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The structure of lithium garnets: cation disorder and clustering in a new family of fast Li\textsuperscript{+} conductors†

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The structure of the fast lithium-ion conducting garnets Li\textsubscript{5}La\textsubscript{3}M\textsubscript{2}O\textsubscript{12} (M = Ta, Nb) reveals Li\textsuperscript{3+} on both tetrahedral and octahedral sites and suggests that the latter are responsible for the observed Li\textsuperscript{+} mobility via a clustering mechanism.

Lithium garnets have recently been reported as potential solid electrolytes for operation in an all solid-state rechargeable lithium battery.\textsuperscript{1,2} These garnets, Li\textsubscript{5}La\textsubscript{3}M\textsubscript{2}O\textsubscript{12} (M = Ta, Nb), show activated lithium ion mobility which rivals that observed in the best ceramic batteries.\textsuperscript{3} All experimental approaches have employed X-ray powder diffraction patterns collected from both samples contained intense peaks which could be indexed using a cubic unit cell, \(a \approx 12.8\) Å, typical of a garnet phase and a number of small peaks which suggested the presence of minority phases. In order to determine accurately the Li\textsuperscript{3+} position in these garnets neutron powder diffraction data were collected over the \(d\)-spacing range 0.5 \(\leq d\) Å \(\leq 8.0\) using the instrument Polaris at Rutherford Appleton Laboratories, Didcot. Data were collected from both compounds at room temperature and additional data sets were collected from Li\textsubscript{5}La\textsubscript{3}Ta\textsubscript{2}O\textsubscript{12} at 300 and 600 °C. The room temperature data showed that the majority phase (>94 wt%) in both samples exhibited systematic absences associated with the space group \(Ia\overline{3}d\). We found no Bragg intensity which required a reduction in the space group symmetry. Initial attempts to fit the data collected from Li\textsubscript{5}La\textsubscript{3}Ta\textsubscript{2}O\textsubscript{12} used a structural model in which the lithium occupied \(\frac{1}{3}\) of the octahedrally coordinated (48\text{a}) site. However this refinement failed to converge and resulted in a poor intensity match and the large residual fit parameters shown in Table 1.

An alternative model was employed in which the lithium was disordered with occupancies of \(\frac{1}{3}\) octahedral sites and \(\frac{1}{3}\) tetrahedral sites (24\text{d}). This structural model improved the fit but a significant intensity mismatch remained which could be readily eliminated by refining the lithium occupancies of these two sites.

<table>
<thead>
<tr>
<th>Li site occupancies</th>
<th>Oh</th>
<th>Td</th>
<th>M</th>
<th>(R_{wp}) (%)</th>
<th>(\chi^2)</th>
<th>Energy/eV\textsuperscript{b}</th>
<th>GII/v.u.\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{1}{3})</td>
<td>0</td>
<td>Ta</td>
<td>3.01\textsuperscript{a}</td>
<td>6.937\textsuperscript{c}</td>
<td>—</td>
<td>0.171</td>
<td></td>
</tr>
<tr>
<td>(\frac{1}{3})</td>
<td></td>
<td>Nb</td>
<td>4.44\textsuperscript{a}</td>
<td>15.69\textsuperscript{c}</td>
<td>5 035.6</td>
<td>0.156</td>
<td></td>
</tr>
<tr>
<td>(\frac{1}{3})</td>
<td>(\frac{1}{3})</td>
<td>Ta</td>
<td>2.17</td>
<td>3.593</td>
<td>—</td>
<td>0.151</td>
<td></td>
</tr>
<tr>
<td>(\frac{1}{3})</td>
<td>(\frac{1}{3})</td>
<td>Nb</td>
<td>3.07</td>
<td>7.507</td>
<td>5 137.0</td>
<td>0.138</td>
<td></td>
</tr>
<tr>
<td>(\frac{1}{3})</td>
<td>(\frac{1}{3})</td>
<td>Ta</td>
<td>0.433(\pm 1)</td>
<td>0.802(\pm 4)</td>
<td>1.272</td>
<td>0.4376</td>
<td>0.119</td>
</tr>
<tr>
<td>(\frac{1}{3})</td>
<td>(\frac{1}{3})</td>
<td>Nb</td>
<td>0.414(\pm 1)</td>
<td>0.836(\pm 4)</td>
<td>2.35</td>
<td>4.376</td>
<td>0.112</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Failed to reach convergence. \textsuperscript{b} Calculated using GULP. No suitable potential is available for Ta\textsuperscript{3+}. \textsuperscript{c} Global Instability Index calculated using Soft BVS.\textsuperscript{d} v.u. = valence units.
with the constraint that the unit cell contained 5Li⁺ per formula unit. The lithium on the 48g site refined to give highly anisotropic displacement parameters indicating that the scattering intensity was disordered along a line between the opposing faces of the octahedron which are shared with neighbouring tetrahedral LiO₄ units. Therefore the refinement was modified to allow the octahedrally coordinated lithium to move off the 48g site and the final refinement employed a model in which the octahedral lithium was disordered with the majority of the lithium displaced away from one shared polyhedral face and towards the opposite linking face. The structural parameters are summarised in Table 2 and a fitted diffraction pattern is shown in Fig. 2.

The lithium occupancies of the tetrahedra (0.802(4)) and octahedra (0.43(2)) imply that face-sharing octahedral and tetrahedral pairs can be occupied simultaneously giving a mean Li···Li separation of only 1.962(3) Å. The majority of lithium on the octahedral site is displaced thus splitting the Li···Li distance to 1.500(15) and 2.381(11) Å. The latter is a physically acceptable value but the former, and the mean value, are clearly too short. The average structure does not exist within the material over the length scale of a unit cell but instead represents clustering of regions of tetrahedral and octahedral Li, reminiscent of the structure of Lisicon.⁴ The size of such domains will be limited by the charge separation associated with the formation of (Td) [Li₃La₃Ta₂O₁₂]²⁻ and (Oh) [Li₈La₃Ta₂O₁₂]³⁺ regions. The surface of a domain containing lithium on the octahedral site must necessarily share faces with occupied tetrahedral sites in a neighbouring domain and the electrostatic repulsion associated with such a short distance is reduced by the observed displacement of some of the octahedral lithium away from one of the shared faces. The LiO₆ octahedra are linked by shared edges which have irregular Li···Li distances. The shortest cation separations are associated with the longest oxide–oxide distances i.e. when the Li⁺ cations are closest the anions provide the least effective screening, as shown in Fig. 3. This suggests that Li⁺ hopping between these sites will be relatively facile. The connectivity between these sites gives rise to a 3-dimensionally connected Li⁺ pathway. Both the elevated temperature data sets and data collected from Li₅La₃Nb₂O₁₂ at room temperature showed the structures were not significantly different and the occupancies of the tetrahedral and octahedral Li⁺ sites all refined to similar values in each data set.

The refined structures were used as input for a series of lattice energy calculations using the General Utility Lattice Program (GULP)¹⁰ and literature values for interatomic potentials.¹¹,¹² The minimised lattice energies, collected in Table 1, show that disorder of Li⁺ over both tetrahedral and octahedral sites increases the lattice stability by ca. 1.7% compared to a structure which accommodates lithium wholly on the octahedral sites.

The observation of mixed Li⁺ coordination environments and clustering shows that the lithium garnets are more complex than previously described. The structural data suggest that the Li⁺ mobility arises from the octahedral sites which contain a minority lithium occupancy.

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Notes and references