Insight into lithium-ion mobility in Li$_2$La(TaTi)O$_7$

Selorm Joy Fanah,$^a$ Ming Yu,$^b$ Ashfia Huq$^c$ and Farshid Ramezanipour$^{d,*a}$

Combination of neutron diffraction, impedance spectroscopy and DFT analysis of lithium diffusion pathways provides an understanding of lithium-ion mobility in layered oxides through a case study of Li$_2$La(TaTi)O$_7$. This new material is a Li-conducting oxide, which contains stacks of (Ta/Ti)O$_6$ octahedra separated by a layer of lithium ions, forming a Ruddlesden–Popper type structure. Experiments show that two strategies, i.e., shortening the Li hopping distance and inducing defects in the Li-layer, can successfully improve the ionic conductivity. The DFT analyses reveal the orientation of lithium diffusion pathways and the energy barriers in these pathways, which are directly correlated with the atomic arrangement of this material. These results have broad implications with regard to the design of a new class of Li-conducting oxides based on Ruddlesden–Popper oxides.

Introduction

The need for development of solid lithium-ion conductors has been recognized in recent years,$^{1-5}$ and there has been intense research on the development of solid electrolytes for lithium ion batteries. Several classes of solids have been investigated for this purpose, including different polymers,$^{6,7}$ perovskites$^{8,9}$ and garnet oxides.$^{10-18}$ Another family of oxides that has the potential to be a good lithium-ion conductor is the Ruddlesden–Popper family. This class of oxides has been studied in view of various properties they exhibit such as ion-exchange,$^{11}$ carbon dioxide capture,$^{12}$ and photocatalytic activities.$^{13}$ However, little work has been done on their potential Li-ion conductivity. Solid electrolytes need to have structures and compositions that allow the conduction of lithium ions, but have negligible electronic conductivity. While it is possible to incorporate Li-ions into a diverse range of solid-state compounds, the conduction pathways that allow the mobility of lithium ions are not available in many lithium-containing compounds. However, Ruddlesden–Popper materials have open spaces in their structure that can be suitable pathways for lithium-ion conductivity. In addition, the diverse range of compositions makes it possible to design Li-containing Ruddlesden–Popper compounds that have negligible electronic conductivity. As shown in Fig. 1, the structure of these materials comprises layers of corner-sharing BO$_6$ octahedra, where B is usually a transition metal. These layers are stacked to form double or triple layer slabs. The general formula for these oxides is A$_{n+1}$B$_n$O$_{3n+1}$, where A is usually an alkaline-earth or lanthanide cation located in spaces within and between the octahedral stacks. The number of layers in each stack is represented by $n = 1, 2$ or 3. Given the large gap between the stacks, it is reasonable to speculate that the inter-stack spaces could be good pathways for transport of ions. If lithium-containing Ruddlesden–Popper compounds can be synthesized, it should be possible to achieve Li-ion conductivity. A small number of $n = 2$ Ruddlesden–Popper oxides containing lithium have been reported,$^{12,14-16}$ where the Li ions reside in spaces between the stacks. The electrical conductivity of a composite system, containing poly(ethylene oxide) and Ruddlesden–Popper compounds, has been investigated recently, suggesting a two-dimensional Li-conduction pathway based on bond valence sum mapping.$^{17}$ Also, the electrical properties of Li$_x$SrTa$_2$O$_7$ have been studied, showing lithium-ion conductivity.$^{18}$ It has been suggested that creating partial cation deficiency in the intra-stack sites can lead to the displacement of some lithium ions at elevated temperatures from inter-stack to intra-stack positions, leaving behind vacant sites.$^{18}$ While the ionic conductivity of Li$_x$SrTa$_2$O$_7$ is not significant, it demonstrates the feasibility of lithium conducton in Ruddlesden–Popper phases. This is reminiscent of the initial stages of research on some other ionic conductors, such as garnet oxides, where the first materials showed low lithium ion mobility,$^4$ but further modifications led to the synthesis of highly conductive materials.$^{5-10}$

Further optimization of Ruddlesden–Popper compounds can lead to enhanced lithium ion conductivity. Given the presence of large cations, such as Sr$^{2+}$, in Li$_x$SrTa$_2$O$_7$, we hypothesized that the ionic conductivity should be enhanced if the synthesis of Ruddlesden–Popper compounds containing smaller cations on both A and B-sites could be achieved. Cations that have smaller ionic radii will lead to smaller unit cells, shortening the hopping distances for lithium ions. Therefore, we planned to synthesize Li$_2$La(TaTi)O$_7$, containing La$^{3+}$ and Ti$^{4+}$, which have smaller ionic radii than Sr$^{2+}$ and Ta$^{5+}$.
respectively. In addition, we sought to enhance the ionic conductivity further by inducing defects directly in the Li-layer to improve the mobility of lithium ions. This paper describes the results of these studies. While the lithium ion conductivity still needs to be improved for practical applications, this work demonstrates the success of the above strategies for enhancing the ionic conductivity in Ruddlesden–Popper oxides.

**Experimental and computational methods**

**Synthesis**

The syntheses were performed by solid-state method using powders of Li₂CO₃ (Alfa Aesar, 99.998%), La₂O₃ (Alfa Aesar, 99.99%), Ta₂O₅ (Alfa Aesar, 99.993%), and TiO₂ (Sigma Aldrich, 99.99%). Stoichiometric amounts of precursors were weighed and mixed together. In order to compensate for Li loss due to evaporation at high temperature, 5% extra Li₂CO₃ was added to the starting mixture. The mixtures were then ground and pressed into pellets and calcined in alumina crucibles at 850 °C for 4 hours. The calcined pellets were ground, re-pelletized and re-fired at 1200 °C for 6 hours in air. The heating and cooling rates in all cases were 100 °C per hour. Both Li₂La(TaTi)O₇ and the A-site deficient Li₁.₈La(Ta₁.₂Ti₀.₈)O₇ were synthesized as single phase products.

**Characterization**

The polycrystalline oxides were studied by powder X-ray diffraction (PXRD) using Cu Kα₁ radiation (λ = 1.54056 Å) in a 2θ range of 5–100°. The crystal structures of all samples were examined by Rietveld refinements using GSAS software and the EXPGUI interface. Microstructural characterization was performed using high-resolution field-emission scanning electron microscopy (SEM).

Neutron diffraction experiments were performed on POWGEN diffractometer at the Spallation Neutron Source in Oak Ridge National Laboratory at 300 K, over the d-range of 0.25–5 Å.

Ionic conductivity measurements on sintered pellets (~1.45 mm in thickness and 9 mm in diameter) were carried out using a computer controlled potentiostat equipped with a frequency response analyzer in the frequency range 0.1 Hz to 1 MHz and temperature range 25 to 400 °C in air. All conductivity measurements were performed under identical conditions for both the parent compound and the A-site deficient analogue.

**Density functional theory calculations**

The overall computational calculations were mainly carried out employing the density functional theory (DFT) framework, as implemented in the Vienna Ab initio Simulation Package (VASP). The electron–ion interactions were described by the Projector Augmented Wave (PAW) method, while electron exchange–correlation interactions were treated by the generalized gradient approximation (GGA) in the scheme of Perdew Burke Ernzerhof (PBE). The spin polarized behaviors were also considered in calculations. The structural relaxation was performed using Conjugate-Gradient algorithm implemented in the VASP. The micro-canonical ensemble was used in the molecular dynamics simulation and all atoms in the unit cell were allowed to move freely during the simulations. The energy cutoff was set at 400 eV for the plane wave basis in all calculations, and the criteria for convergences of energy and force in
relaxation processes were set to be $10^{-5}$ eV and $10^{-4}$ eV Å$^{-1}$, respectively. A $1 \times 1 \times 1$ primitive cell was chosen and the Brillouin zones (BZ) were sampled using $5 \times 5 \times 5$ $k$-point meshes generated in accordance with the Monkhorst–Pack scheme\cite{28} in all calculations.

Results and discussions

Crystal structure

Both Li$_2$La(TaTi)O$_7$ and Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ have a double-layered Ruddlesden–Popper structure type, $A_{n+1}B_nO_{3n+1}$, where $n = 2$. Double-layered Ruddlesden–Popper materials usually have tetragonal\cite{14,29,30} or orthorhombic\cite{15,16,31} structures. The common space groups are $I4/mmm$, $P4_2/mmm$, $Fmmm$\cite{15,12,32} and $Cmcm$\cite{16,31}.

For Li$_2$La(TaTi)O$_7$, the tetragonal structure is readily ruled out due to the splitting of the X-ray diffraction peaks at $2\theta = 58.8$, 68.0, 77.4, 81.5, 92.8, and 96.1°, indicating that this material crystallizes in an orthorhombic space group. Given the angle-dependence of the peak intensities in X-ray diffraction, the peaks at a high $2\theta$ angle (low $d$-spacing) are not pronounced. However, this problem does not exist in neutron diffraction, which allows for careful examination of the peaks in the low $d$ region. The neutron diffraction data show small peaks at $d = 1.115$ Å and 1.505 Å, which cannot be described by the $Fmmm$ space group, but are an excellent match with $Cmcm$. Fig. 2 and 3 show the refinement profile of Li$_2$La(TaTi)O$_7$ using the $Cmcm$ model with both X-ray and neutron diffraction data, respectively.

The accurate determination of oxygen and lithium positions in Li$_2$La(TaTi)O$_7$ was performed using neutron diffraction. The limitations of laboratory powder X-ray diffraction in the study of light atoms such as lithium and oxygen should be noted. These limitations can lead to the observation of unrealistic distortions in the coordination environment of lithium. However, neutron diffraction can readily identify and study these light atoms. Table 1 lists the refined structural parameters for Li$_2$La(TaTi)O$_7$.

Interestingly, the A-site deficiency leads to a change in the space group of Li$_2$La(TaTi)O$_7$. The A-site deficient compound, Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$, does not show the orthorhombic peak splitting discussed above. This material has a tetragonal structure, with a space group $I4/mmm$, as shown in Fig. 2. The insets in this figure highlight the difference between the powder diffraction data for Li$_2$La(TaTi)O$_7$ and the A-site deficient Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$. The refined structural parameters for Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ are listed in Table 2.

In both parent and the A-site deficient compounds, the (Ta/Ti)O$_6$ octahedra form double-layer stacks by corner-sharing. The octahedra are distorted in both compounds. The La atoms are located in spaces within the stacks, while Li atoms reside in inter-stack spaces, as shown in Fig. 1. The Li atoms have a distorted tetrahedral coordination geometry and form a layer of edge-sharing tetrahedra between the octahedral stacks. As described later, the ionic conduction occurs through this lithium layer.

![Fig. 2](image2.png)  
Fig. 2 Rietveld refinement profile for powder X-ray diffraction data (a) Li$_2$La(TaTi)O$_7$ in the $Cmcm$ space group. (b) Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$ in the $I4/mmm$ space group. The black crosses represent experimental data, red line shows the fit, vertical tick marks show the Bragg peak positions, and the lower blue line is the difference plot.

![Fig. 3](image3.png)  
Fig. 3 Neutron diffraction Rietveld refinement profile for Li$_2$La(TaTi)O$_7$ in the $Cmcm$ space group.
Table 1 Refined structural parameters from Rietveld refinement with powder neutron diffraction data for Li$_2$La(TaTi)O$_7$. Space group Cmcm, a = 18.2384(5), b = 5.5126(2), c = 5.4996(2) Å, $R_p = 0.0440$, w$R_p = 0.0185$

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$U_{iso}$</th>
<th>Multiplicity</th>
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<td>0.7543(9)</td>
<td>0.25</td>
<td>0.002(3)</td>
<td>8</td>
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</tr>
<tr>
<td>Ti1</td>
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<td>0.7543(9)</td>
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<td>0.002(3)</td>
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<tr>
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<tr>
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</tbody>
</table>

Table 2 Refined structural parameters from Rietveld refinement with powder X-ray diffraction data for Li$_{1.8}$La(Ta$^{1.2}$Ti$^{0.8}$)O$_7$. Space group: I4/mmm, $a = 3.8986(0)$ Å, $c = 18.4520(3)$ Å, $R_p = 0.0736$, w$R_p = 0.0977$

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$U_{iso}$</th>
<th>Multiplicity</th>
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<tr>
<td>Ti2</td>
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<td>0.032(4)</td>
<td>8</td>
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</table>

The scanning electron microscopy data in Fig. 4 show that the microstructure of Li$_2$La(TaTi)O$_7$ remains nearly unaffected due to A-site deficiency. However, the ionic conductivity improves significantly, as discussed below.

### Lithium-ion conductivity

Variable temperature electrochemical impedance spectroscopy shows an increase in ionic conductivity as a function of temperature, as listed in Table 3. The impedance plots of Li$_2$La(TaTi)O$_7$ in the Nyquist plane in the temperature range 100–400 °C are presented in Fig. 5. The observed spike (tail) in the low-frequency region indicates the blocking of mobile lithium ions at the electrodes. The appearance of a semicircle in the high-frequency region was observed only at temperatures above 100 °C. There was no semicircle and measurable conductivity at room temperature, which can be due to the restriction of lithium ion mobility, since all lithium sites between the layers are occupied, as seen from the crystal structure in Fig. 1. A similar behavior, i.e., lack of room temperature conductivity, was reported for the layered perovskite Li$_2$Sr$_{1.5}$Nb$_3$O$_{10}$, even though some defects had been introduced in the crystal structure. We will show later that, for Li$_2$La(TaTi)O$_7$, lack of ionic conductivity at room temperature can be overcome by introducing vacancies in some lithium sites. The increase in conductivity with temperature is expected due to an increase in mobility of ions and a decrease in grain boundary resistance.

Table 3 Variable temperature conductivity of Li$_2$La(TaTi)O$_7$ and Li$_{1.8}$La(Ta$^{1.2}$Ti$^{0.8}$)O$_7$

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Li$_2$La(TaTi)O$_7$</th>
<th>Li$<em>{1.8}$La(Ta$</em>{1.2}$Ti$_{0.8}$)O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>N/A</td>
<td>$4.08611 \times 10^{-9}$</td>
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<tr>
<td>100</td>
<td>$1.82184 \times 10^{-8}$</td>
<td>$2.92558 \times 10^{-7}$</td>
</tr>
<tr>
<td>200</td>
<td>$1.78362 \times 10^{-7}$</td>
<td>$1.45776 \times 10^{-5}$</td>
</tr>
<tr>
<td>300</td>
<td>$3.50991 \times 10^{-6}$</td>
<td>$1.83973 \times 10^{-4}$</td>
</tr>
<tr>
<td>400</td>
<td>$2.55058 \times 10^{-5}$</td>
<td>$1.034851 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The two processes correspond to contributions from the bulk and grain boundary. To estimate these contributions, we built an electrical model as seen in the inset of Fig. 6. Here the first RC unit ($R_1 = 1.71 \times 10^5$ Ω and $CPE1 = 5.9 \times 10^{-11}$ F) corresponds to the bulk (grain), and the second set ($R_2 = 1.2 \times 10^6$ Ω and $CPE2 = 3.0 \times 10^{-10}$ F) corresponds to the grain boundary. As expected, the respective capacitance values for the bulk, grain boundary and electrode (CPE3) are in the order of $10^{-14}$, $10^{-10}$ and $10^{-7}$ F, respectively. The same model can be used for fitting at 300 °C.

**Fig. 4** Scanning electron microscopy data for (a) Li$_2$La(TaTi)O$_7$ and (b) Li$_{1.8}$La(Ta$_{1.2}$Ti$_{0.8}$)O$_7$. 

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J. Mater. Chem. A
leading to smaller resistances (R) for both the bulk, $2.67 \times 10^4 \ \Omega$, and grain boundary, $3.94 \times 10^4 \ \Omega$, compared to the resistances at 200 °C, which were discussed above.

The importance of composition design is demonstrated when Li$_2$La(TaTi)O$_7$ is compared to another compound with the same structure-type, Li$_2$SrTa$_2$O$_7$. The conductivity of Li$_2$SrTa$_2$O$_7$ has been reported at 300 °C. At this temperature, Li$_2$SrTa$_2$O$_7$ shows a conductivity of $5.0 \times 10^{-7} \ \text{S cm}^{-1}$. However, at the same temperature, the conductivity value for Li$_2$La(TaTi)O$_7$ is $3.5 \times 10^{-6} \ \text{S cm}^{-1}$, one order of magnitude greater than that of Li$_2$SrTa$_2$O$_7$. The enhanced conductivity of Li$_2$La(TaTi)O$_7$ can be due to the smaller ionic radii of the A-site and B-site cations in this material’s composition, leading to shorter hopping distances for Li$^+$. The distance between two neighboring Li-sites is as short as ~2.75 Å, while the same distance for Li$_2$SrTa$_2$O$_7$ is ~2.80 Å. This indicates the success of our strategy in designing Li$_2$La(TaTi)O$_7$ composition.

We also examined the effect of creating vacant sites in the Li layer by synthesizing Li$_{1.8}$La$_{0.2}$Ti$_{0.8}$O$_7$. This was done in an attempt to allow lithium ions to move more freely in the interstack spaces. In this material, 10% Li vacancies were introduced and charge neutrality was maintained by changing the Ta/Ti ratio from 1/1 to 1.2/0.8. This lithium deficient compound showed significantly enhanced ionic conductivity compared to the parent Li$_2$La(TaTi)O$_7$. The conductivity values, derived from the intercept with the real axis in the low frequency region of the Nyquist plot, are listed in Table 3. As seen here, the conductivity of the Li-deficient compound is one to two orders of magnitude greater than that of Li$_2$La(TaTi)O$_7$ at different temperatures, reaching $1.08 \times 10^{-3} \ \text{S cm}^{-1}$ at 400 °C. Note that the Li-deficient compound shows measurable conductivity and a semicircle in the Nyquist plot even at room temperature, as shown in Fig. 7. This semicircle, at both 25 °C and 100 °C, could be described by three RC elements (Fig. 8), similar to some other ionic conductors such as lithium lanthanum titanate perovskite, where the third RC element has been attributed to electrode interface. This electrode RC unit has resistance and capacitance values of $R_3 = 1.23 \times 10^7 \ \Omega$ and CPE3 = $1.40 \times 10^{-7} \ \text{F}$, respectively. The first ($R_1 = 1.15 \times 10^6 \ \Omega$ and CPE1 = $5.099 \times 10^{-11} \ \text{F}$) and second ($R_2 = 5.37 \times 10^5 \ \Omega$ and CPE2 = $6.53 \times 10^{-10} \ \text{F}$) RC elements correspond to the bulk and grain boundary, respectively. As expected, all three resistance contributions at 100 °C are smaller than those at 25 °C, where the bulk, grain boundary and electrode interface resistances are
4.33 \times 10^6, 2.19 \times 10^7 and 4.10 \times 10^7 \, \Omega, respectively. As seen in Fig. 5 and 7, for both compounds, the semicircles gradually shrink with an increase in temperature and the contributions from the bulk and grain boundary cannot be separated beyond 300 °C for the parent compound and above 100 °C for the Li-deficient material. The disappearance of semicircles due to the increase in temperature is commonly observed in ionic conductors such as garnets.\textsuperscript{35,37,39,40}

As shown in Table 3, the conductivity of the Li-deficient compound increases significantly above room temperature, rising from 4.08 \times 10^{-9} to 1.08 \times 10^{-3} \, \text{S} \, \text{cm}^{-1} at 400 °C. The activation energy for the rise in conductivity as a function of temperature can be obtained using the Arrhenius equation for thermally activated conductivity:\textsuperscript{41–43}

\[
\sigma T = \sigma_0 e^{-\frac{E_a}{kT}}
\]

where \(\sigma_0\) is the pre-exponential factor, characteristic of the material and \(E_a\), \(k\) and \(T\) are the activation energy, the Boltzmann constant, and the absolute temperature, respectively. The Arrhenius plots of the electrical conductivity of both Li\(_2\)La(TaTi)O\(_7\) and the Li-deficient Li\(_{1.8}\)La(Ta\(_{1.2}\)Ti\(_{0.8}\))O\(_7\) are shown in Fig. 9. The activation energy \((E_a)\) decreases when vacancies are introduced in the lithium layers. Activation energies are 0.61 eV and 0.57 eV for Li\(_2\)La(TaTi)O\(_7\) and Li\(_{1.8}\)La(Ta\(_{1.2}\)Ti\(_{0.8}\))O\(_7\), respectively.

The differences between the ionic conductivity of the A-site deficient and the parent compound, and the large increase in

\[
\text{Fig. 7 Nyquist impedance plots of Li}_{1.8}\text{La(Ta}_{1.2}\text{Ti}_{0.8})\text{O}_7.
\]

\[
\text{Fig. 8 Typical fit to the Nyquist impedance plot of Li}_{1.8}\text{La(Ta}_{1.2}\text{Ti}_{0.8})\text{O}_7 at 100 °C.
\]

\[
\text{Fig. 9 Arrhenius plots of Li}_2\text{La(TaTi)}\text{O}_7 (red) and Li}_{1.8}\text{La(Ta}_{1.2}\text{Ti}_{0.8})\text{O}_7 (blue).
\]
conductivity due to A-site vacancies indicate that the pathway for lithium ion conduction is through the inter-stack layer. As discussed below, the lithium conduction pathway is confirmed by a computational study.

Density functional theory calculations

To study the lithium ion diffusion, a DFT optimized structure was needed. Therefore, the Li$_2$La(TaTi)O$_7$ crystal structure was optimized. Various configurations with different Ta/Ti distributions were considered. The crystalline structure for each configuration was fully relaxed and the lattice constants corresponding to each configuration were optimized. The optimized structures and the total energies corresponding to each configuration are shown in Fig. 10. It was found that the optimized lattice constants for various configurations were the same and within 1% of the values obtained using neutron diffraction experiments, indicating an excellent match. From comparing the total energies for different distributions of Ta and Ti, it was found that several configurations had similar energies, but among them the first configuration shown in Fig. 10 was the most favorable. This optimized structure was used for electronic density of states (DOS), electronic band structure, and Li-diffusion studies. In this configuration all Ta and Ti atoms are alternately distributed within the layers and between layers such that identical metal atoms are separated from each other. A truly randomized distribution of Ta and Ti, similar to that determined from neutron diffraction, would require performing the calculations over hundreds or even thousands of unit cells, which is impractical.

The DOS and band structure of the optimized Li$_2$La(TaTi)O$_7$ configuration are shown in Fig. 11, and the system shows a large band gap of 2.0276 eV.

To study the degree of Li mobility in the optimized Li$_2$La(TaTi)O$_7$ structure, the diffusion energy barrier was calculated along b- and c-axes, as shown in Fig. 12. The diffusion energy barrier is defined as the relative energy at a particular site along the diffusion pathway with respect to the energy at the initial position. The corresponding energy barriers for displacement of lithium by different distances from the original

![Fig. 10](image-url) DFT optimized structures for Li$_2$La(TaTi)O$_7$ and their corresponding total energy per unit cell. The top left configuration has the lowest energy. Gray and blue octahedra represent TaO$_6$ and TiO$_6$. Lithium atoms are shown as small spheres between the stacks.

![Fig. 11](image-url) Calculated electronic band structure (left panel) and DOS (right panel) of the optimized Li$_2$La(TaTi)O$_7$ structure. The red dashed line indicates the Fermi energy, and the inset shows the Brillouin zone with special high symmetry k points.
Fig. 12 Energy barrier as a function of displacement of Li atoms from their original sites. The insets show the structures at the maximum and minimum energy barriers.

The diagonal Li diffusion in the bc plane was also investigated, leading to huge energy barriers, in the order of 38 eV. Therefore, it is clear that lithium ions cannot diffuse in the diagonal direction.

The diffusion pathway is therefore along the b and c directions. The main barrier to the Li diffusion along these pathways is the proximity of Li to O atoms at some positions along the conduction pathway. These results reveal that such short distances in inter-stack spaces should be eliminated in order to design structures with enhanced Li mobility. One way to achieve this goal can be the incorporation of a small amount of a large cation, such as Sr$^{2+}$ or La$^{3+}$, in inter-layer spaces, which can push the layers apart and open more space between them. Although, this will lead to a slightly lower Li concentration in inter-layer spaces, the formation of wider channels can prevent close interactions between Li and O atoms, and can increase Li-ion conductivity.

Conclusions

The study of lithium-ion mobility in Li$_2$La(TaTi)O$_7$ and its A-site deficient analogue shows the potential of Ruddlesden–Popper oxides for Li-ion conductivity. The enhanced ionic conductivity of Li$_2$La(TaTi)O$_7$ and further improvement due to the A-site deficiency indicate the success of two strategies: (a) designing compositions where Li hopping distances are shortened. (b) Creating defects in the lithium layer to enhance the mobility of lithium ions. The latter also indicates that lithium-ion conductivity pathway is within the inter-stack spaces. This is confirmed by DFT calculations which show the direction of the pathways for lithium mobility and determine the energy barriers for each conduction pathway. These findings can be used for future research to design Ruddlesden–Popper oxides with enhanced lithium-ion conductivity.

Conflicts of interest

The authors declare no conflicts of interest.

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