Fluoride induced cubic LLZO: Enhanced Li diffusion at low temperatures

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The lithium stuffed garnet $Li_7La_3Zr_2O_{12}$ (LLZO), when suitably doped, is a promising candidate material for use as a solid state electrolyte. While pure LLZO displays excellent thermal and mechanical stability, the ionic conductivity of Li is only significant at higher temperatures when the material transitions from tetragonal to cubic symmetry. Usually, stabilization of the cubic phase at lower temperatures is achieved *via* cation doping.[1,2] Anion doping of LLZO is rarely considered, but may present an interesting alternative route to stabilization of the cubic phase at lower temperatures.[3] Consequently, we have employed classical potentials-based simulation techniques to investigate the incorporation energy of fluoride anion defects into LLZO.

Extensive point defect calculations were performed using the Mott-Littleton method and the energy to incorporate fluoride ions was calculated to be 1.9 eV. The most favorable compensating mechanism that was identified was the generation of lithium ion vacancies,[2] which is also the compensating mechanism for doping with many cation species, suggesting stabilization of the cubic phase with fluoride defects would be possible.

Molecular dynamics (MD) calculations were used to analyze the phase stability of both pure and F-doped systems. Results showed a clear stabilization of the cubic phase when ~4% of oxygen sites were substituted with fluoride ions at all temperatures. Conversely, the pure system displayed a tetragonal-cubic phase transition at approximately 700 K in line with experimental transition temperatures.[3] These results support the use of fluoride doping to stabilize the cubic phase of LLZO, in accordance with the experimental paper by Cai *et al.*[3]

Additional MD simulations were also conducted to evaluate the lithium ion diffusion in both pure and F-doped systems. The pure LLZO system displayed a marked increase in diffusion once the material became cubic (i.e. above the phase transition temperature). The F-doped system however retains a linear profile across all temperatures, suggesting faster Li ion diffusion at lower temperatures (< 700 K) and comparable diffusion to pure cubic LLZO at higher temperatures (i.e. > 700 K).

Acknowledgements:
This work recognises the use of the "Hydra" and "Athena" High Performance Systems at Loughborough University and the ARCHER UK National Supercomputing Service.

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