A study on the influence of crystal structure and its effects on Li diffusion in $Li_{0.29}La_{0.57}TiO_3$ single crystal grown by optical floating zone technique.

S. Uthayakumar[1,3] *, D.G. Porter[2], T.J. Willis[1], A. Ewings[3], J. P. Goff[1]
* s.uthayakumar@rhul.ac.uk

[1]Department of Physics, Royal Holloway, University of London, Egham, TW20 0EX, United Kingdom.
[2]Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, United Kingdom.
[3]ISIS Pulsed Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire OX11 0QX, United Kingdom.

Solid-state lithium-ion electrolytes have recently been proposed as a future development for battery technology, with the benefits of enhanced stability and safety over the currently used organic electrolytes [1]. $Li_{0.29}La_{0.57}TiO_3$ (LLTO) has attracted much attention due to its high Li-ion conductivity [2] but despite over two decades of studies, the crystal structure and behaviour of this system are still not fully explained, due to the complexity of the solid-solution of La ions in a distorted perovskite structure and the difficulty in measuring low atomic number Li ions. LLTO exhibits a perovskite structure where TiO_6 octahedra are separated on a cubic lattice by a solid solution of La ions and mobile Li Ions. Lithium is expected to diffuse through La-free pathways, although it is evidenced that Li ions do not hop between vacant La sites but reside away from the high symmetry sites [3]. Consequently, the La-rich layers tend to block lithium-ion conduction and such conduction pathways hinder the kinetics of ionic transport. Therefore, to achieve high ionic conductivity it is highly essential to get a deep insight into the relationship between the crystal structure and its diffusion mechanism. When LLTO is realized in polycrystalline form, the grain boundaries deteriorate the ionic conductivity by 2-3 orders of magnitude owing to its grain boundary resistance [4]. There is no clear consensus on the mechanism of the conduction pathway. The ambiguity is certainly due to the unavailability of high-quality bulk single crystals for atomic-scale studies by deploying emerging advanced characterization studies.

To mitigate, bulk single crystals of $Li_{0.29}La_{0.57}TiO_3$ were grown using a 4-lamp Optical floating zone technique. The successful optimization of growth parameters yielded high-quality single crystals. This has enabled us to perform a new class of experiments to study dynamics in this technologically important material which has not been reported so far. Through the studies, we investigated the relationship between the crystal structure and Li-ion conductivity for the first time using the I16 beamline at the Diamond light source. Our studies will highlight the importance of the I16 beamline to probe the structure, investigate the microscopic variation in phases and study the effects of Li ion diffusion by comparing the structure at different temperatures. The results of the growth and characterization will be presented in detail.

References

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