Atomic-scale investigation of doping effects in the anti-perovskite Na3OCl sodium-ion battery material

Solid-state batteries present potential advantages over their liquid-based electrolyte equivalents, including enhanced safety and increased energy density. In the search for novel solid electrolytes, the anti-perovskite family of materials are attracting growing interest. However, while there is significant work on Li-rich anti-perovskites, their Na-based counterparts and the atomistic effects of aliovalent doping on these materials are not fully characterised. Here, we investigate the effects on Na-ion conductivity of doping with divalent (Mg, Ca, Sr and Ba) and trivalent cations (Al and Ga), and of possible dopant-vacancy clustering in the anti-perovskite Na3OCl by employing atomistic simulation techniques. Our results highlight the potential of Mg2+, Ca2+, Al3+ and Ga3+ doping due to their favourable incorporation and increased Na-ion vacancy concentration. Local defect clustering and binding energies are analysed, and such effects inhibit Na-ion conductivity in the doped Na3OCl solid electrolyte at operating temperatures. These results provide a framework to guide future work on anti-perovskites to enhance their solid electrolyte properties.