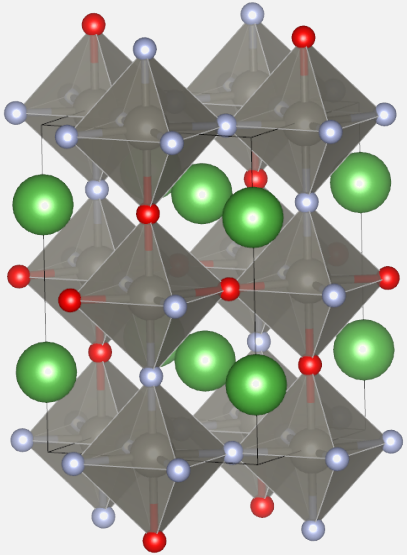

Thermodynamic Stability and Anion Ordering of Perovskite Oxynitrides

Samuel D. Young; Amitava Banerjee; Bryan Goldsmith; Ghanshyam Pilania

ACS Fall 2022 — 23 Aug 2022

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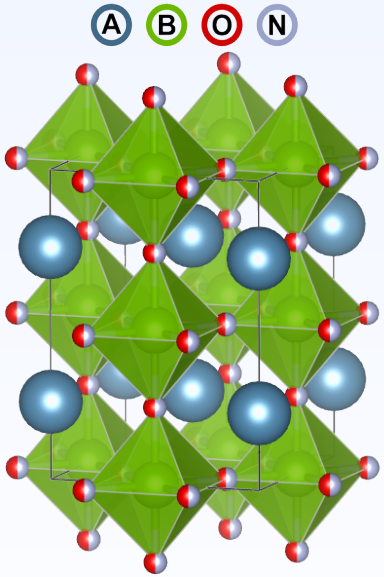
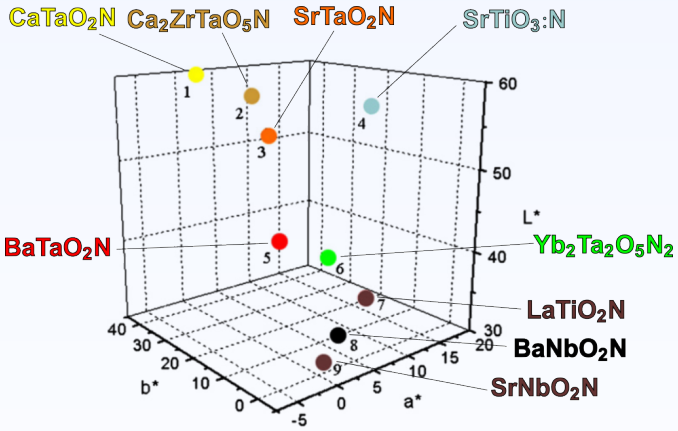
http://cheresearch.engin.umich.edu/goldsmith/

Perovskite oxynitrides (PONs) are important for many applications



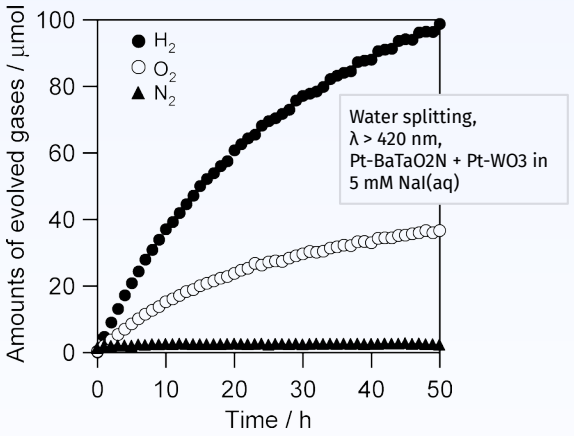
$\sqrt{2} \times \sqrt{2} \times 2$ supercell

Visible-spectrum pigments



Aguiar, R. *et al. Dyes and Pigments* **76**, 70–75 (2008).

Photocatalysis

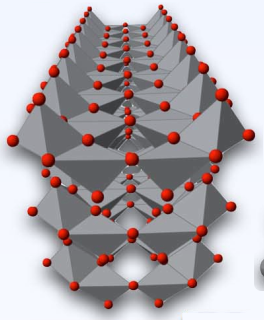


Higashi, M., *et al. Chem. Mater.* **21**, 1543–1549 (2009).

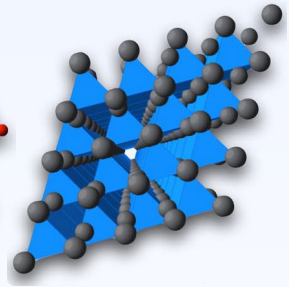
The structure and composition of a PON strongly impacts its performance and stability.

Fuertes, A. Chemistry and applications of oxynitride perovskites. *J. Mater. Chem.* **22**, 3293–3299 (2012).

PON structure, anion ordering, and stable compositions are not well explored



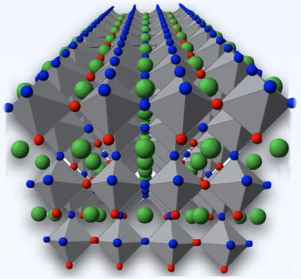
Metal oxide



Metal nitride

Less tunable

More tunable



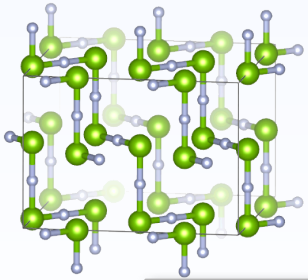
Perovskite oxynitride

ABO_xN_{3-x}

A	Ca	Ca	La	La	⋯	?
B	Ti	Cr	Cr	Re	⋯	?

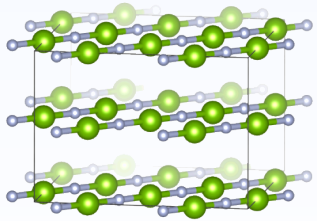
Which cation pairs?

Mostly *cis*



or

Mostly *trans*



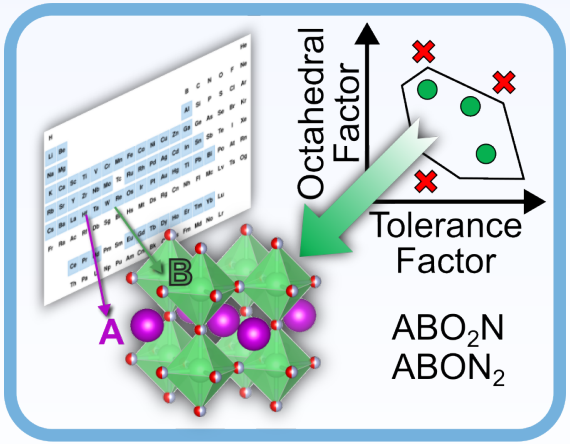
or ?

Which anion orderings? Trends?

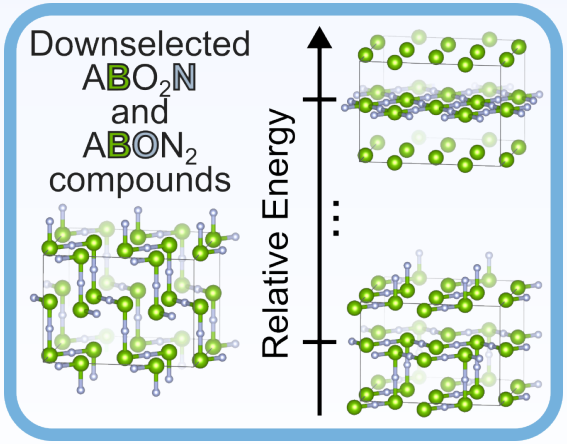
Goal: determine thermodynamic stability and anion ordering in ABO_2N and $ABON_2$ perovskite oxynitrides

Our workflow

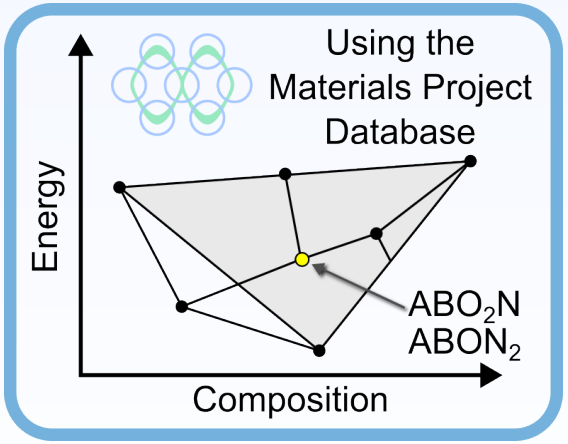
(a) Cation Pair Selection



(b) Anion Ordering Selection



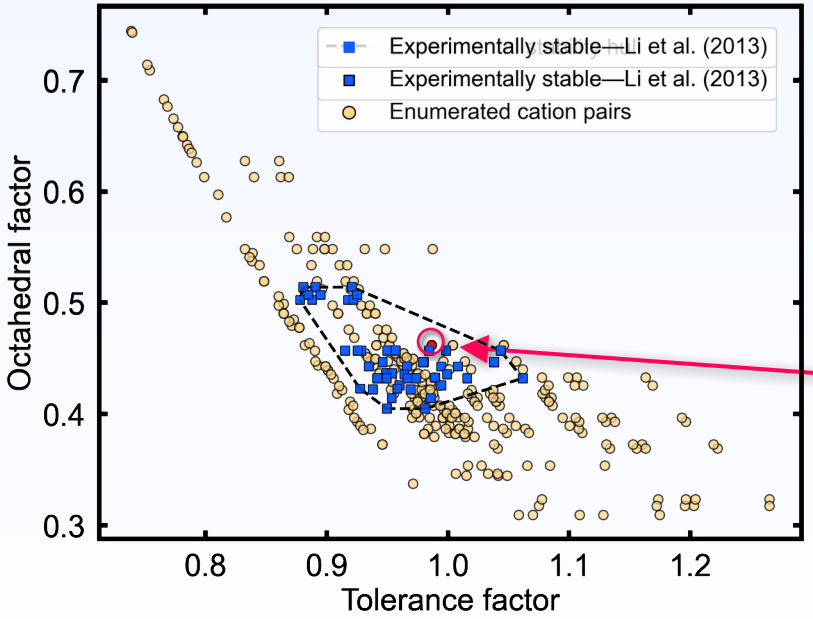
(c) Energy-Above-Hull Analysis

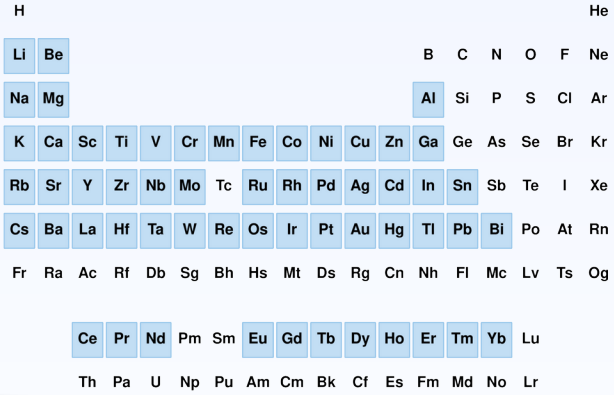


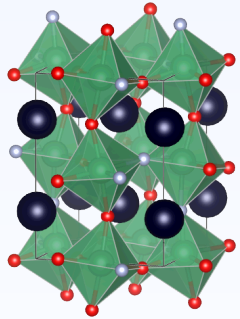
Select cation pairs

- We build an experimental stability hull from known stable PONs.[1, 2]

Stoichiometry	Goldschmidt tolerance factor	Octahedral factor
ABO_2N	$\frac{[(r_A+r_O)^8(r_A+r_N)^4]^{1/12}}{\sqrt{2}[(r_B+r_O)^4(r_B+r_N)^2]^{1/6}}$	$\frac{r_B}{(r_O^4 r_N^2)^{1/6}}$
$ABON_2$	$\frac{[(r_A+r_O)^4(r_A+r_N)^8]^{1/12}}{\sqrt{2}[(r_B+r_O)^2(r_B+r_N)^4]^{1/6}}$	$\frac{r_B}{(r_O^2 r_N^4)^{1/6}}$







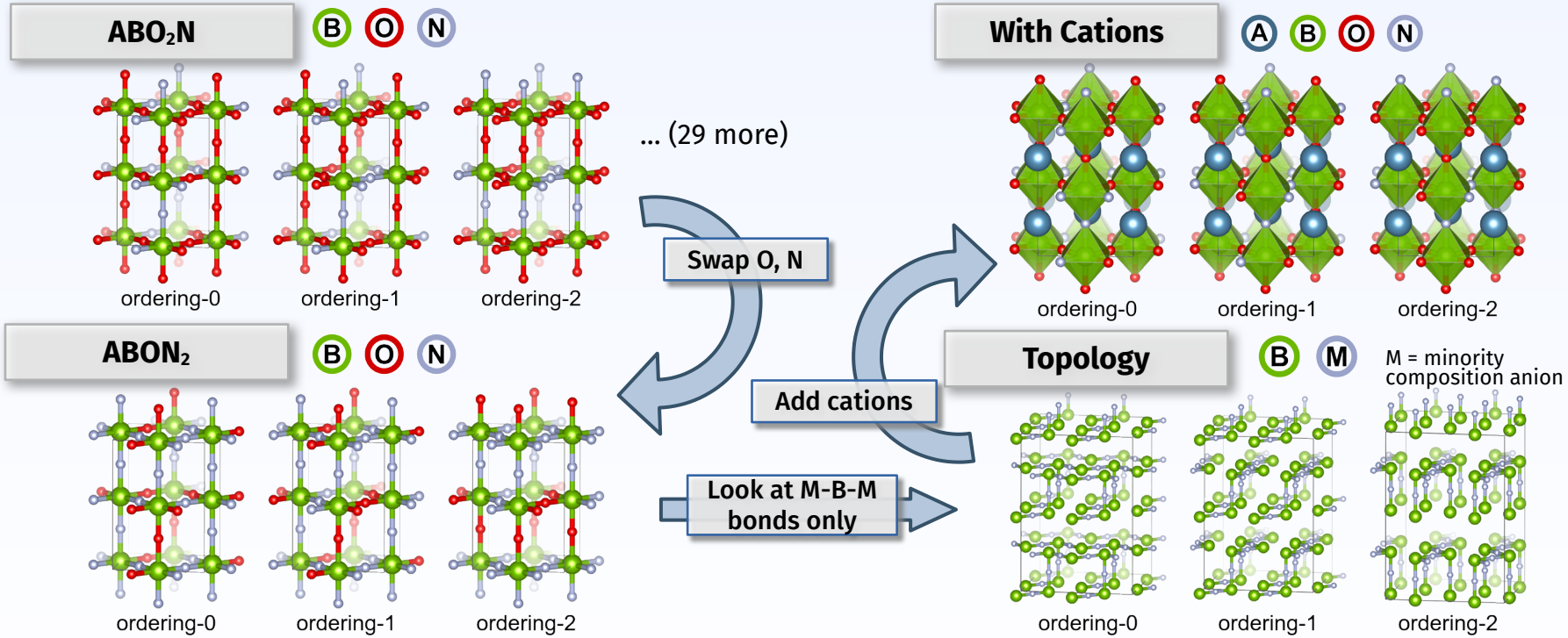
$SrNbO_2N$

351 enumerated compounds total
114 (32.4%) inside hull; 237 (67.5%) outside hull

1. Li, W., Ionescu, E., Riedel, R. & Gurlo, A. Can we predict the formability of perovskite oxynitrides from tolerance and octahedral factors? *J. Mater. Chem.* ***A*** 1, 12239 (2013).
2. Wang, H.-C., Schmidt, J., Botti, S. & L. Marques, M. A. A high-throughput study of oxynitride, oxyfluoride and nitrofluoride perovskites. *J. Mater. Chem. A* **9**, 8501–8513 (2021).

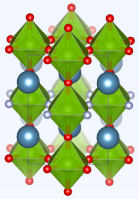
We aim to identify preferred anion orderings

- For $\sqrt{2} \times \sqrt{2} \times 2$ supercell, there are 32 total symmetrically distinct anion orderings.[1]



1. Hart, G. L. W., Nelson, L. J. & Forcade, R. W. Generating derivative structures at a fixed concentration. *Computational Materials Science* **59**, 101–107 (2012).

We identified anion orderings that are consistently stable across 16 cation pairs



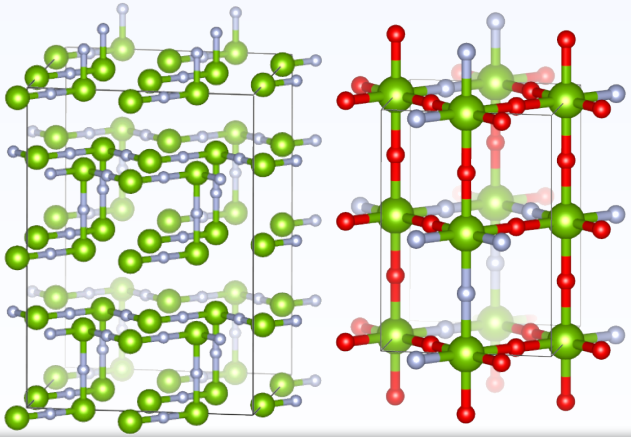
Full structure

DFT

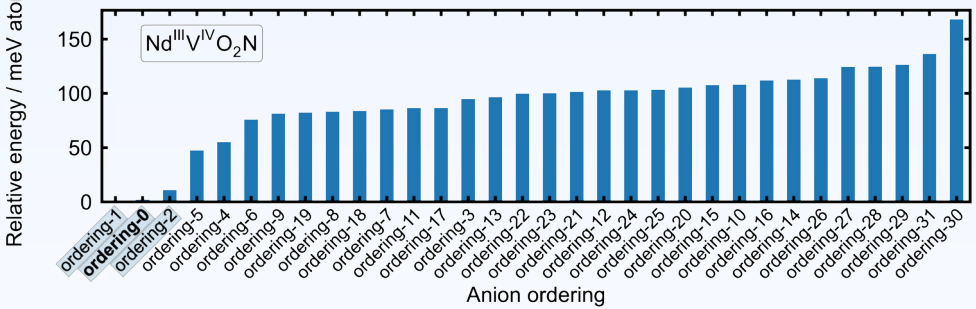
ΔE_{DFT} = 3.61 meV/atom above minimum-energy ordering for this cation pair

- The most stable anion ordering contains *cis* bonding as both straight and branched chains.

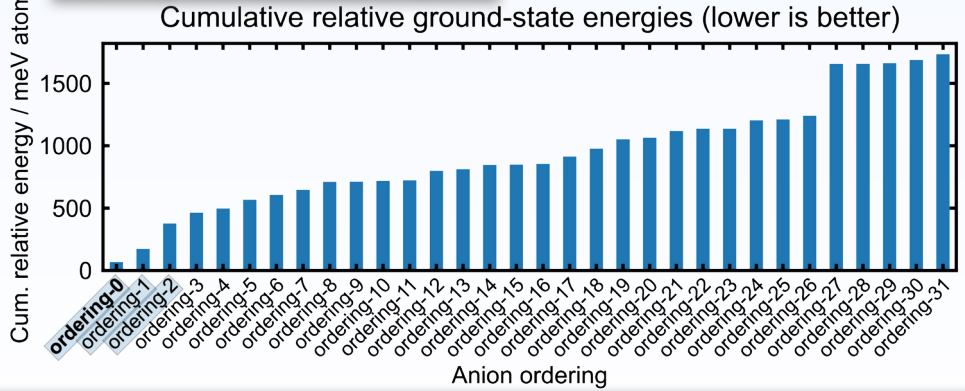
A B O N **ordering-0**



Ranking for single cation pair

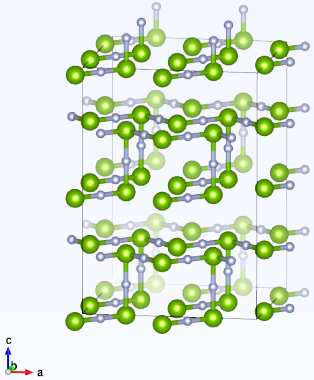


Ranking over all 16 cation pairs

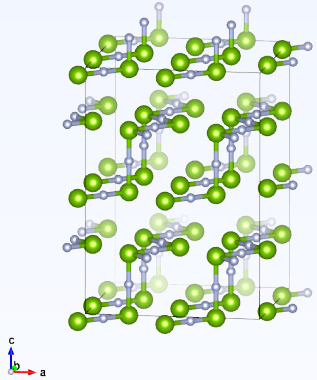


Calculate degree of *cis* ordering

B M

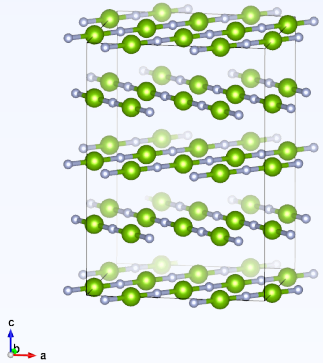


ordering-0
100% global cis bonding
Cis counts: 1, 0, 3, 1
3/4 octahedra with cis bonds

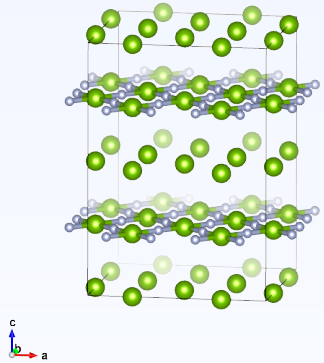


ordering-1
100% global cis bonding
Cis counts: 1, 0, 3, 1
3/4 octahedra with cis bonds

•••



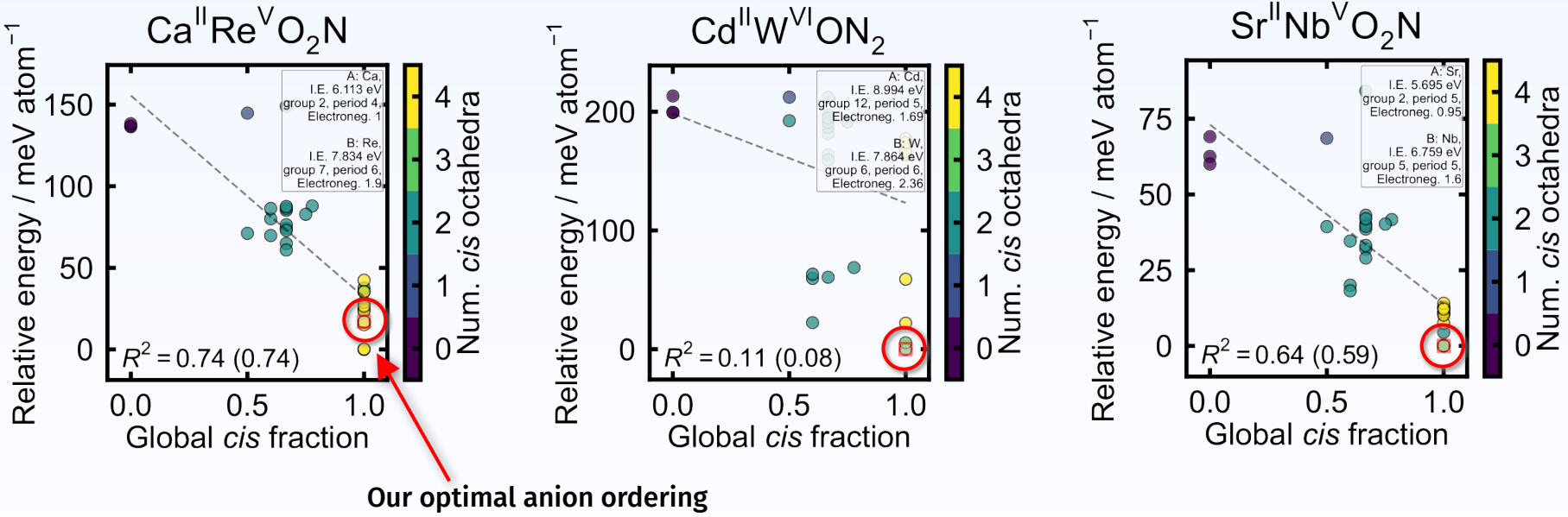
ordering-30
0% global cis bonding
Cis counts: 0, 0, 0, 0
0/4 octahedra with cis bonds



ordering-31
67% global cis bonding
Cis counts: 4, 0, 4, 0
2/4 octahedra with cis bonds

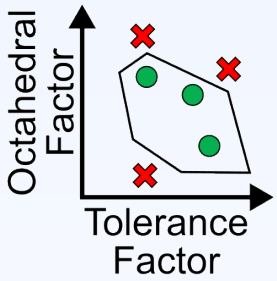
Most favorable ← → **Least favorable**

A global *cis* fraction of 1 leads to the most stable anion ordering, for all cation pairs

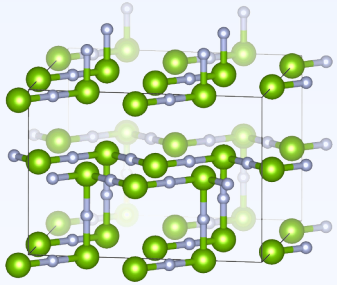


Correlations not strong across all cation pairs, but high fraction of global *cis* ordering is important.

We screen 295 PON compounds and group by stability above convex hull

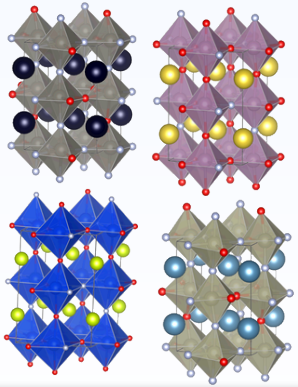


+



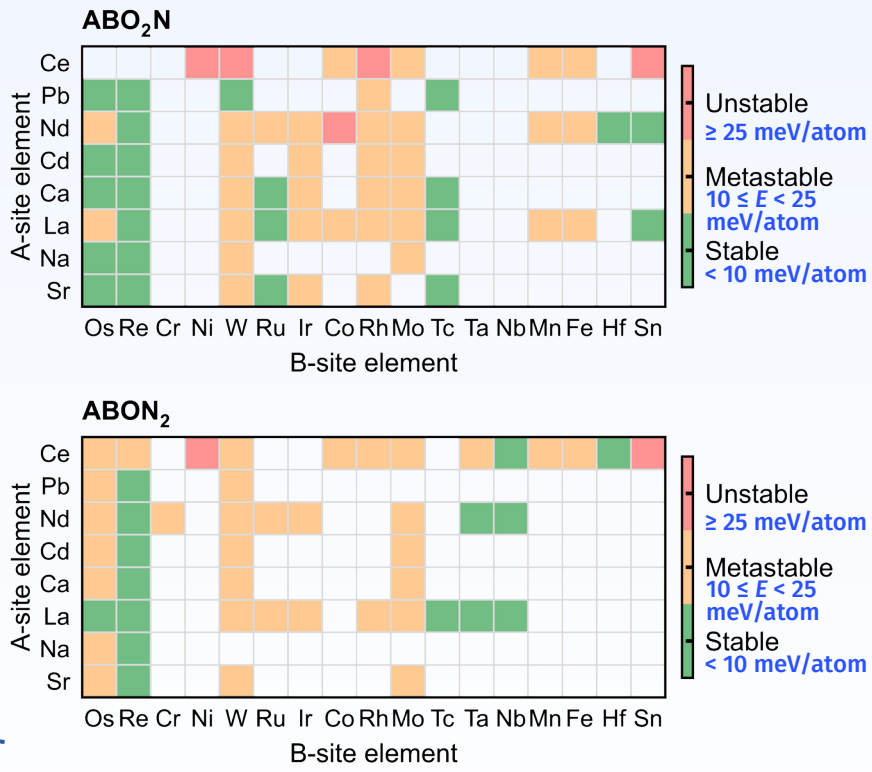
Cation pairs

Optimal anion ordering



DFT, energy-above-hull search using Materials Project

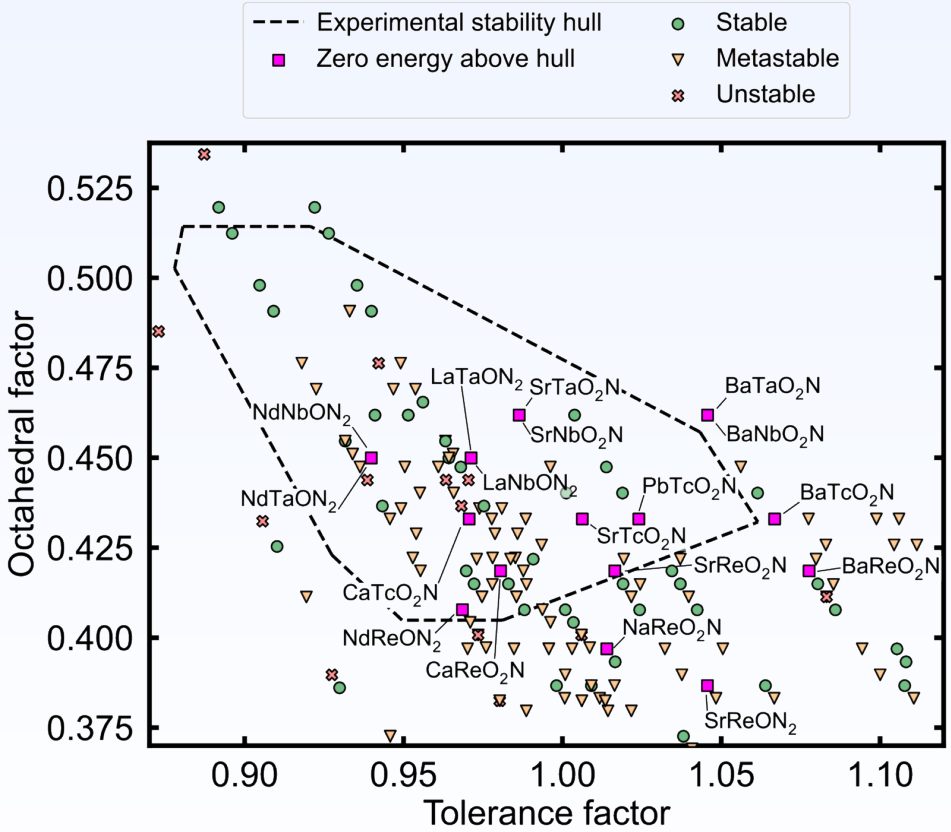
... 291 more full structures



1. Jain, A. et al. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Materials* **1**, 011002 (2013).

DFT-predicted hull identifies new possible stable PON compounds for exploration

- B = Re compounds
- A = La, Ca, Pb compounds
- Many stable compounds are outside southeast border of experimental stability hull.

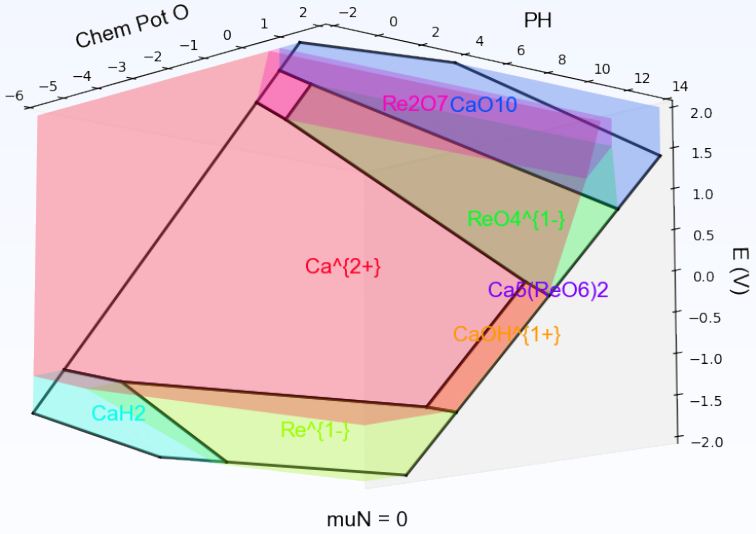


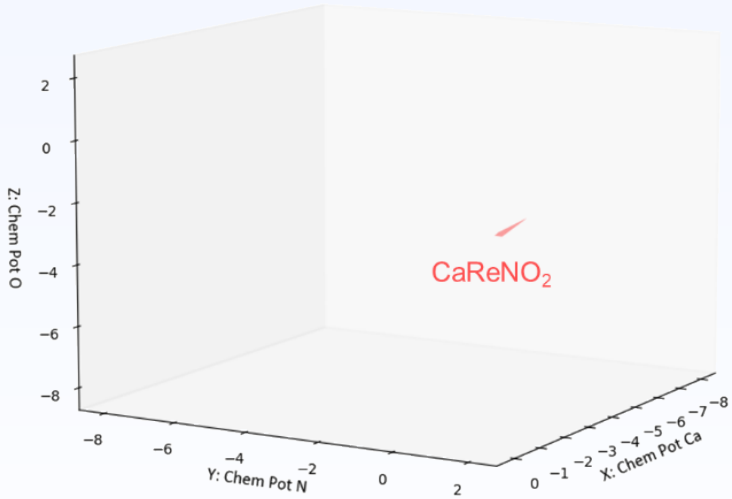
We generate a Pourbaix diagram for $CaReO_2N$

Pourbaix diagram, $\mu_{Ca} = \mu_{Re} = 0$

Animation

Stability region for solid PON





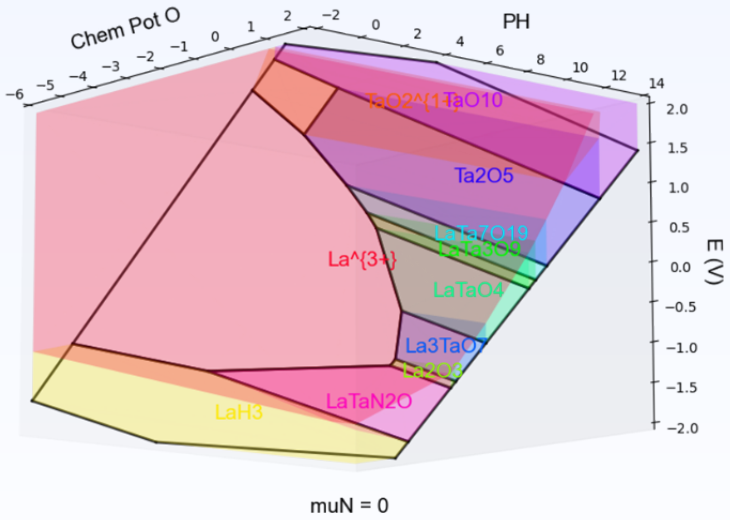
Jiadong Chen
Sun Research Group
Materials Science
University of Michigan

Synthesis could require very high partial pressures of NH_3 or N_2 precursor.

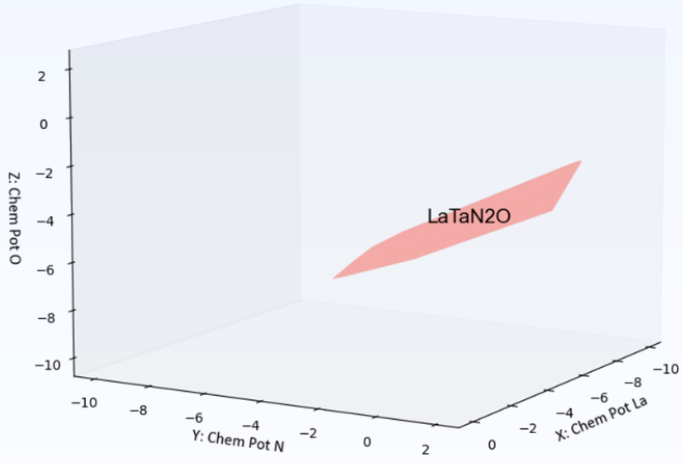
We generate a Pourbaix diagram for $LaTaO_2N$

Pourbaix diagram, $\mu_{La} = \mu_{Ta} = 0$

Animation



Stability region for solid PON



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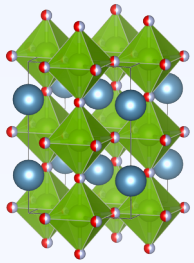
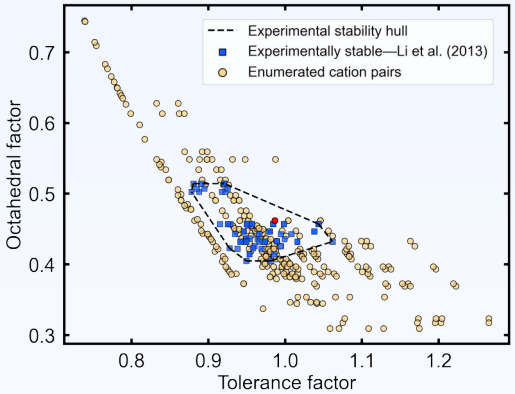
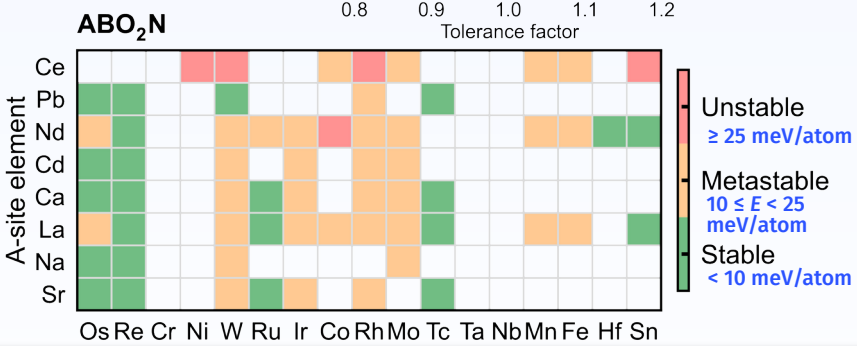
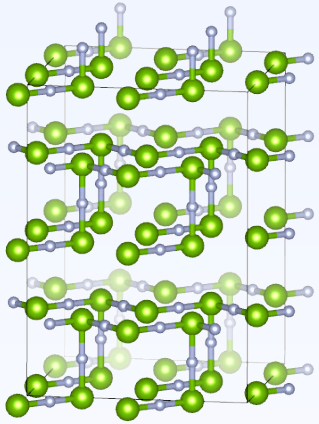
$LaTaO_2N$ should be much easier to synthesize with lower pressures and NH_3 flowrates.

Conclusions and Next Steps

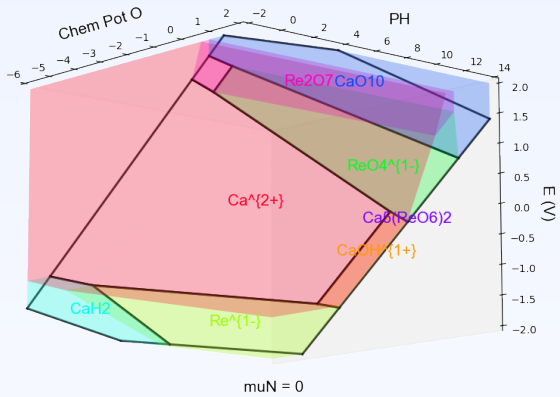


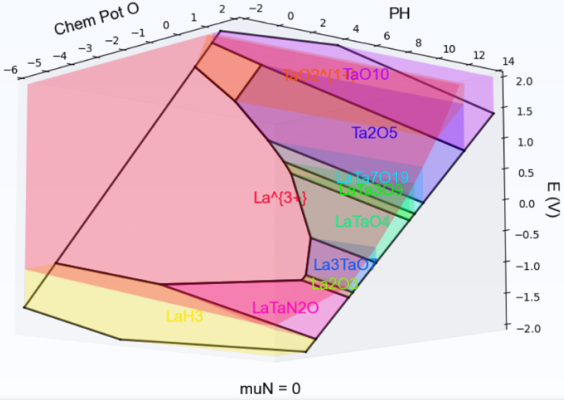






ordering-0
100% global cis bonding
Cis counts: 1, 0, 3, 1
3/4 octahedra with cis bonds





Next steps: synthesis!! Collaborating with LANL experimentalists making $CaReO_2N$, $LaTaO_2N$.

Acknowledgments

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Questions?