
This version is available at https://strathprints.strath.ac.uk/10286/

Strathprints is designed to allow users to access the research output of the University of Strathclyde. Unless otherwise explicitly stated on the manuscript, Copyright © and Moral Rights for the papers on this site are retained by the individual authors and/or other copyright owners. Please check the manuscript for details of any other licences that may have been applied. You may not engage in further distribution of the material for any profitmaking activities or any commercial gain. You may freely distribute both the url (https://strathprints.strath.ac.uk/) and the content of this paper for research or private study, educational, or not-for-profit purposes without prior permission or charge.

Any correspondence concerning this service should be sent to the Strathprints administrator: strathprints@strath.ac.uk
The structure of lithium garnets: cation disorder and clustering in a new family of fast Li⁺ conductors†

Edmund J. Cussen

Received (in Cambridge, UK) 17th October 2005, Accepted 2nd November 2005

The structure of the fast lithium-ion conducting garnets Li₃LaₓMₓO₁₂ (M = Ta, Nb) reveals Li⁺ on both tetrahedral and octahedral sites and suggests that the latter are responsible for the observed Li⁺ mobility via a clustering mechanism.

Lithium garnets have recently been reported as potential solid electrolytes for operation in all solid-state rechargeable lithium battery.¹ ² These garnets, Li₃LaₓMₓO₁₂ (M = Ta, Nb), show activated lithium ion mobility which rivals that observed in the best crystalline Li⁺ conductors and, most importantly, the garnets are chemically stable when exposed to moisture, air and metallic lithium. Lithium-containing garnets have been known for over 35 years and a number of small peaks which suggested the presence of minority phases. In order to determine accurately the Li⁺ position in these garnets neutron powder diffraction data were collected over the d-spacing range 0.5 ≤ dÅ ≤ 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 Li₃LaₓTa₂O₁₂ 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 Ia3d. We found no Bragg intensity which required a reduction in the space group symmetry. Initial attempts to fit the data collected from Li₃LaₓTa₂O₁₂ used a structural model in which the lithium occupied ½ of the octahedrally coordinated (48d) 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 ½ octahedral sites and ½ tetrahedral sites (24d). 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 1 The fit parameters, lattice energies and global instability indices of a range of structural models for Li₃LaₓMₓO₁₂ at room temperature

<table>
<thead>
<tr>
<th>Li site occupancies</th>
<th>Oh</th>
<th>Td</th>
<th>M</th>
<th>Rwp (%)</th>
<th>χ²</th>
<th>Energy/eV</th>
<th>GII/v.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>½Ta</td>
<td>0</td>
<td>Ta</td>
<td>3.01°</td>
<td>6.937°</td>
<td>—</td>
<td>0.171</td>
<td></td>
</tr>
<tr>
<td>½Ta</td>
<td>0</td>
<td>Nb</td>
<td>4.44°</td>
<td>15.69°</td>
<td>5</td>
<td>0.156</td>
<td></td>
</tr>
<tr>
<td>½Nb</td>
<td>0</td>
<td>Ta</td>
<td>2.17</td>
<td>3.593</td>
<td>—</td>
<td>0.151</td>
<td></td>
</tr>
<tr>
<td>½Nb</td>
<td>0</td>
<td>Nb</td>
<td>3.07</td>
<td>7.507</td>
<td>5</td>
<td>0.138</td>
<td></td>
</tr>
<tr>
<td>0.433(1) 0.802(4)</td>
<td>Ta</td>
<td>1.72</td>
<td>2.269</td>
<td>—</td>
<td>0.139</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.414(1) 0.836(4)</td>
<td>Nb</td>
<td>2.35</td>
<td>4.376</td>
<td>5</td>
<td>0.129</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Electronic supplementary information (ESI) available: Full details of the synthetic methods, lattice energy calculations, crystal structures and Rietveld refinements. See DOI: 10.1039/b514640b
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 1.9626(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. The size of such domains will be limited by the charge separation associated with the formation of (Td)⁶LiO₄₆⁻ and (Oh) [Li₆La₃Ta₂O₁₂]⁺ 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 oxide−oxide distances (GULP) and literature values for interatomic potentials. The refined structures were used as input for a series of lattice energy calculations using the General Utility Lattice Program (GULP) and literature values for interatomic potentials. 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.

The author is grateful to The Royal Society for the provision of a University Research Fellowship and to Dr R. Smith at RAL for assistance with the neutron scattering experiments and Dr J. D. Gale for providing the GULP code.

Notes and references