

Slowly but Surely—Pathways of Ultraslow Lithium Diffusion in γ -LiAlO₂

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The ultraslow lithium-ion conductor γ -LiAlO₂ is used as substrate for epitaxial growth of III-V semiconductors, as coating material, and as additive in electrolytes. Our research on this material aims at gaining insight into the most basic principles of lithium diffusion in solids.

In γ -LiAlO₂, the metal ions are tetrahedrally coordinated by oxygen; each LiO₄ shares an edge with an AlO₄ tetrahedron. These pairs are connected *via* common vertices to form a 3D network, in which the lithium ions may diffuse (as suggested by ⁷Li-NMR and conductivity measurements).[1]

Rietveld refinements of powder neutron-diffractograms acquired up to 1500 °C allowed modelling of Debye-Waller factors including anharmonic terms for the lithium ion. Probability-density functions (PDFs) and one-particle potentials (OPPs) were derived.

At high temperatures, the PDF sprawls through two tetrahedron boundaries into octahedral voids that form channels along the principal axes (see Fig. 1). The OPP landscape shows an activation energy of 1.25 eV for the diffusion into channels and barriers of ca. 1.5 eV/1.7 eV for undulated paths along $\langle 100 \rangle / [001]$. Direct jumps between two neighboring lithium sites are forbidden.

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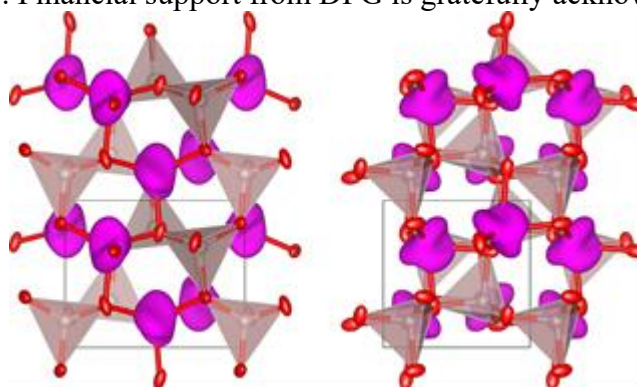


Figure 1: Crystal structure of γ -LiAlO₂ at 1202 °C (left: view along $[01; \bar{0}]$, right: view along $[001]$). Pink: lithium as isosurface plot of PDF, brown: aluminium, red: oxygen as ellipsoids for 50 % probability.

References

- [1] a) S. Indris, P. Heitjans, R. Uecker, T. Bredow, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *74*, 245120; b) S. Indris, P. Heitjans, R. Uecker, B. Roling, *J. Phys. Chem. C* **2012**, *116*, 14243–14247.