SODIUM-RICH ANTIPEROVSKITE STUDIES

Modern studies relating to conductivity

LEGEND: EXP. | DFT DEF. | PB DEF. | DFT NEB | PB NEB | DFT AIMD | PB MD

PAPER	FOCUS	MATERIALS	SYNTHESIS/MODEL	CONCLUSIONS
Structural manipulation approaches towards enhanced sodium ionic conductivity in Na-rich antiperovskites WANG, 2015	Developing a facile and timesaving synthetic route; improving conductivity of antiperovskite via alio- and isovalent doping	$Na_3OCl_{1-x}Br_x$ (x = 0 – 1) $Na_3OBr_{1-x}I_x$ (x = 0 – 1) $Na_{2.9}M_{0.05}OBr_{0.6}I_{0.4}$ (M = Ca, Sr) Na_3OX (X = Cl, Br, I)	Solid-state reaction + heating @ 350 °C for 3h CASTEP for NEB	Facile, timesaving route successful; alio- and isovalent doping is a promising mean of increasing conductivity: NSOBI in the mS/cm range @ 200 °C
Sodium ion transport mechanisms in antiperovskite electrolytes Na_3OBr and Na_4OI_2: an in situ neutron diffraction study ZHU, 2016	Understanding the sodium transport pathway in bulk and layered antiperovskites, via neutron diffraction and maximum entropy method	Na_3OBr Na_4OI_2 Na_3OBr Na_4OI_2	Solid-state reaction + heating @ 400 °C for 4h CASTEP for NEB	Main sodium transport pathway between nearest sodium ions in Na_6O octahedra (both cubic and layered); in layered I^- ions act as bridges between octahedra
Experimental and computational evaluation of a sodium-rich anti-perovskite for solid state electrolytes NGUYEN, 2016	Increase ionic conductivity in antiperovskites via a post-processing method, spark plasma sintering (SPS)	Na_3OBr Na_3OBr	Solid-state reaction + heating @ 450 °C for 24h, then SPS VASP for DEFECTS	SPS reduces interfacial impedance and activation energy, but conductivity in 10^{-7} S/cm range, due to lack of defects
A first principle study of the phase stability, ion transport and substitution strategy for highly ionic conductive sodium antiperovskite as solid state electrolytes for sodium ion batteries WAN, 2018	Improving understanding of defects in antiperovskites an improving conductivity in these materials via aliovalent doping with alkaline earth ions	Na_3OCl Na_3OCl $Na_3M_{1/\infty}OCl$ (M = Mg, Ca, Sr, Ba) $Na_{2.875}OCl$ $Na_{2.75}Ca_{0.125}OCl$	VASP for DEFECTS, NEB and AIMD	NaCl Schottky is most favourable; alkaline earth doping increases activation energy of vacancy hops, but also increases defect concentration, so overall it can affect conductivity positively
Theoretical design of a double-antiperovskite Na_6SOI_2 as a super-fast ion conductor for solid Na^+ ion batteries YU, 2018	Exploration of a sodium double antiperovskite as a solid state electrolyte, observing stability, conductivity and and compatibility with electrodes	Na_6SOI_2 $Na_{25}S_5O_4I_7$ $Na_{23}S_4O_4I_8$ $Na_{25}O_9Cl_7$ $Na_{23}O_8Cl_8$	VASP for DEFECTS and AIMD	Off-stoichiometric double-antiperovskites are predicted with low activation barriers and ultra-fast conductivity around 10 ms/cm; stability was also good
Composititon screening of lithium- and sodium-rich anti-perovskites for fast-conducting solid electrolytes DAWSON, 2018	Investigation of defect formation energies and sodium ion transport capabilities in Li/Na antiperovskites with alkali-mixing and isovalent doping of the halides	$Na_{3-x}Li_xOX$ (x = 1, 2; X = Cl, Br) $Na_3OCl_{1-x}Br_x$ (x = 0, 0.5, 1) $Na_{3-x}Li_xOX$ (x = 1, 2; X = Cl, Br) $Na_3OCl_{1-x}Br_x$ (x = 0, 0.5, 1) $Na_{3-x}Li_xOX$ (x = 1, 2; X = Cl, Br) $Na_3OCl_{1-x}Br_x$ (x = 0, 0.5, 1)	GULP for DEFECTS and NEB LAMMPS for MD	Schottky MCl defect are favourable; mixed Li\Na systems do not provide enhanced conductivity; mixing halides could be used to finetune activation energies; max conductivity was still only around 5 mS/cm at 500K
Sodium superionic conductors based on clusters FANG, 2019	Improving conductivity via cluster anions, that **i,** have good tolerance factor **ii,** create large channels **iii,** soften the lattice	$Na_3S(BCl_4)$ $Na_{2.875}OX$ (X = Br, BF_4, AlH_4) $Na_{2.875}S(BCl_4)$ $Na_{2.875}S(BCl_4)_{0.5}I_{0.5}$	VASP for NEB and AIMD	Substitution of cluster anions is effective in creating larger channels and softer lattices that lead to conductivities of mS/cm at RT for $Na_3S(BCl_4)$ and $Na_3S(BCl_4)_{0.5}I_{0.5}$
Rotational cluster anion enabling superionic conductivity in sodium-rich antiperovskite Na_3OBH_4 SUN, 2019	Attempting synthesis of antiperovskites with best tolerance factor from Na_3XY (X = O, S; Y = BH_4, BF_4)	Na_3OBH_4	Solid-state reaction?	The rotation of the tetrahydroborate failitates ion movement hence increasing conductivity significantly
Theoretical tuning of Ruddlesden-Popper type anti-perovskite phases as superb ion conductors and cathodes for solid sodium ion batteries YU, 2019	Investigation of a range of sodium-rich Ruddlesen-Popper antiperovskites for solid state electrolyte applications, in terms of conductivity and stability	$Na_4O_{1-x}S_xCl_{1-y}I_y$ (x = 0, 1; y = 0, 1, 2) Na_4OI_2 Na_4OICl $Na_4S_{0.5}O_{0.5}I_2$ $Na_3LiS_{0.5}O_{0.5}I_2$	VASP for DEFECTS and AIMD	'Superb' electrolyte $Na_3LiS_{0.5}O_{0.5}I_2$ with RT conductivity of 6.3 mS/cm; electrolyte is predicted to be compatible with sodium anode both electrochemically and thermodynamically
Correlating lattice distortions, ion migration barriers, and stability in solid electrolytes KIM, 2019	Probing the connection between ionic mobility, thermodynamic stability and symmetry-lowering distortions	Na_3OX (X = F, Cl, Br, I) Na_3SX (X = F, Cl, Br, I) Na_3SeX (X = F, Cl, Br, I)	VASP for NEB	Increasing the degree of distortion (deviating tolerance factor for ideal) leads to lower migration energy, but also lower stability; Na_3SI could be the balance
Mechanochemical synthesis and ion transport properties of Na_3OX (X = Cl, Br, I and BH_4) andtiperovskite solid electrolytes AHIAVI, 2020	Investigation of synthesis and experimental conductivity of various sodium antiperovskites; test of ball-milling method	Na_3OX (X = Cl, Br, BH_4) $Na_3OX_{0.5}(BH_4)_{0.5}$ (X = Cl, Br) $Na_3OCl_{0.33}Br_{0.33}(BH_4)_{0.33}$ Na_3OX (X = Cl, Br, I, BH_4)	Soli-state reaction with ball-milling + heating @ 200 °C for 13h VASP for AIMD	Ball-milling works well as cheap and effective synthesis; larger (super)halogens lead to lower activation energy with both channel size and polarizability
Mechanism of enhanced ionic conductivity by rotational nitrite group in antiperovskite Na_3ONO_2 GAO, 2020	Attempt at synthesissing and measuring the conductivity of cluster antiperovskite Na_3ONO_2	Na_3ONO_2	Solid-state reaction + heating @ 210 °C for 12h	Rotation of the anion unlocked above 200 °C, at which point activation is 0.385eV and conductivity of 0.37 mS/cm
Theoretical study of Na^+ transport in the solid-state electrolyte Na_3OBr based on deep potential molecular dynamics LI, 2020	Exploration of the DeePMD approach for antiperovskites	Na_3OBr Na_3OBr	DeePMD for NEB and MD	DeePMD produces data with good consitstency with previous experiments, while provodong a cheaper alternative to ab initi methods

A Na-rich fluorinated sulfate anti-perovskite with dual doping as solid electrolyte for Na metal solid state batteries FAN, 2020	Synthesising and investigating the structure and conductivity of a novel sulfate-based antiperovskite	Na_3SO_4F $Na_{2.98}Mg_{0.01}SO_4F_{0.95}Cl_{0.05}$	Ball-milling with alcohol + heating @ 500 °C for 36h	Material is promising with conductivities in the 0.01 mS/cm range when doped with alkaline earth and large halide ions
Facile synthesis and electrochemical properties of Na-rich anti-perovskite solid electrolytes FENG, 2020	A low-temperature synthesis method for antiperovskites	$Na_3OBr_{1-x}I_x$ (x = 0, 0.3, 0.5, 0.7, 1)	Solid-state reaction with ball-milling + heating @ 250 °C for 12h	Sharp drop in conductivity as temperature is lowered, possibly from change of structural symmetry and Na sites
Superionic conduction in low-dimensional-networked anti-perovskites LU, 2020	Investigating the effect of dimensionality on alkali ion connectivity in antiperovskites	Na_3OX (X = Br, I) Na_4OX_2 (X = Br, I)	VASP for AIMD	Reducing the dimensionality of the octahedral networks effectively lowers the Li diffusion barrier, due to the enlarged
Hydride-based antiperovskites with soft anionic sublattices as fast alkali ionic conductors GAO, 2021	Soft anions for stability of cubic structure and softening of phonon mode of octahedral rotation	Na_3HCh (Ch = S, Se, Te) $Na_{2.9}HSe_{0.9}I_{0.1}$ Na_3HCh (Ch = S, Se, Te) Na_3HCh (Ch = S, Se, Te)	Solid-state reaction with SPS-like processing VASP for DEF. (natural) and NEB	NEB calculations showed low activations; after doping conductivity of $Na_{2.9}HSe_{0.9}I_{0.1}$ showed conductivities in the 10^{-4} S/cm at 100 °C

SODIUM-RICH ANTIPEROVSKITE STUDIES

Early studies and modern studies relating to structural properties

LEGEND: EXP. DFT

PAPER	FOCUS	MATERIALS	SYNTHESIS/MODEL	OUTCOMES
New investigations of Na_3NO_3 JANSEN, 1977	Discovering the structural properties of Na_3ONO_2	Na_3ONO_2	?	Cubic antiperovskite with a = 4.605 Å
The crystal-structure of kogarkoite, Na_3SO_4F FANFANI, 1980	Discovering the structural properties of Na_3SO_4F	Na_3SO_4F	?	Monoclinic antiperovskite with a = 18.074, b = 6.958, c = 11.443 Å
Na_3OCl and Na_3OBr, the 1st alkali-metal chalcogenide halides SABROWSKY, 1988	Discovering the structural properties of Na_3OCl and Na_3OBr	Na_3OX (X = Cl, Br)	Sintering between 793 and 892 K	Both structures were cubic antiperovskite, with a = 4.500 and 4.573 Å, for the Cl and Br variant
Na_4OI_2 - A new type of alkali-metal chalcogenide halide SABROWSKY, 1989	Discovering the structural properties of Na_4OI_2	Na_4OI_2	Sintering between 773 and 823 K	Tetragonal antiperovskite with a = 4.677 and c = 26.020 Å
Structure of Na_3OCl HIPPLER, 1990	Discovering the structural properties of Na_3OCl	Na_3OCl	Sintering between 573 K and 873 K	Cubic antiperovskite with a = 4.496 Å
Crystal-structure of Na_4OBr_2 HIPPLER, 1990	Discovering the structural properties of Na_4OBr_2	Na_4OBr_2	Sintering between 723 K and 773 K	Tetragonal antiperovskite with a = 4.521, c = 14.908 Å
Structure of Na_4OI_2 SABROWSKY, 1990	Discovering the structural properties of Na_4OI_2	Na_4OI_2	Sintering at 830 K	Tetragonal antiperovskite with a = 4.655 and c = 15.940 Å
$Na_3O(CN)$ - The 1st alkali-metal chalcogenide pseudohalide HIPPLER, 1990	Discovering the structural properties of $Na_3O(CN)$	$Na_3O(CN)$	Sintering between 640 K and 770 K	Cubic antiperovskite with a = 4.56 Å
$(CN)ONa_3$, crystal structure and sodium ion conductivity MULLER, 1990	Measuring the structural properties sodium conductivity of $Na_3O(CN)$	$Na_3O(CN)$	?	Above 230°C exceptionally high sodium ion conductivity (10^{-2} S/cm) from the rotational disorder of the CN^-
On the quasi-binary systems $NaNO_2/Na_2O$ and $NaCN/Na_2O$, phase diagrams and sodium ion conductivity of $Na_3O(NO_2)$ and $Na_3O(CN)$ JANSEN, 1992	Improving understanding on the temperature-depend phase-transitions and their effect on conductivity in Na_3ONO_2 and Na_3OCN	Na_3ONO_2 $Na_3O(CN)$	?	Sharp increase in conductivity at 200-250 °C as a consequence of a "melting" of the sodium sublattice or the rotational disorder of complex anions
Lattice dynamics of antiperovskite structure compounds A_3OX (A = Na, K; X = Cl, Br) ZIENKO, 2001	Exploring the lattice dynamics of antiperovskite structures	Na_3OX (X = Cl, Br)	DFT	Elastic moduli constants and dielectric constants
Ab inbitio study of electronic structure, elastic and optical peoperties of anti-perovskite type alkali metal halides RAMANNA, 2013	Exploring elastic and optical properties for antiperovskite structures via both GGA and LDA methods	Na_3OX (X = Cl, Br)	CASTEP for DFT	Elastic properties including bulk moduli, shear moduli, Young's moduli, Poisson's ratio, anisotropy factor and Cauchy's pressure
Order-disorder phase transition in the antiperovskite-type structure of synthetic kogarkoite, Na_3SO_4F AVDONTCEVA, 2015	Improving understanding on the temperature-induced structural transformations in kogarkoite	Na_3SO_4F	Evaporation from aqueous solution at 25 °C	Transofrmation involves complete disordering of the sulfate tetrahedra, antiperovskite octahedral framework intact
Elastic properties of alkali superionic conductor electrolytes from first principles calculations DENG, 2016	Exploring elastic and optical properties for antiperovskite structures	Na_3OX (X = Cl, Br)	VASP for DFT	Elastic properties including bulk moduli, shear moduli, Young's moduli, Poisson's ratios and Pough's ratios

Robust high pressure stability and negative thermal expansion in sodium-rich antiperovskites Na_3OBr and Na_4OI_2 WANG, 2016	Investigation of structural variability of antiperovskites under high pressures and low temperatures	Na_3OBr Na_4OI_2 Na_3OBr Na_4OI_2	Solid-state reaction + heating @ 350 °C for 3h CASTEP for DFT	Both structures stable up to 23 GPa; negative thermal expansion at very low temperatures; phase stability, symmetry preferences explained qualitatively
Electronic, elastic, lattice dynamic and thermal conductivity properties of Na_3OBr LV, 2017	Investigation of various structural properties for the antiperovskite Na_3OBr	Na_3OBr	CASTEP for DFT	Properties include bulk, shear, and Young's moduli, Poisson's and Pough's ratios; static + hf dielectric constant; thermal conductivity
Computational predictions of stable phase for antiperovskite Na_3OCl PHAM, 2018	Investigation of stability of non-cubic phases in antiperovskites, with potentially lower activations	Na_3OCl	VASP for DFT	14 tilted structures energetically more stable than cubic $Pm\bar{3}m$, with $P2_1/m$ being most stable; the two phases have similar band gaps
Electronic structure, thermomechanical and phonon properties of inverse perovskite oxide (Na_3OCl): An ab initio study KHANDY, 2020	Investigation of various structural properties for the antiperovskite Na_3OCl	Na_3OCl	Wien2K for DFT	Properties include bulk, shear, and Young's moduli, Poisson's and Pough's ratios, anisotropy factor; thermal conductivity
The structural stability, lattice dynamics, electronic, thermophysical, and mechanical properties of inverse perovskites A_3OX: A comperative first-principles study SATTAR, 2020	Investigation of various structural properties for the antiperovskites Na_3OX (X = Cl, Br, I)	Na_3OX (X = Cl, Br, I)	Wien2K for DFT	Properties include bulk, shear, and Young's moduli, Poisson's and Pough's ratios, anisotropy factor; thermal conductivity
Synthesis of Antiperovskite Solid Electrolytes: Comparing Li_3SI, Na_3SI, and Ag_3SI YIN, 2020	Attempt at synthesising iodide-based antiperovskites for larger channel size and faster conductivity	Na_3OI	Solid-state reaction + heating @ up to 600 °C (with a 3 stage profile)	In the case of Na_3SI (and Li_3SI), the adoption of bcc anion packing in the reactants does not occur below melting point, which makes formation difficult