the La-poor upper layers of models 1 and 2

2La+1Li+1 layer of model 2:

1D paths along the [100] rows of La-free A-type cavities

activation energy: 0.42 eV
La+1Li+2 layer of model 1:

→ 1D paths possible but unfavoured (activation energy: 0.67 eV)

→ 2D paths more favourable (activation energy: 0.47 eV)
2D pathway in the 1La+1Li+2\(\square\) layer of model 1:

→ 'straight' and '90° turn' steps in the ‘easy’ and ‘difficult’ A-type hollows

→ saddle points 0.19 and 0.47 eV high for the two steps

→ the 90° detour reduces the hopping barrier by 0.2 eV in the difficult A hollow

→ the 2D pathway should be more frequent than the 1D one, as model 1 is much more populated than model 2

→ the hopping barrier of 0.47 – 0.42 eV compares favourably with the experimental activation energy of 0.35 eV for Li_{0.36}La_{0.55}TiO_3

Starting ordered models for the LLTO local structure

→ **Li-rich phases:**

- \( x=5/16 \) \( \text{Li}_{0.3125}\text{La}_{0.5625}\text{TiO}_3 \) four layers
  
  \( 2a_p \times 2a_p \times 4a_p \) supercell (\( Z=16 \))

  layer sequence:  \( 3\text{La}+1\text{Li} / 2\text{La}+1\text{Li}+1\Box / 3\text{La}+1\text{Li} / 1\text{La}+2\text{Li}+1\Box \)

- average La occupancies along [001]:  \( \text{occ.}(\text{La}1)=0.375, \text{occ.}(\text{La}2)=0.750 \)

- Rietveld-refined values in \( \text{Li}_{0.3}\text{La}_{0.567}\text{TiO}_3 \):  \( \text{occ.}(\text{La}1)=0.357, \text{occ.}(\text{La}2)=0.778 \)

  54 atoms in the asymmetric unit

Energy minimization:

  128 atomic coordinates relaxed within the \( Pm \) space group

Least-energy $Pm$ model of \( \text{Li}_{0.3125}\text{La}_{0.5625}\text{TiO}_3 \)

\[ 2a_p \times 2a_p \times 4a_p \text{ cell} \]

optimized structure of the four (001) layers:

(a) 3La+1Li
(b) 2La+1Li+1
(c) 3La+1Li
(d) 1La+2Li+1

The \( a^0a^0c^0 \) tilt of the NPD structure of \( \text{Li}_{0.3}\text{La}_{0.567}\text{TiO}_3 \)
is correctly reproduced.
Li atoms take two different locations, according to the La-Li-□ layer composition:

- **Li n.1:**
  close to vertical windows separating A-type cages

- **Li n.2:**
  close to horizontal windows separating A-type cages

**Li n. 1 in La-poor and Li n. 2 in La-rich layers**

Li n.1  →  Li1

of the experimental *P4/nbm* structure of Li$_{0.3}$La$_{0.567}$TiO$_3$

Li n.2  →  Li2
• Li goes to site n.1 in A-type cages belonging to La-poor layers
  
  Li goes to site n.2 in A-type cages surrounded by La atoms

  ↓

  the experimental Li1 and Li2 positions can be associated to different locally ordered layer configurations

• The site n.2 is unfavourable for the ionic mobility of Li (‘trapping site’)

• Ionic transfer occurs by hopping between sites n.1
Simulated pathways of Li$^+$ ion diffusion in Li$_{5/16}$La$_{9/16}$TiO$_3$

\[ \Rightarrow \text{Li-stripped ionized system: } (\text{La}_{0.5625\pm0.4375}\text{TiO}_3)^{-0.3125} \]

layers 2La$^+$2\ and 1La$^+$3\th

maps of the electrostatic potential

at fixed (experimental) structure
Electrostatic potential of \((\text{La}_{0.5625} \square_{0.4375} \text{TiO}_3)^{-0.3125}\) layer \(2\text{La}+2\) 

- \(2a_p \times 2a_p \times 4a_p\) reference unit-cell
- contour line separation: 0.002 a.u. (0.054 V).
- A, A' (saddle points): centres of empty A-type cavities
- * (minima): centres of windows separating adjacent cavities

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Electrostatic potential of \((\text{La}_{0.5625}\text{TiO}_3)^{-0.3125}\) layer 1La+3

- \(2a_p \times 2a_p \times 4a_p\) reference unit-cell
- Contour line separation: 0.002 a.u. (0.054 V).
- A (saddle points), A' (maximum): centres of empty A-type cavities
- B (minima)
- * : centres of windows separating adjacent cavities
A-type sites:

maxima or saddle points of the electrostatic potential

electrostatic potential minima:

- located either at the window centres or slightly displaced
- closer to O atoms than actual Li$^+$ ion positions
  (neglect of electron exchange repulsion)

one- or two-dimensional Li$^+$ mobility pathways according to the La/$\Box$ ratio
Conclusions

→ By least-energy structure optimization, ordering schemes consistent with the experimental average structure can be determined.

→ Suitable ordered models of the $x=1/8$ and $5/16$ terms have proved to account for the disordered structures of Li-poor and Li-rich LLTO perovskites ($\text{Li}_x\text{La}_{2/3-x/3}^{1/3} \text{TiO}_3$).

→ The equilibrium sites of Li atoms in LLTO have been located and associated to the local La composition.

→ Mobility pathways of Li$^+$ ions can be determined by energy minimization techniques, and the associated activation barriers are predicted.