Atomic-scale studies of structural and cation effects in fast-ion conductors

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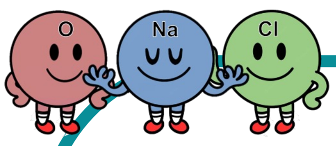

Anti-perovskite Na_3OCl

AIM: Atomistic modelling of Na_3OCl solid electrolyte to gain insight into:

- aliovalent doping to increase Na-vacancy concentration.
- Na-ion conduction mechanism and performance.

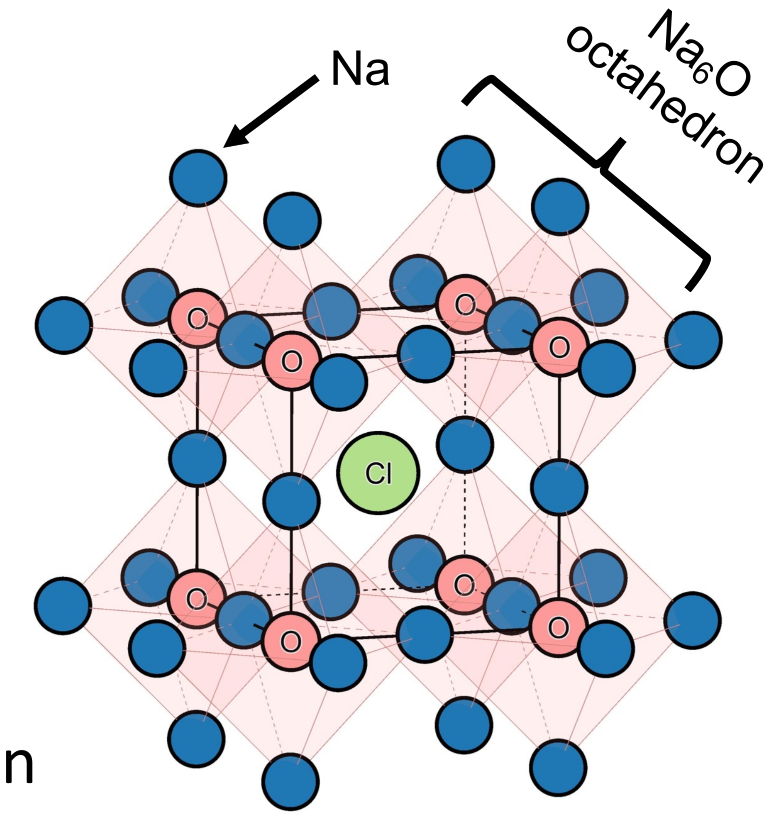

Fig. 1 – The anti-perovskite Na_3OCl structure.

Doping and Na-ion Conduction

- Favourable dopants: Mg^{2+}, Ca^{2+}, Al^{3+} and Ga^{3+}
- Max. Na-ion cond. with Mg dopant
- Doped materials: higher activation energy (E_a) than undoped material → clustering

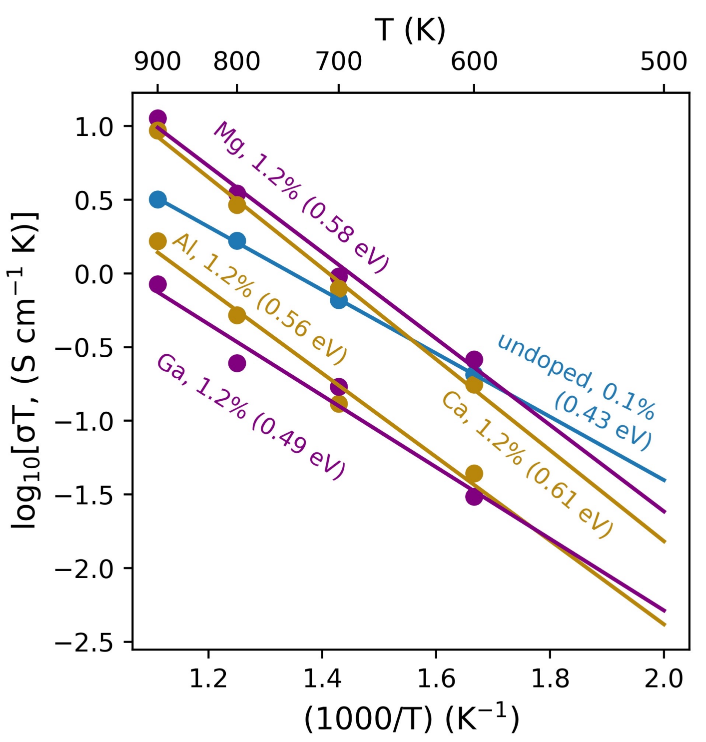

Fig. 2 – Temperature-dependent Na^+ conductivities for doped Na_3OCl with 1.2% vacancy concentration.

Defect Clustering Effects

- Doping → dopant-Na vacancy clustering → higher E_a than undoped with NaCl Schottky
- Clustering trend: $Al^{3+} > Ga^{3+} > Ca^{2+} > Mg^{2+}$
- Clustering minimised: ~1.2% vacancy conc.

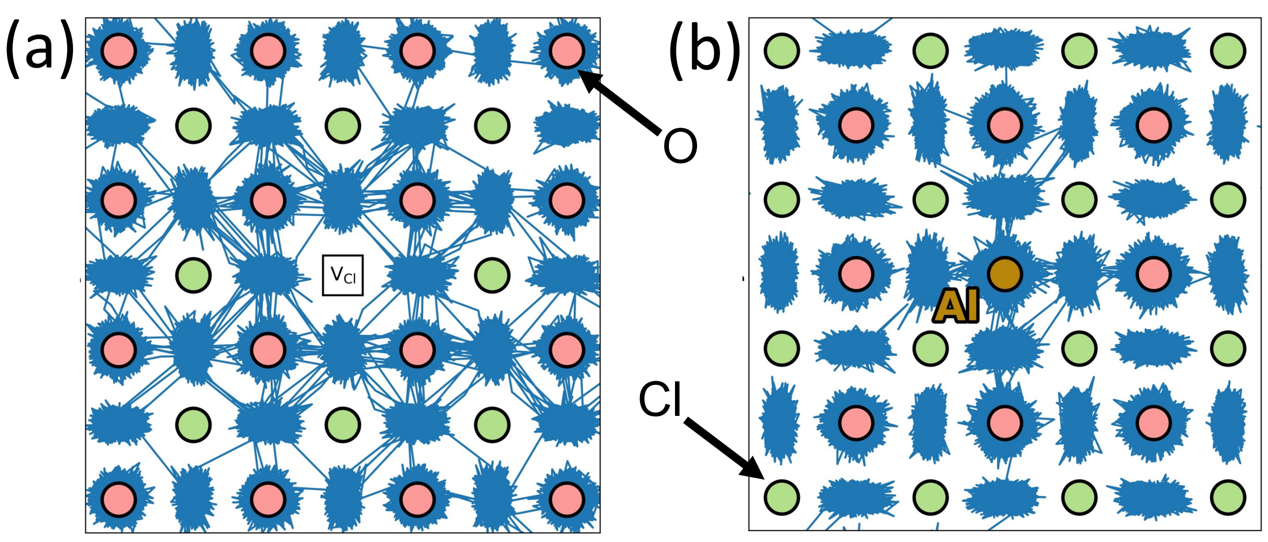

Fig. 3 – Na ion trajectories (blue) in (a) undoped and (b) Al-doped Na_3OCl.

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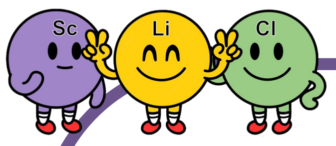

Li_3ScCl_6 Structures

AIM: Machine-learning assisted modelling of ccp-based Li_3ScCl_6 structures to gain insight into the effect of cation ordering on Li-ion conduction mechanism and performance.

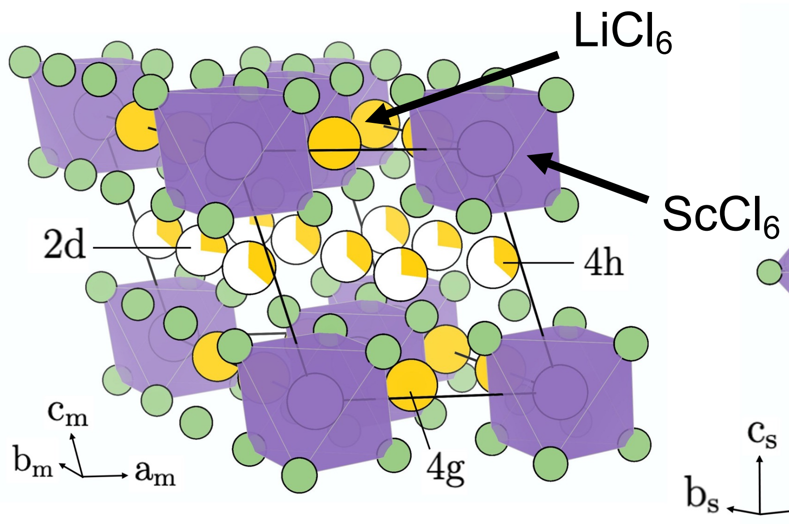

Fig. 4 – Layered monoclinic Li_3ScCl_6. (Bohnsack,1997)

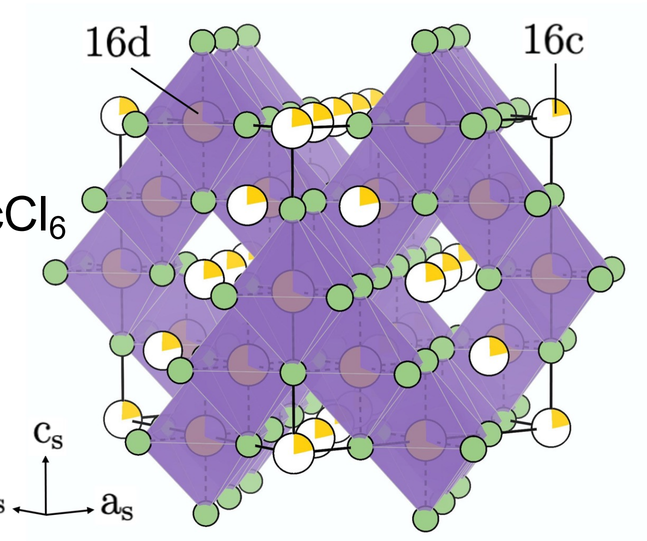

Fig. 5 – Spinel-like cubic Li_3ScCl_6. (Nazar, 2020)

Stacking Faults in Monoclinic

- ccp lattice + no C_3 symmetry in Sc-rich layers → 3 different stacking → stacking faults
- No significant energy penalty
- Stacking fault monoclinic can appear similar to cubic via spectroscopy

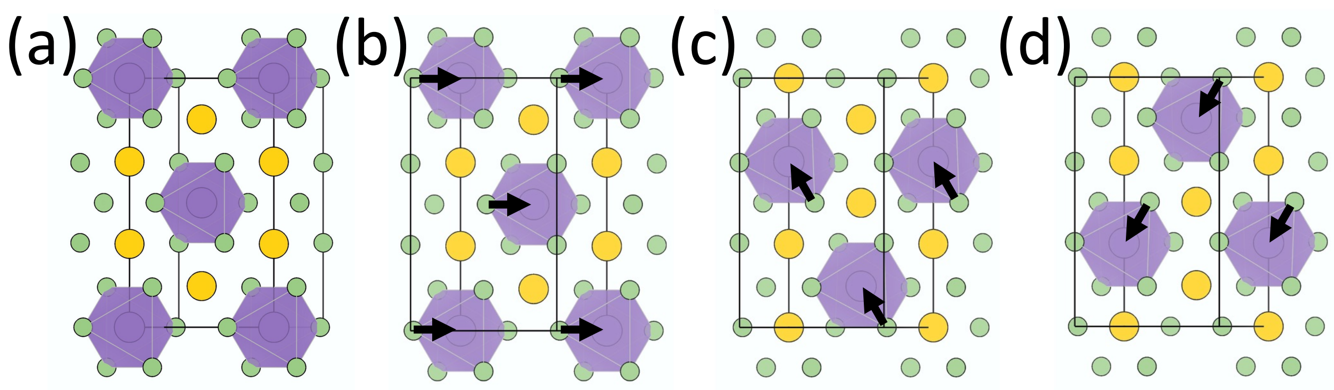

Fig. 6 – Stacking faults in layered monoclinic Li_3ScCl_6. (b-d) Three different stacking relative to (a) looking down the ccp layers.

Li-ion Conduction vs Structure

- Monoclinic with all levels of stacking fault (0, 33, 67, 100%): ~ 2.3 mS/cm RT cond. → all Li sites used for migration
- Cubic: ~ 1.3 mS/cm RT cond. → fully occupied Li sites highly trapping → 65% of Li immobile

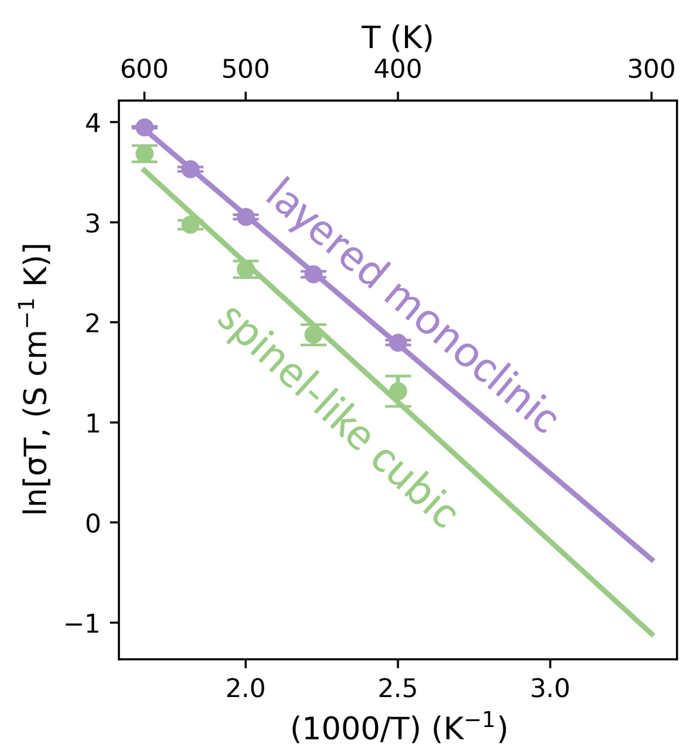

Fig. 7 – Temperature-dependent Li^+ conductivities for layered monoclinic and spinel-like cubic Li_3ScCl_6.