# Computational exploration of the fluoride chemical space for beyond lithium-ion batteries

SAI GAUTAM GOPALAKRISHNAN, DEREJE BEKELE TEKLIYE, DEBOLINA DEB

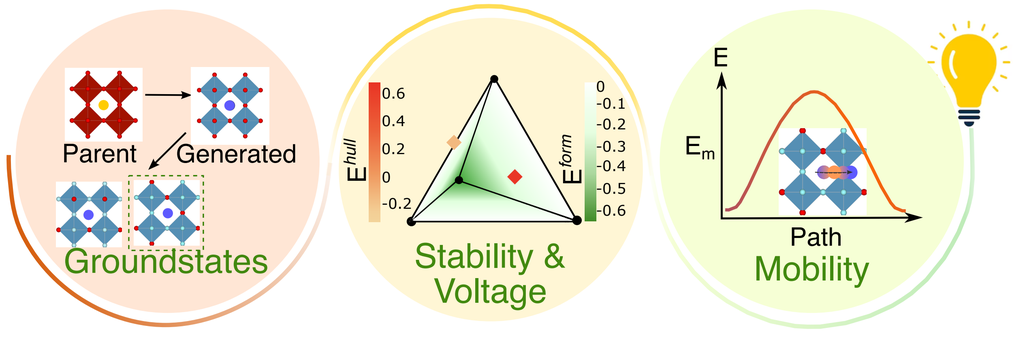
Department of Materials Engineering, Indian Institute of Science, Bengaluru 560012, India

saigautamg@iisc.ac.in
https://sai-mat-group.github.io

## INTRODUCTION

- Next generation of energy storage technologies require both high energy and power densities
  - Multivalent systems (e.g., calcium) can enhance volumetric energy density; sodium can be cheaper and less resource-constrained
- Need good positive electrode materials (cathodes) for both calcium and sodium
  - Inductive effect[1] of fluorine can boost voltages (hence energy densities)

Are there promising fluoride-based cathode materials for calcium and sodium-ion batteries?




## METHODS

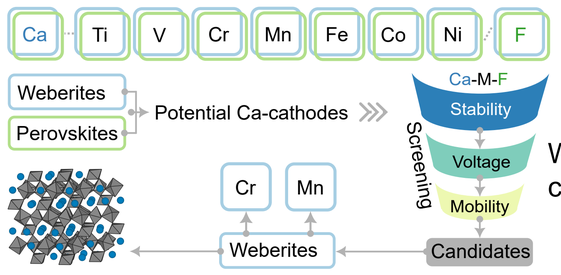
- All density functional theory (DFT) calculations done with Vienna ab initio simulation package (VASP[2])
- Ground state structure identification
  - Ionic substitution, lattice scaling, and DFT calculations
- 0 K thermodynamic stability and average voltages
  - Construction of convex hulls based on structures from the inorganic crystal structure database[3] and using pymatgen[4]
- Ionic mobility using nudged elastic band (NEB)[5]
  - Seven or five images

Exchange-correlation

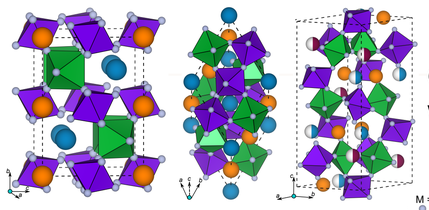
- Hubbard $U$[6] corrected Strongly constrained and appropriately normed (SCAN+$U$)[7,8]
  - Ground state, stability, and voltage
- Generalized gradient approximation (GGA)[9]
  - Perdew-Burke-Ernzerhof version
  - Better convergence in NEB[10]

## WORKFLOW and SYSTEMS

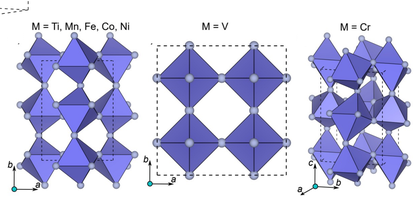
- Fluoride weberites and perovskites for calcium
  - $Ca_xM_2F_7$ and $Ca_xMF_3$
  - M = Ti, V, Cr, Mn, Fe, Co, or Ni; $0 \leq x \leq 1$
- Oxyfluoride perovskites for sodium
  - $Na_xMOF_2$ (F-rich) and $Na_{1+x}MO_2F$ (O-rich)
- Choice of system motivated by availability of 'large' cationic voids and evidence of Na/Ca-containing structures



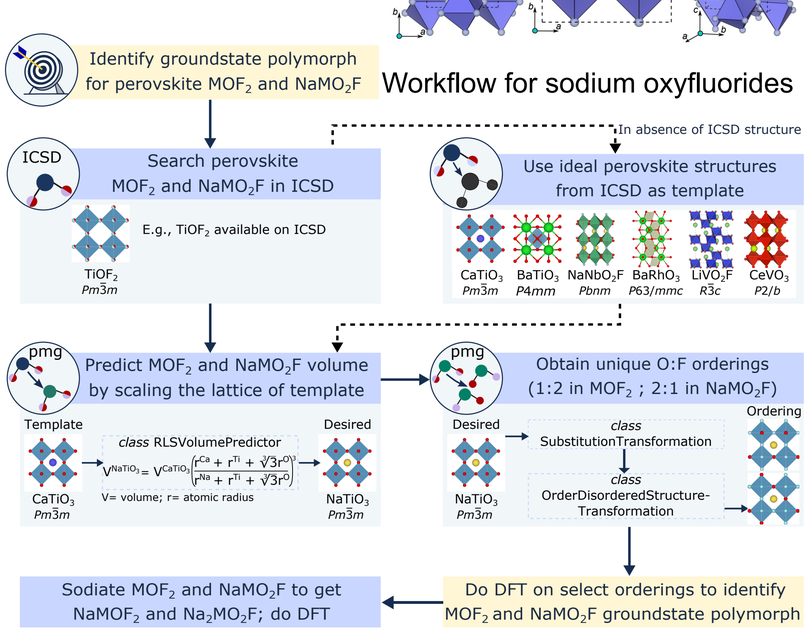

Workflow for calcium fluorides



Orthorhombic and trigonal weberites

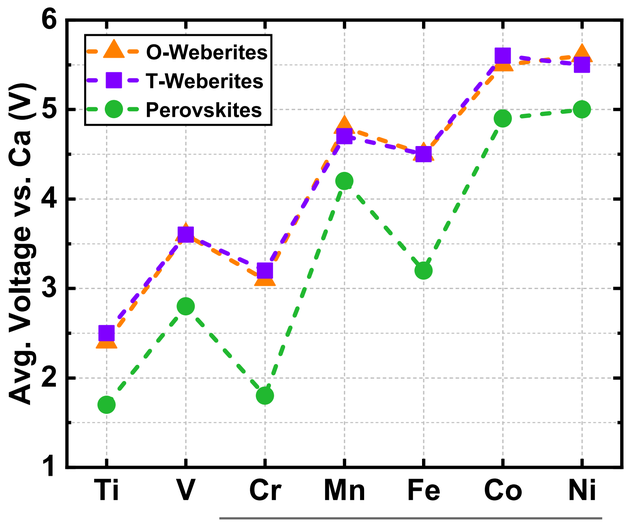



Orthorhombic, cubic, and triclinic perovskites




Workflow for sodium oxyfluorides

## RESULTS: CALCIUM FLUORIDES




Voltage increase from Ti to Ni: standard reduction potentials

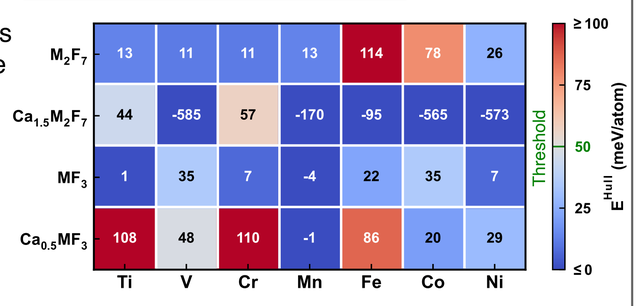
Weberite > Perovskite, higher M oxidation states

"Local" minima at Fe and Cr: stability of $Fe^{3+}$ and $Cr^{3+}$

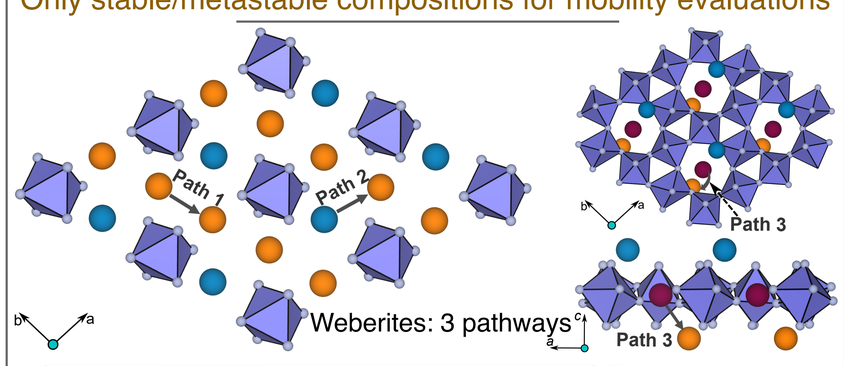
Several structures stable/metastable

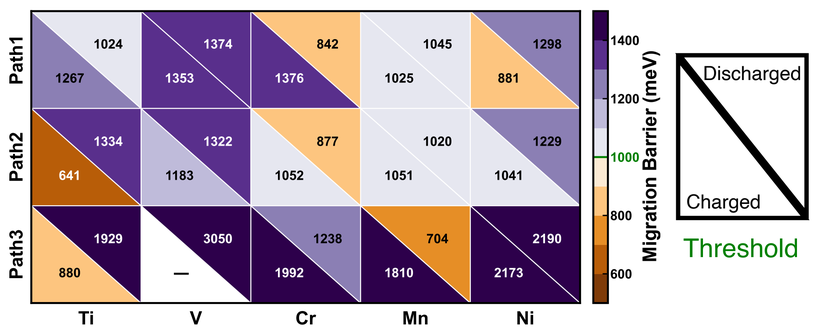
Weberites: Ti, V, Cr, Mn, Ni

Perovskites: V, Mn, Co, Ni




Only stable/metastable compositions for mobility evaluations



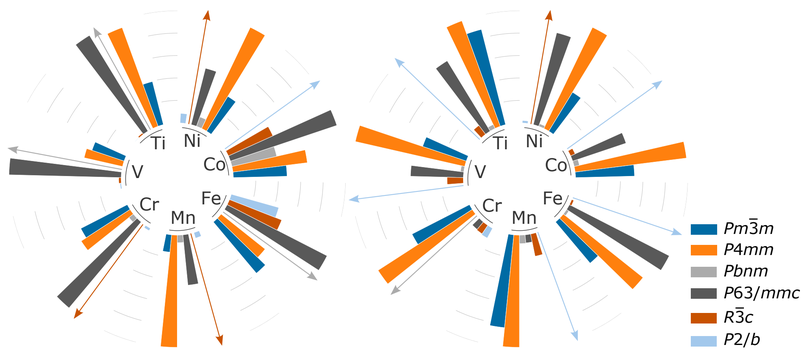

All perovskites, V, Ti, and Ni weberites (discharged) > threshold

$Ca_xCr_2F_7$ and $Ca_xMn_2F_7$: feasible candidates

### KEY TRENDS

- Fluorine addition can cause a significant increase in voltages
- Higher voltage systems are typically unstable
- Higher barriers for migration with both sodium and calcium, due to stronger bonding with fluorine

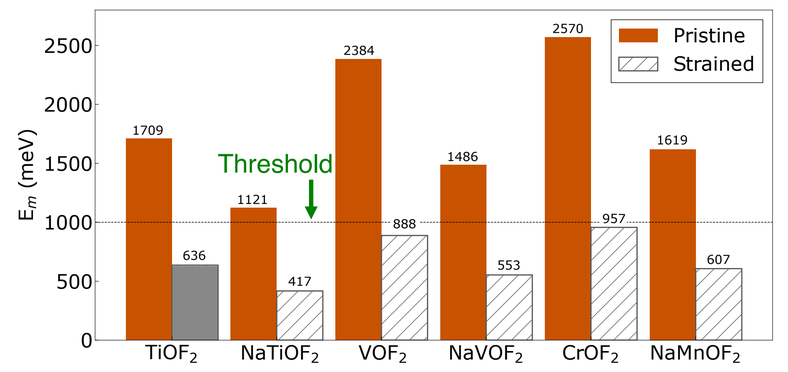
## RESULTS: SODIUM OXYFLUORIDES




Arrows indicate ground state configurations: dependent on M


Monotonic increase from Ti to Ni; F-rich > O-rich


6 possible compositions: stable/metastable $TiOF_2$-$NaTiOF_2$, $VOF_2$-$NaVOF_2$, $CrOF_2$, and $NaMnOF_2$




Na-mobility poor in pristine oxyfluorides
5% hydrostatic strain causes significant reduction in barriers

Ti, V, Cr, and Mn oxyfluorides are candidates under strained (thin film) battery geometries

## CONCLUSION

Design of next generation of energy storage technology is crucial: cathode design is critical

We used high-throughput DFT-based screening to identify novel fluoride-based cathodes for Ca and Na-ion batteries

- Use SCAN+$U$ to screen through 0 K thermodynamic stabilities and average intercalation voltages
- Use GGA to compute migration barriers

Ca: weberite $Ca_xCr_2F_7$ and $Ca_xMn_2F_7$ are promising

Na-ion: Ti, V, Cr, and Mn oxyfluorides can be useful

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4. National Supercomputing Mission, India
5. Supercomputing at University of Paderborn, Germany

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