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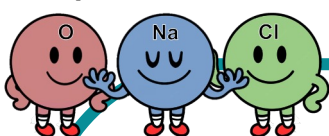


# Atomic-scale studies of structural and cation effects in fast-ion conductors

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## Anti-perovskite $\text{Na}_3\text{OCl}$

**AIM:** Atomistic modelling of  $\text{Na}_3\text{OCl}$  solid electrolyte to gain insight into:

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

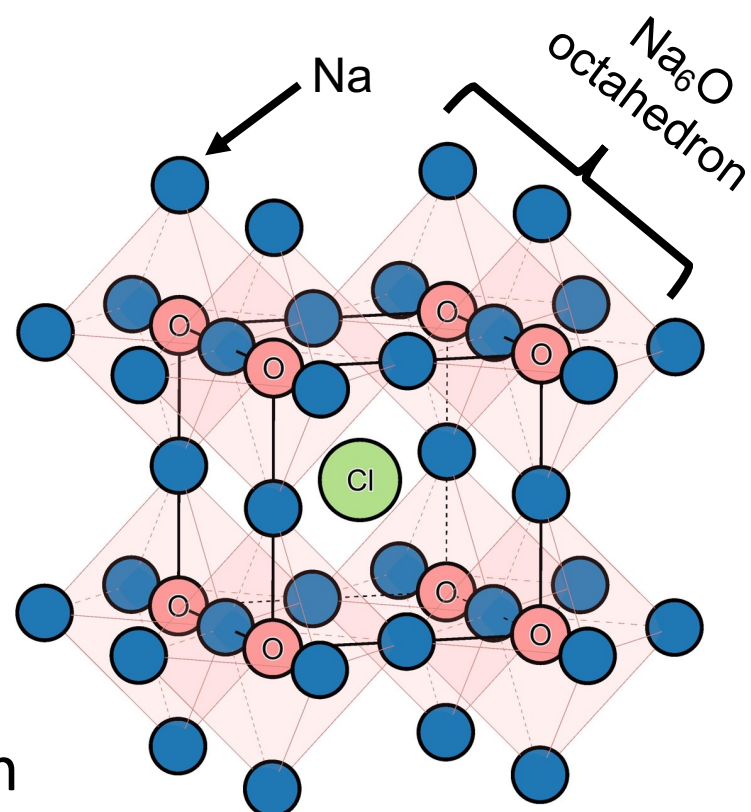


Fig. 1 – The anti-perovskite  $\text{Na}_3\text{OCl}$  structure.

## Doping and Na-ion Conduction

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

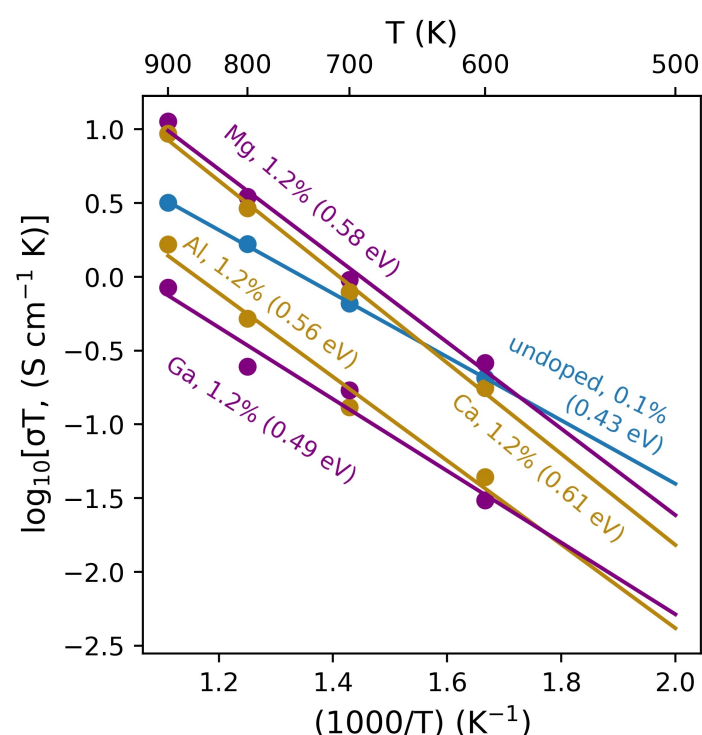


Fig. 2 – Temperature-dependent  $\text{Na}^+$  conductivities for doped  $\text{Na}_3\text{OCl}$  with 1.2% vacancy concentration.

## Defect Clustering Effects

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

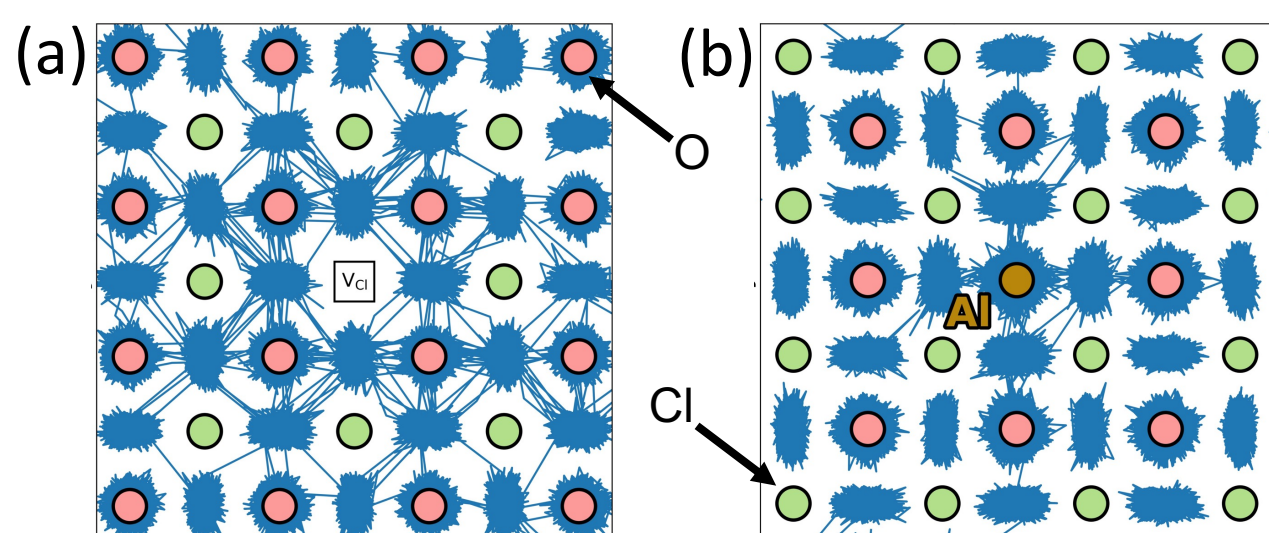


Fig. 3 – Na ion trajectories (blue) in (a) undoped and (b) Al-doped  $\text{Na}_3\text{OCl}$ .

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## $\text{Li}_3\text{ScCl}_6$ Structures

**AIM:** Machine-learning assisted modelling of ccp-based  $\text{Li}_3\text{ScCl}_6$  structures to gain insight into the effect of cation ordering on Li-ion conduction mechanism and performance.

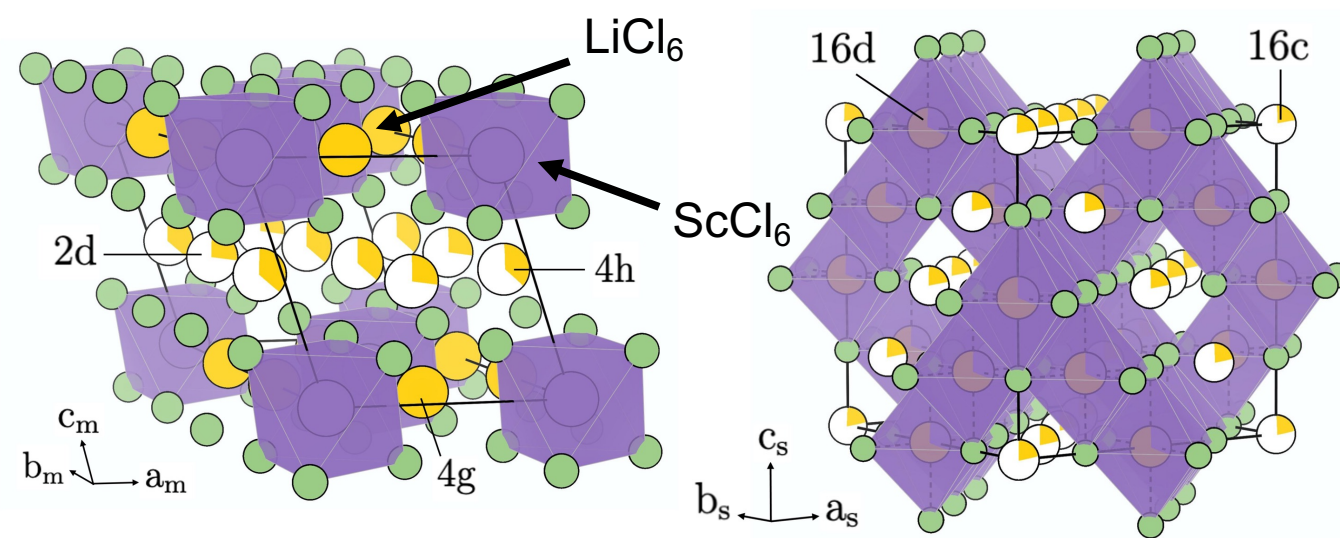


Fig. 4 – Layered monoclinic  $\text{Li}_3\text{ScCl}_6$ . (Bohnsack, 1997)

Fig. 5 – Spinel-like cubic  $\text{Li}_3\text{ScCl}_6$ . (Nazar, 2020)

## Stacking Faults in Monoclinic

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

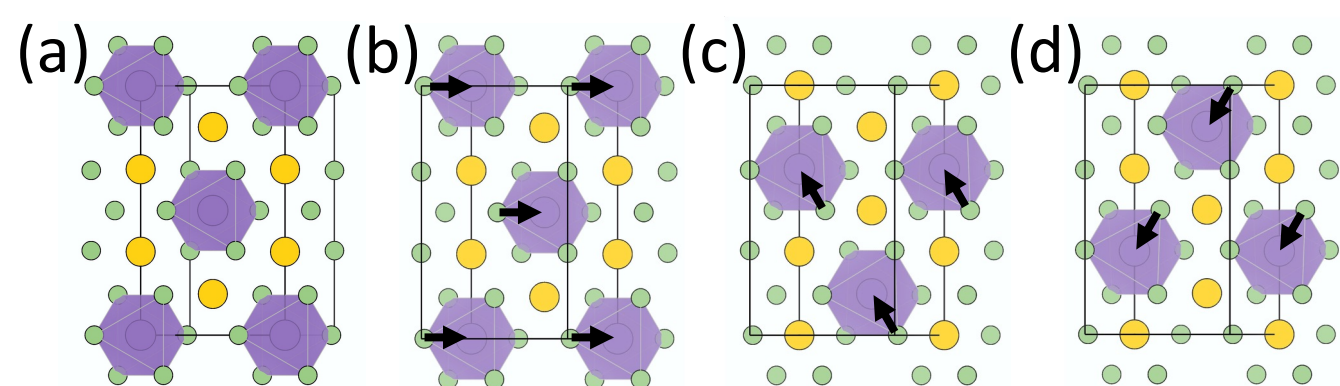


Fig. 6 – Stacking faults in layered monoclinic  $\text{Li}_3\text{ScCl}_6$ . (b-d) Three different stacking relative to (a) looking down the ccp layers.

## Li-ion Conduction vs Structure

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

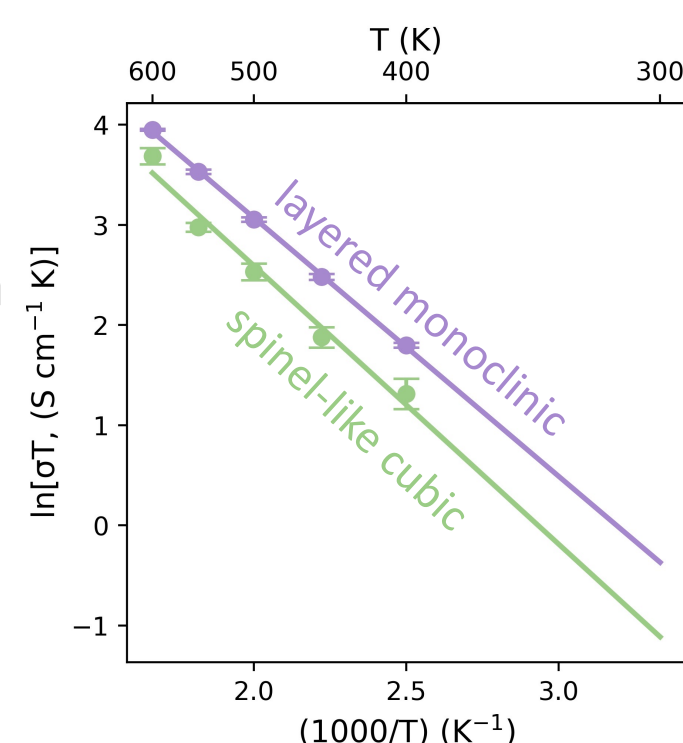


Fig. 7 – Temperature-dependent  $\text{Li}^+$  conductivities for layered monoclinic and spinel-like cubic  $\text{Li}_3\text{ScCl}_6$ .