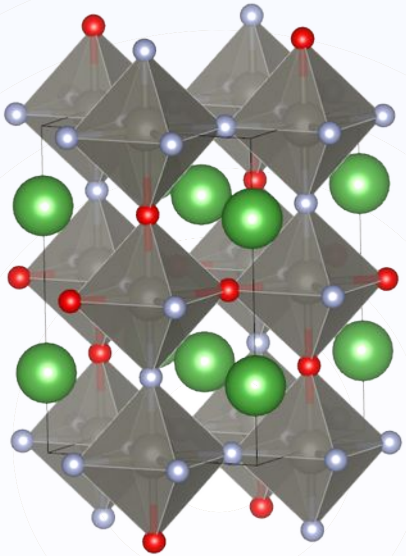

Thermodynamic Stability and Anion Ordering of Perovskite Oxynitrides

Samuel D. Young, Jiadong Chen, Wenhao Sun, Bryan Goldsmith, Ghanshyam Pilania

AIChE National Meeting 2022 – 18 Nov 2022

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Nitrogen chemistry can address nitrate fertilizer pollution

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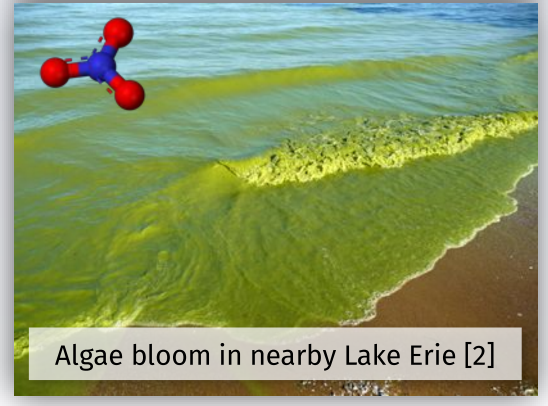

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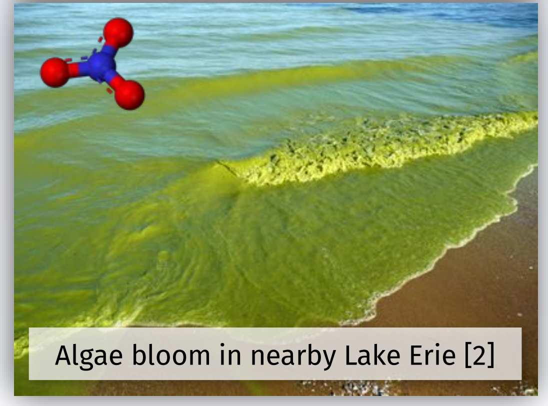

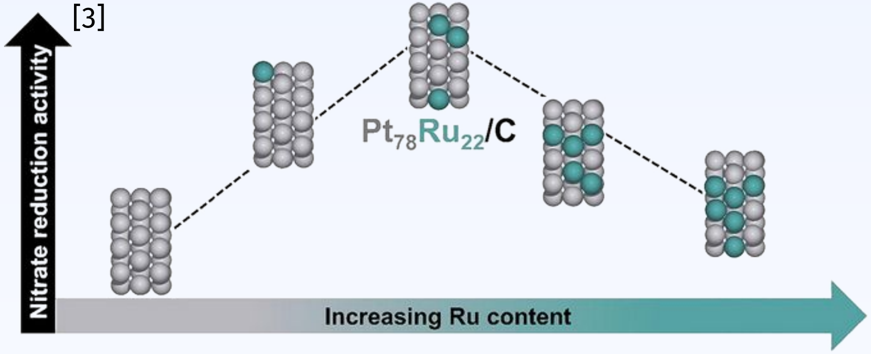

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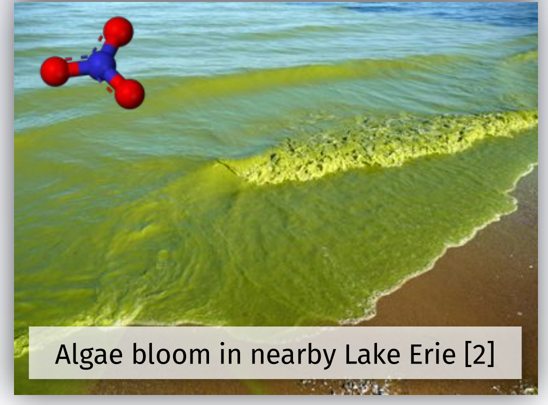

Algae bloom in nearby Lake Erie [2]

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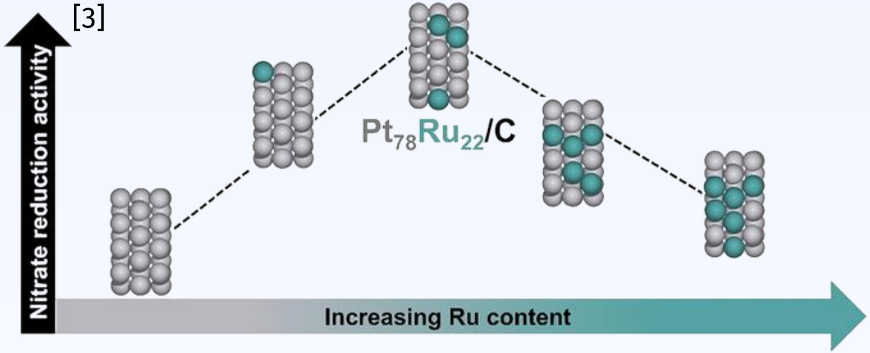

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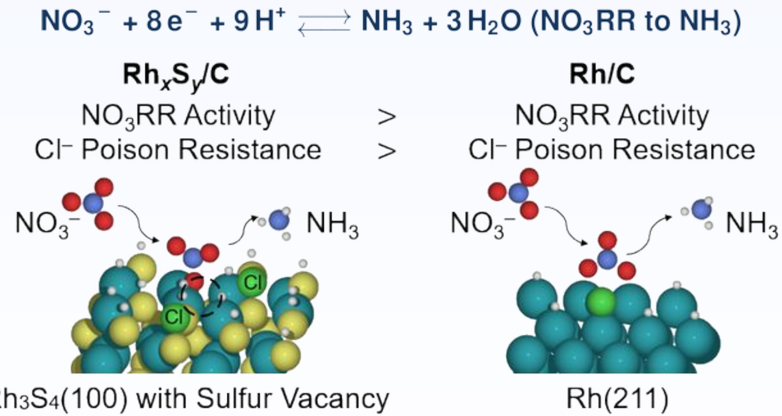

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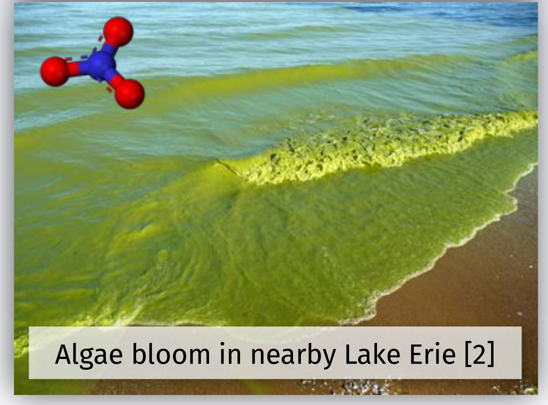

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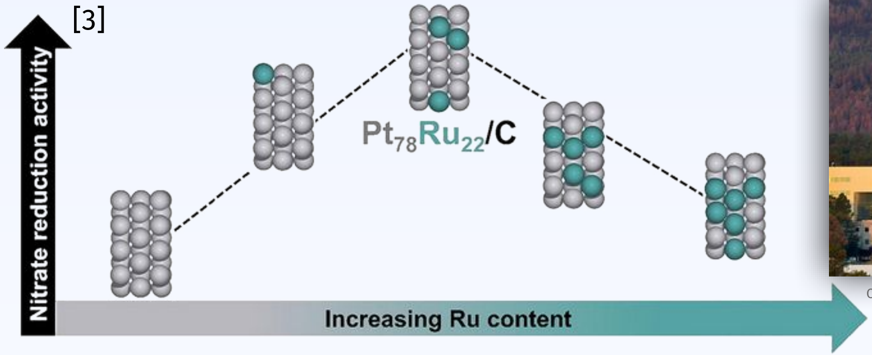

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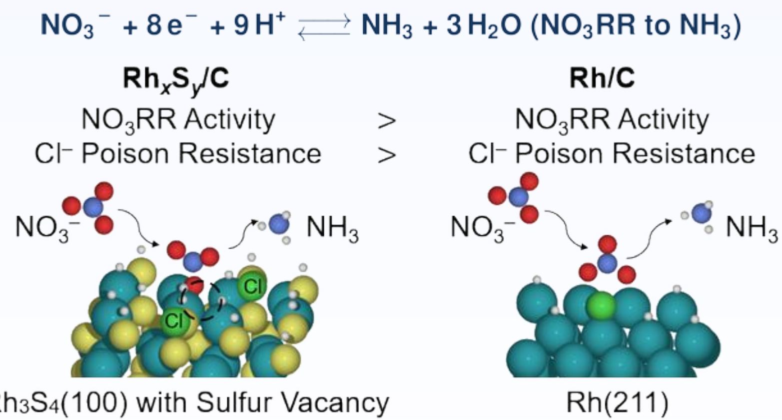
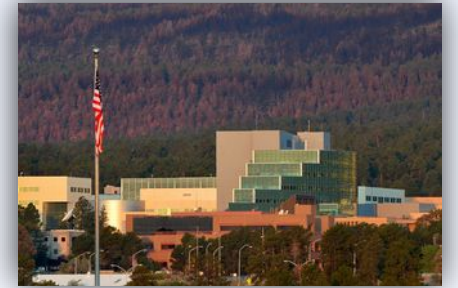
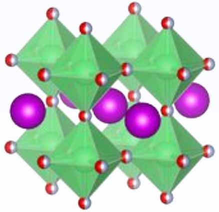




Ghanshyam Pilania



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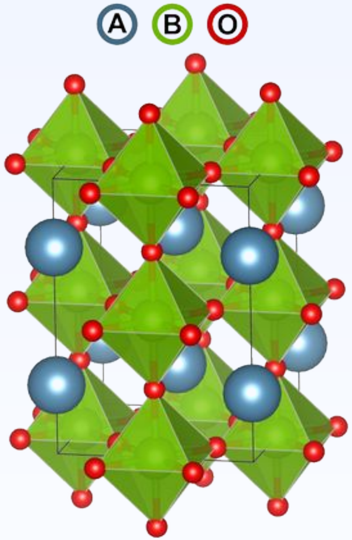

Perovskite oxide

ABO_3

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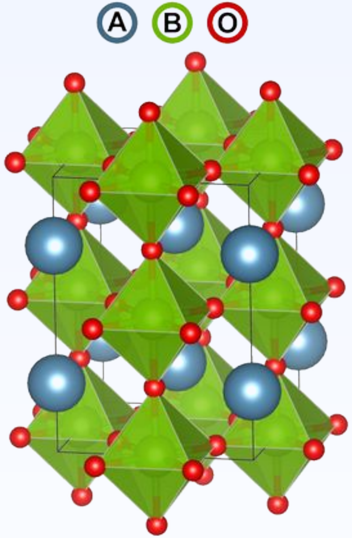

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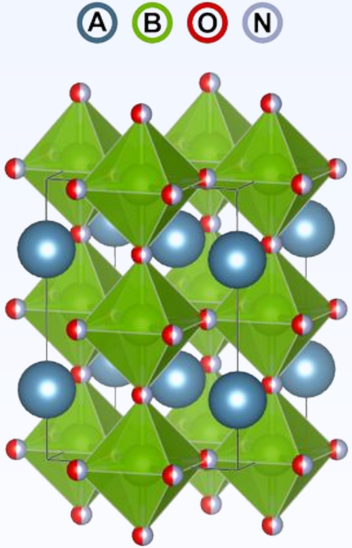

$\sqrt{2} \times \sqrt{2} \times 2$ PON supercell

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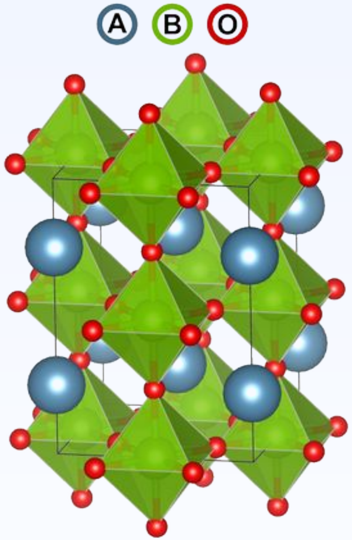

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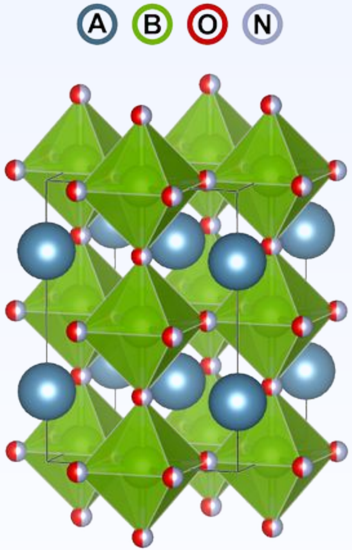

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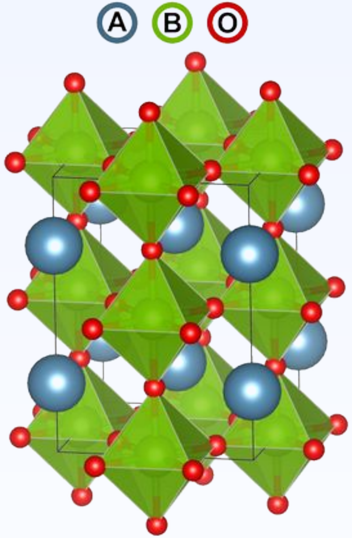

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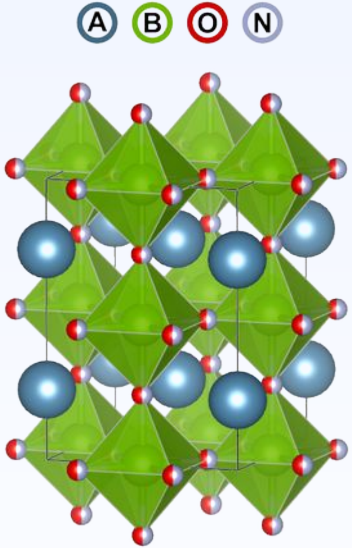

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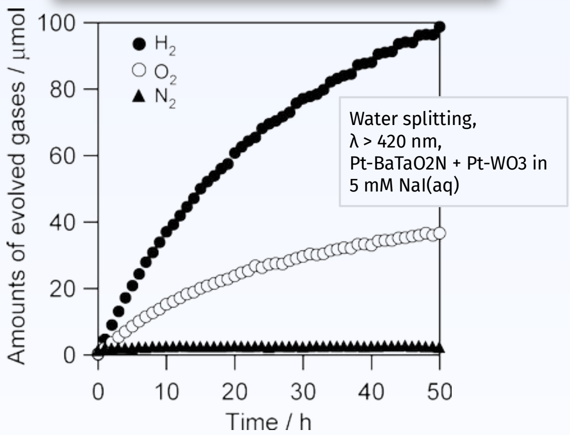
Photocatalysis



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

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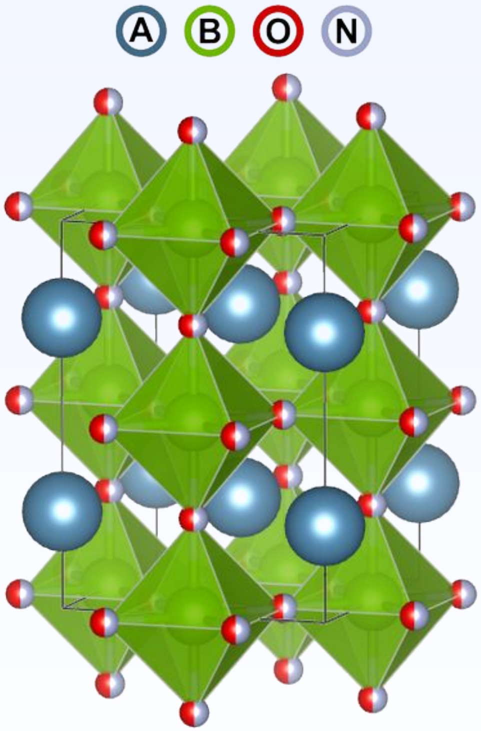

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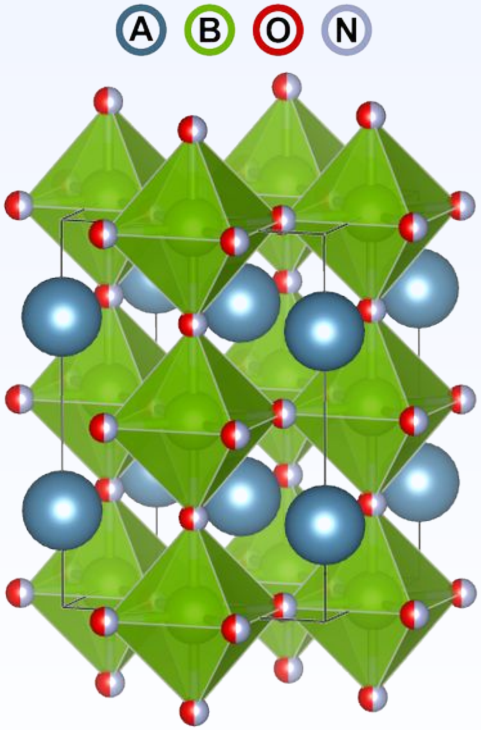

How should we choose the chemistry and structure to maximize stability?

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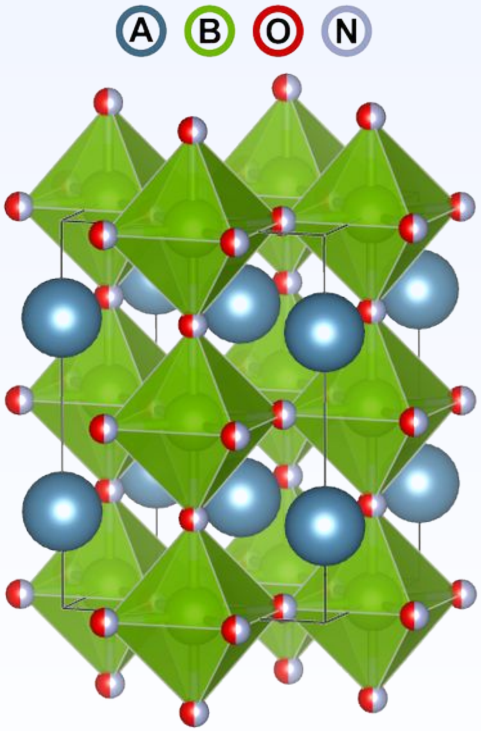

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ABO_xN_{3-x}

A	Ca	Ca	La	La	···	?
B	Ti	Cr	Cr	Re	···	?

Which cation pairs?

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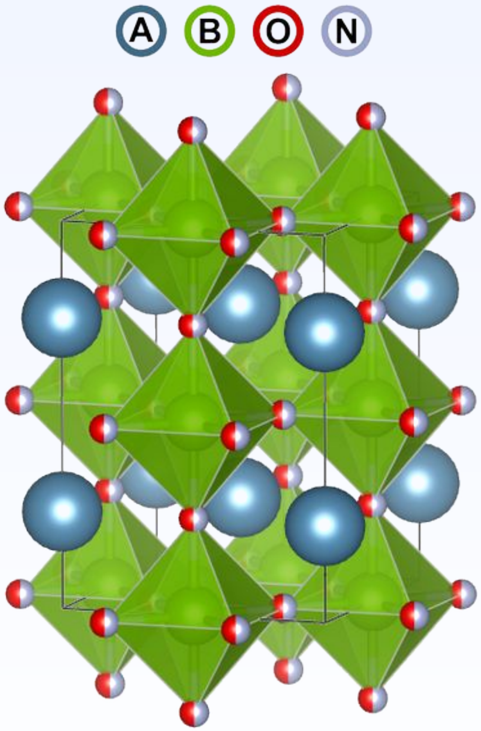

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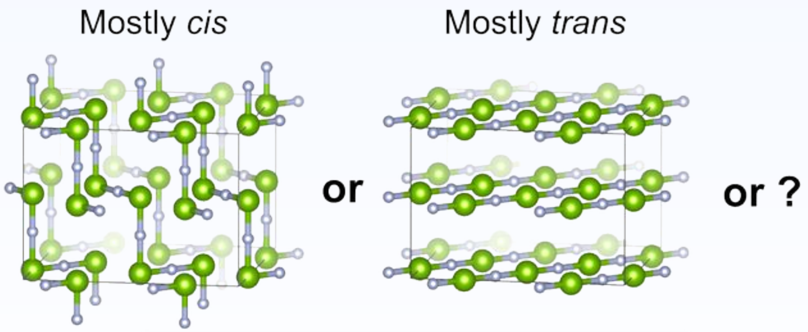

Which anion orderings? Trends?

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

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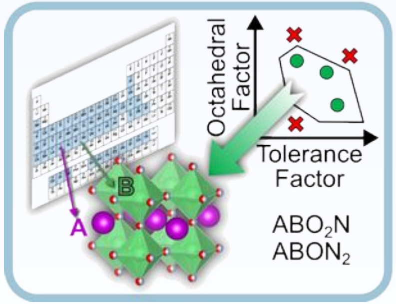

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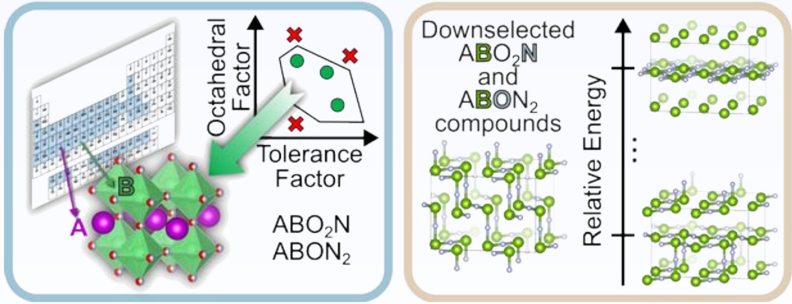

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- Pair 295 cation pairs with optimal anion ordering
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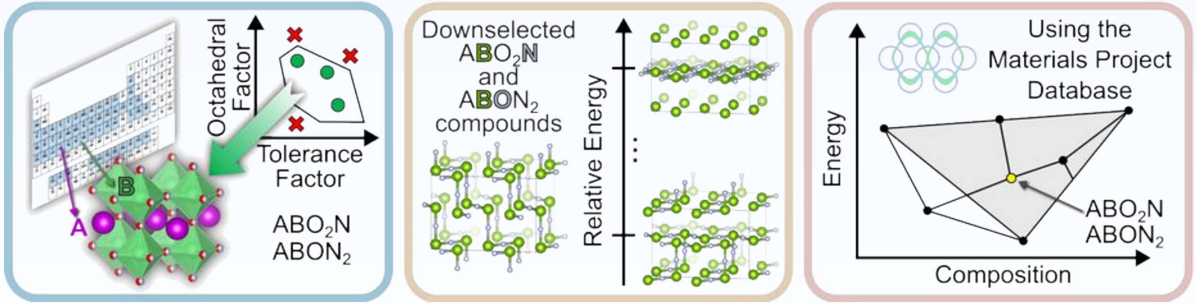

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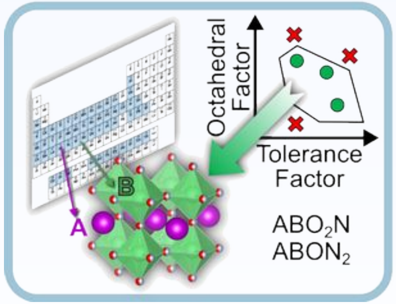

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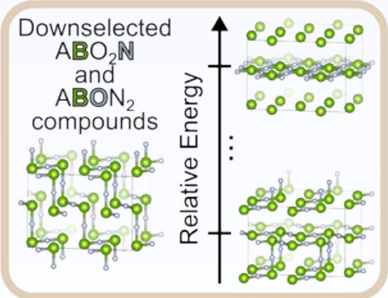

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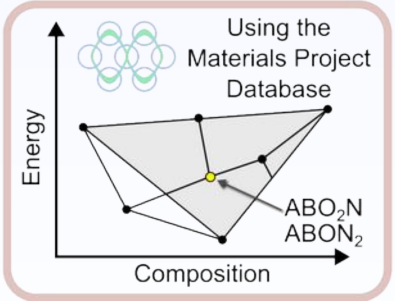
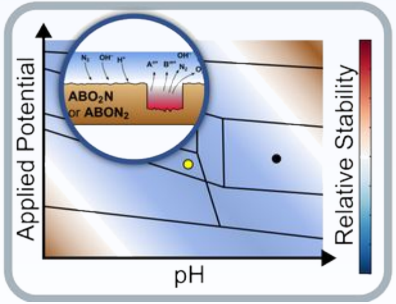


(d) Electrochemical Stability Analysis

- Construct multidimensional Pourbaix diagrams
- Identify regions of stability and corresponding operating conditions



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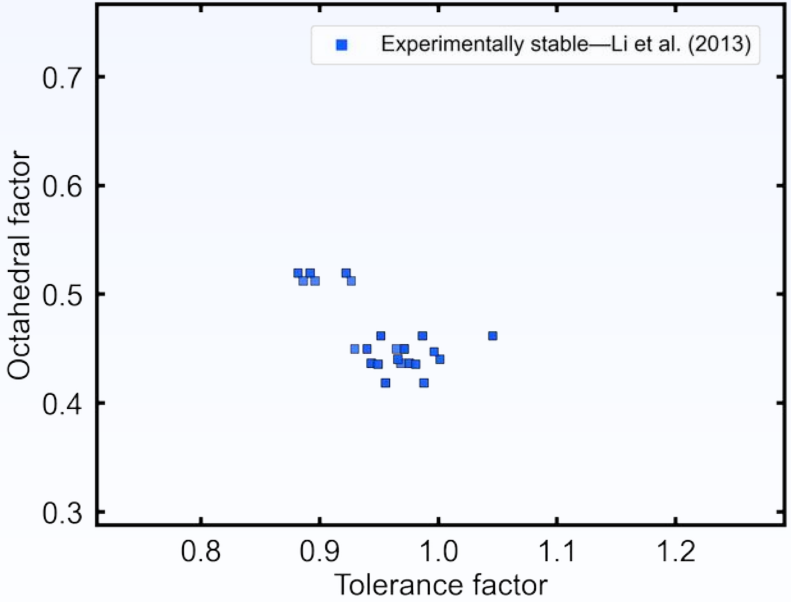

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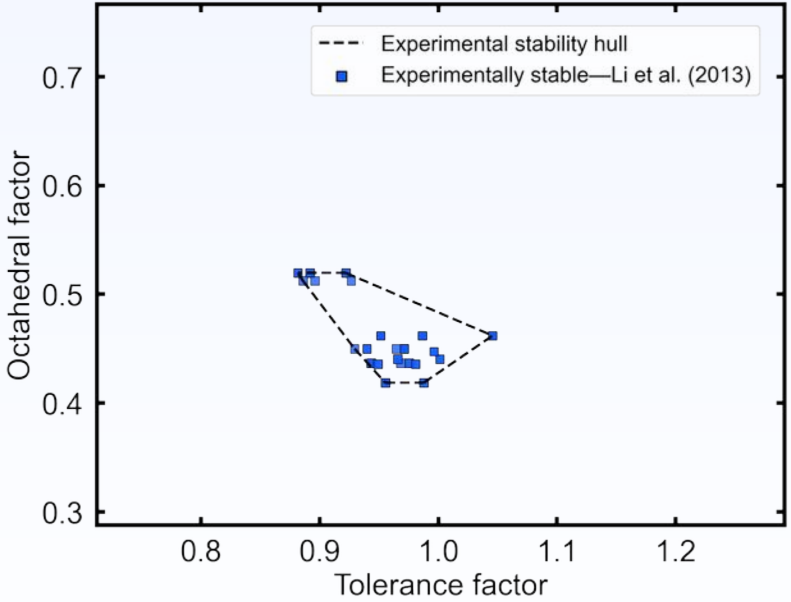

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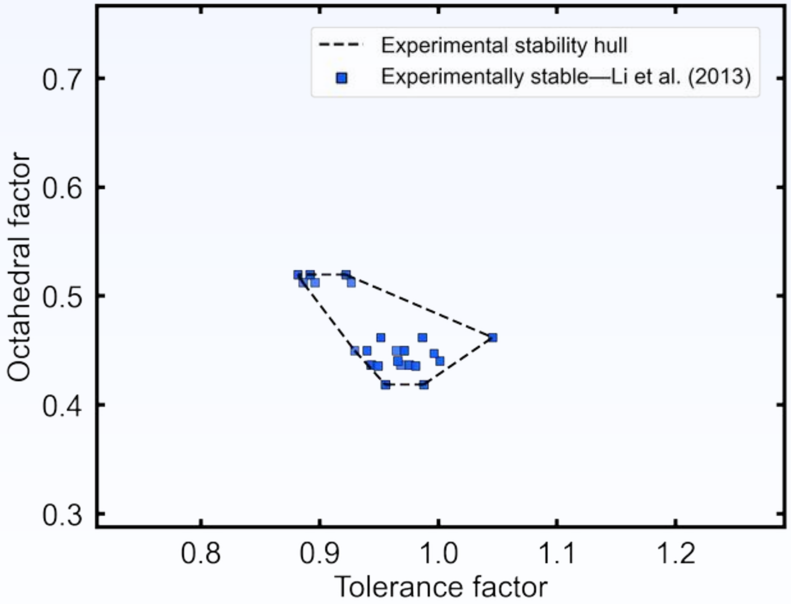

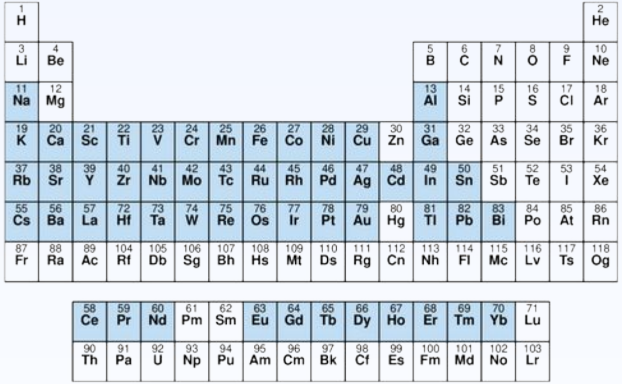

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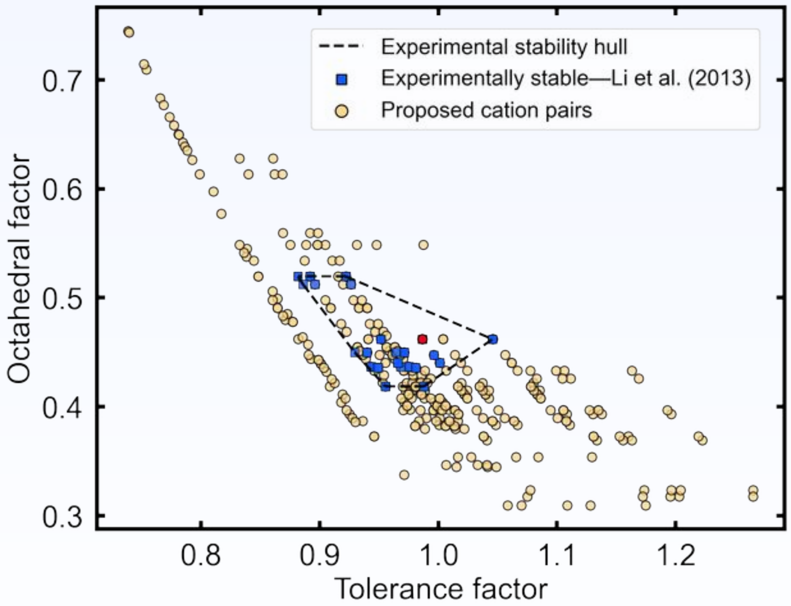

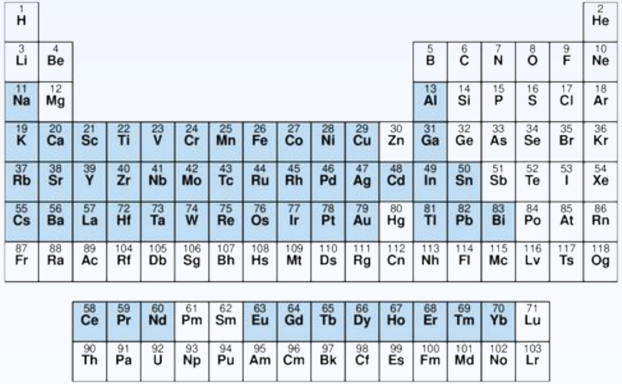

316 enumerated compounds
101 (32%) inside hull; 215 (68%) outside hull

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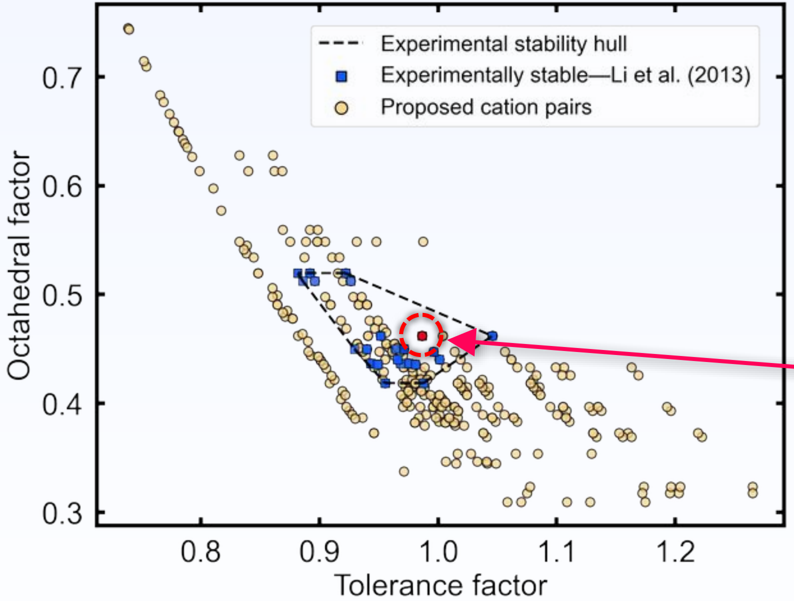
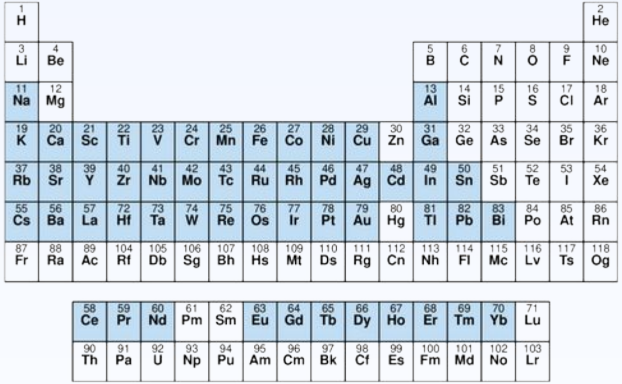
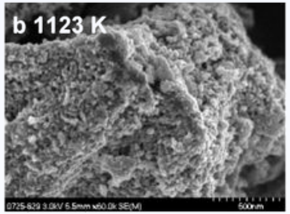
$ABON_2$	$\frac{[(r_A+r_O)^4(r_A+r_N)^8]^{1/12}}{\sqrt{2}[(r_B+r_O)^2(r_B+r_N)^4]^{1/6}}$	$\frac{r_B}{(r_O^2 r_N^4)^{1/6}}$

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







$SrNbO_2N$ [3]

316 enumerated compounds
101 (32%) inside hull; 215 (68%) outside hull

1. Li, W., Ionescu, E., Riedel, R. & Gurlo, A. *J. Mater. Chem.* ***A*** 1, 12239 (2013).
2. Wang, H.-C., Schmidt, J., Botti, S. & L. Marques, M. A. *J. Mater. Chem. A* **9**, 8501–8513 (2021).
3. Higashi, M., *et al. Chem. Mater.* **21**, 1543–1549 (2009).

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]

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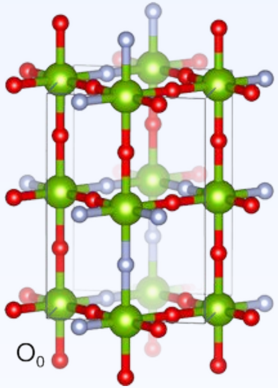
ABO_2N

Low energy



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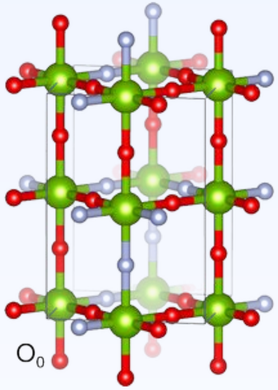
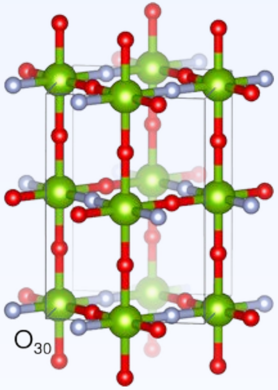


...30 more structures...



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ABO_2N

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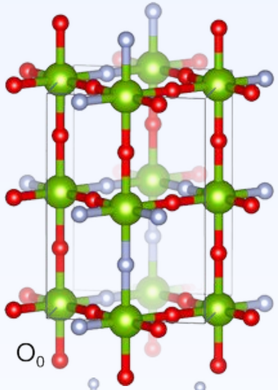

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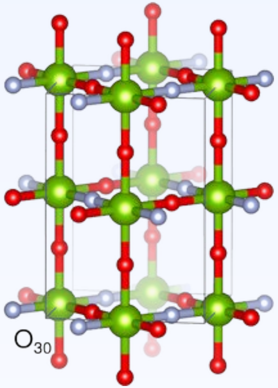


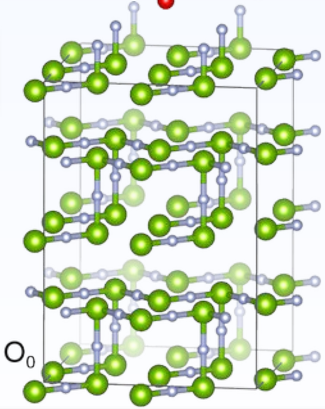
High energy

Topology

B M

M = minority composition anion

Low energy



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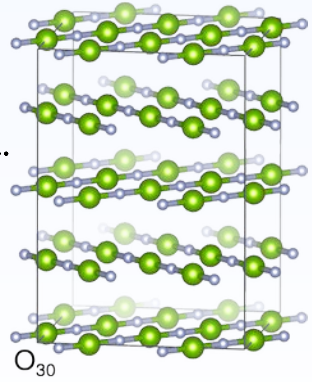

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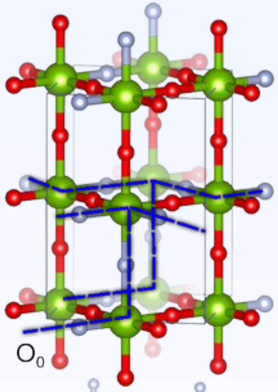

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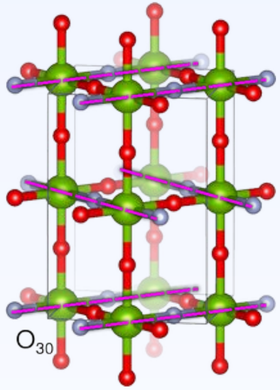

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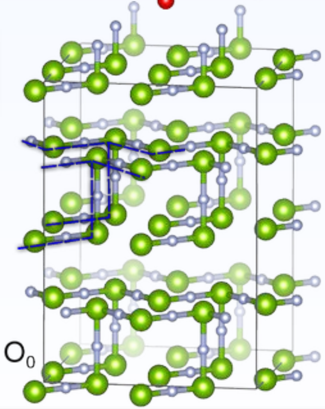

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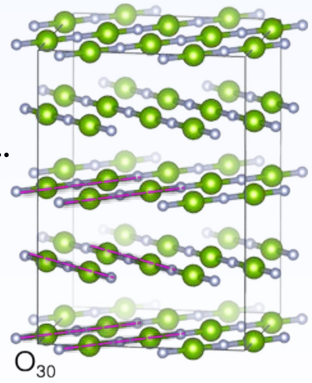

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One anion ordering is consistently stable across 16 cation pairs

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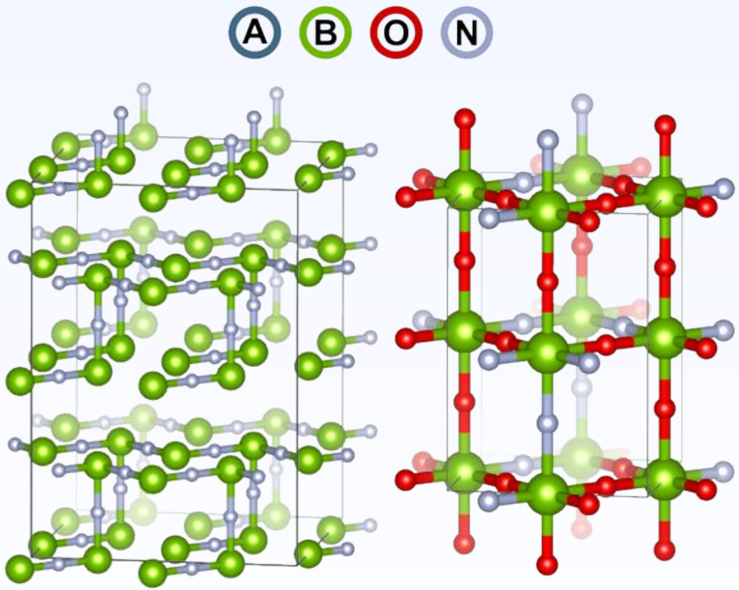
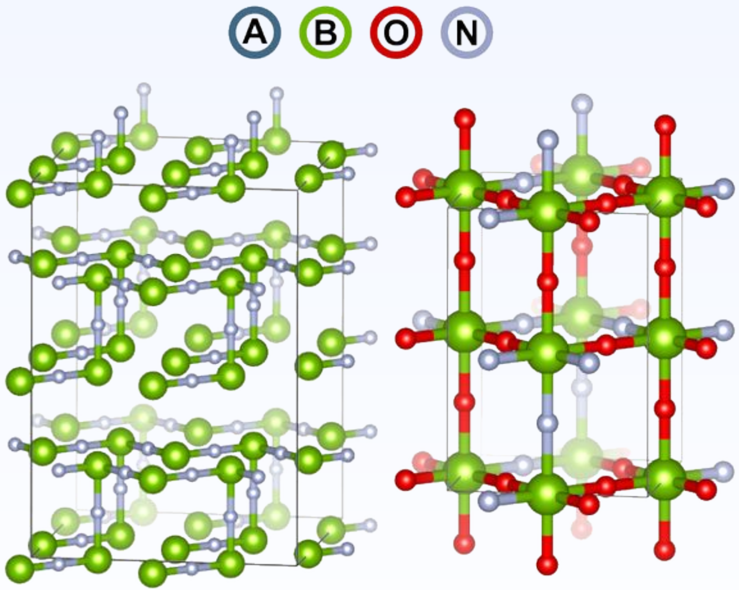
The most stable anion ordering contains *cis* bonding across B atoms.



Ordering O_0

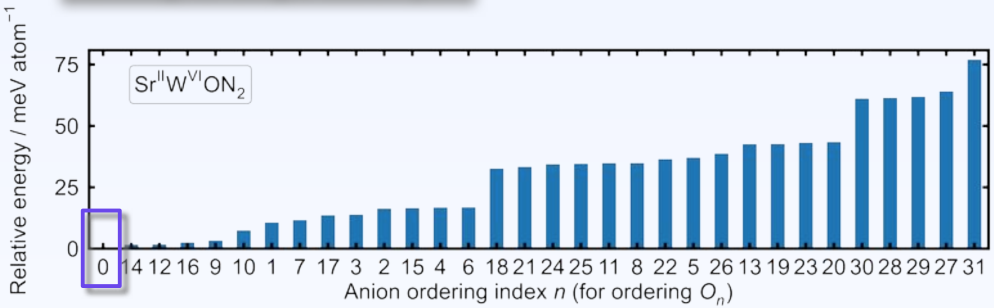
One anion ordering is consistently stable across 16 cation pairs

The most stable anion ordering contains *cis* bonding across B atoms.



Ordering O_0

Ranking for single cation pair



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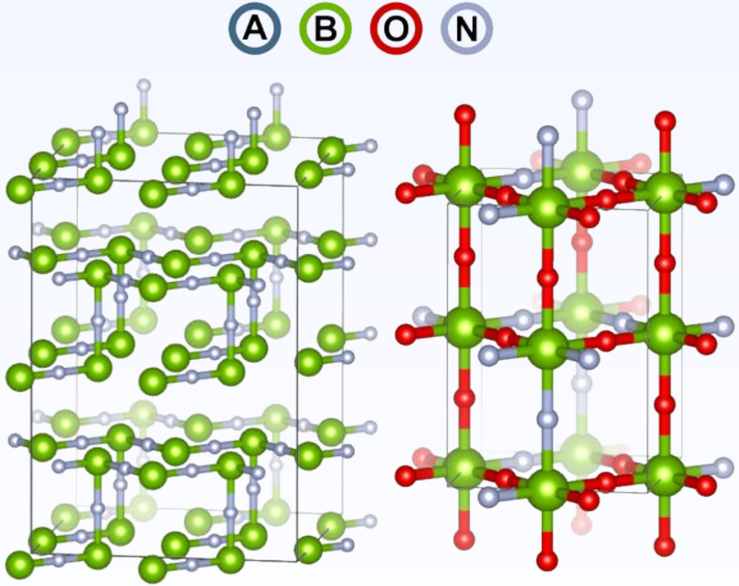

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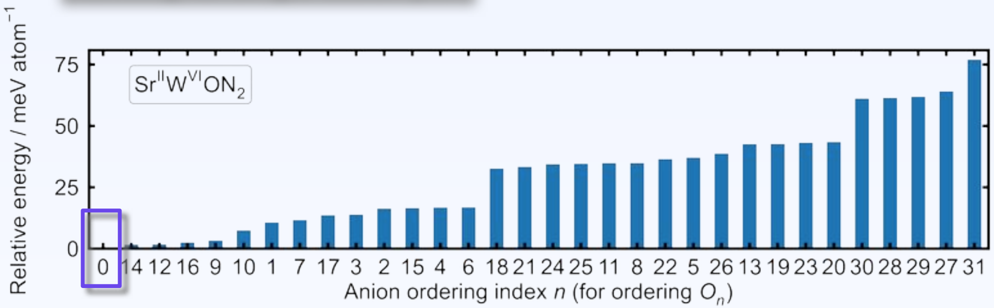
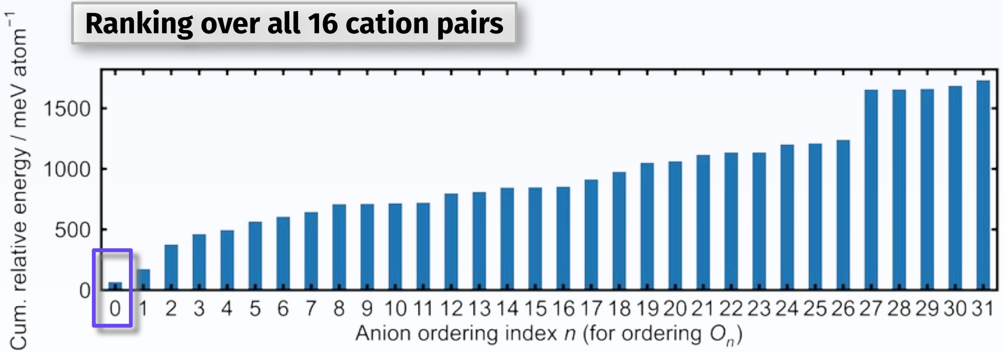


Ranking over all 16 cation pairs



Low-energy orderings have a high degree of *cis* bonding

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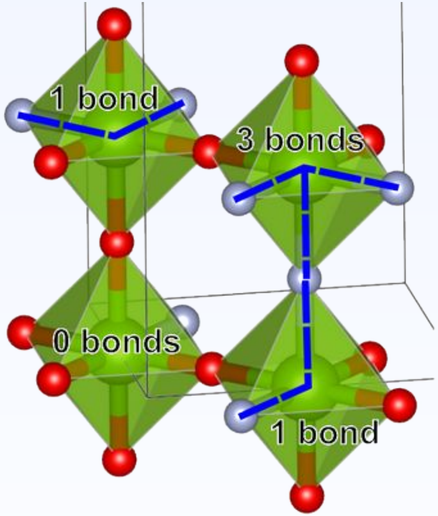
Count the M—B—M bonds



O_0 unit cell
All *cis* bonds

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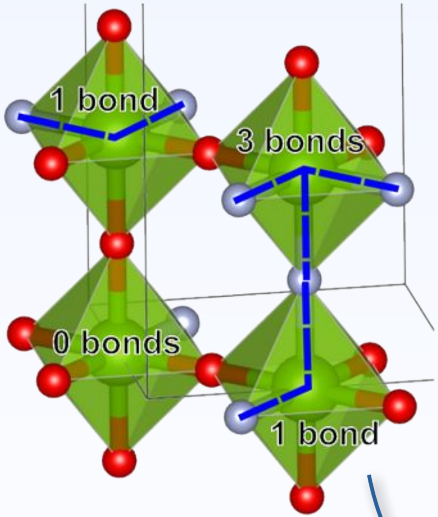

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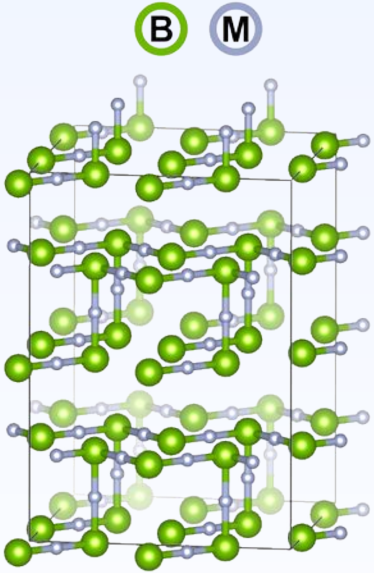
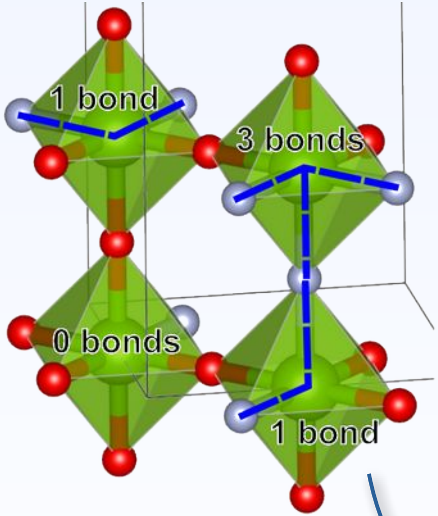


O_0
100% global cis bonding
Cis counts: 1, 0, 3, 1
3/4 octahedra with cis bonds

Low-energy orderings have a high degree of *cis* bonding

Count the M—B—M bonds



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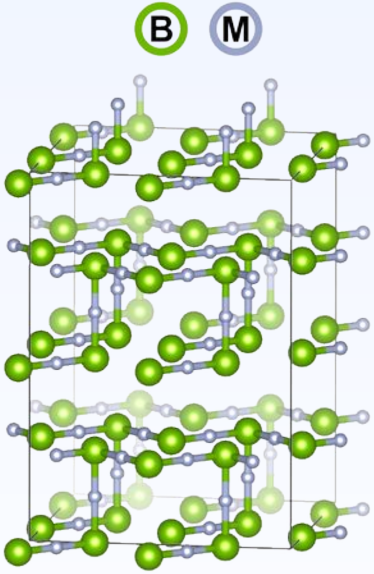

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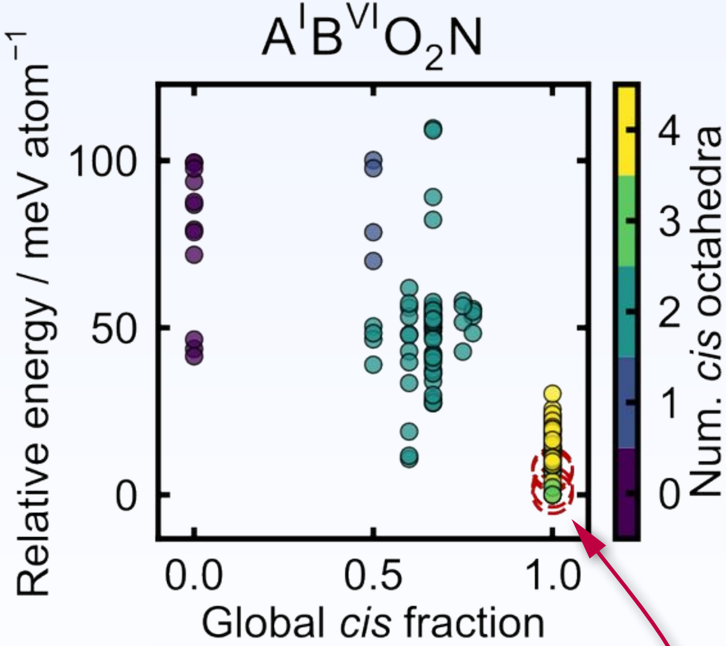

O_0 always has 100% global cis fraction

We identify 66 stable ABO_2N PON materials

1. Wang, H.-C., Schmidt, J., Botti, S. & L. Marques, M. A. A high-throughput study of oxynitride, oxyfluoride and nitrofluoride perovskites. *Journal of Materials Chemistry A* **9**, 8501–8513 (2021).

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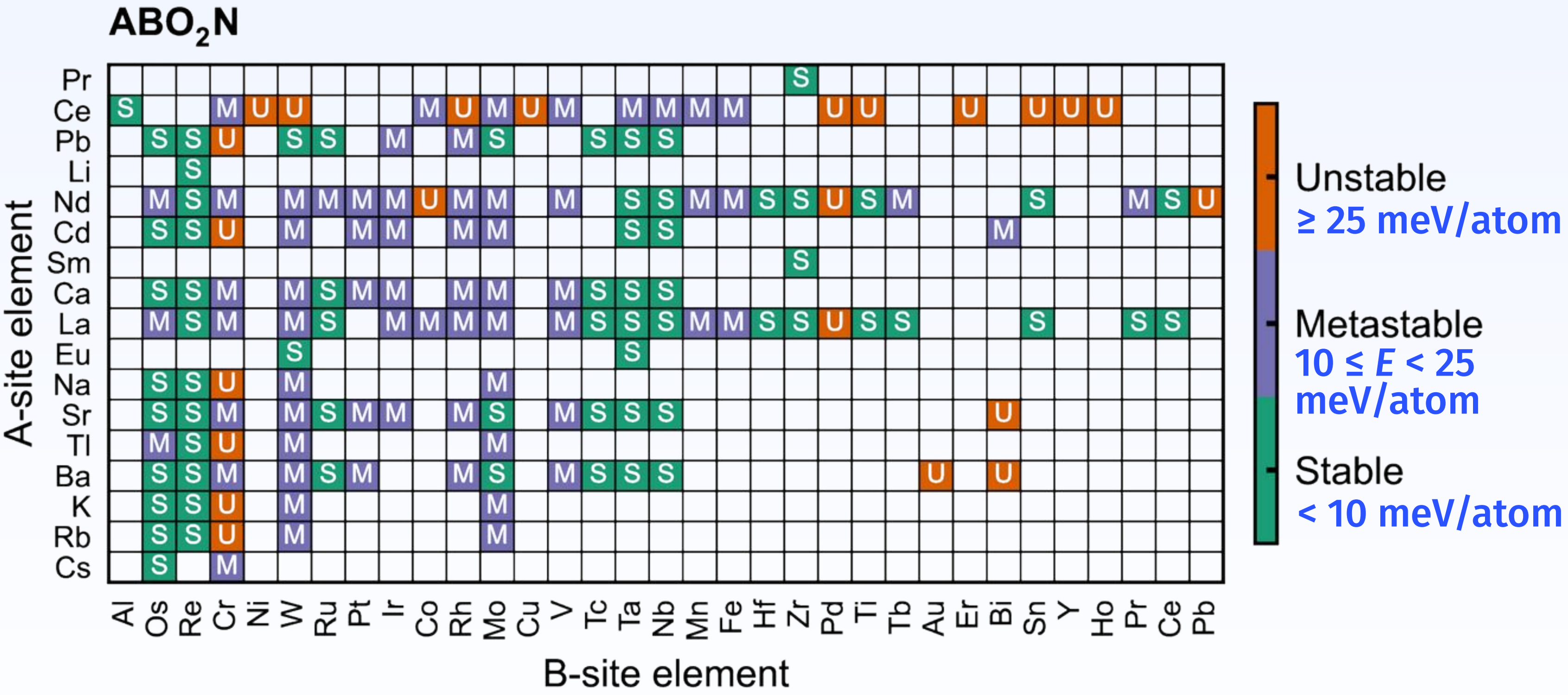

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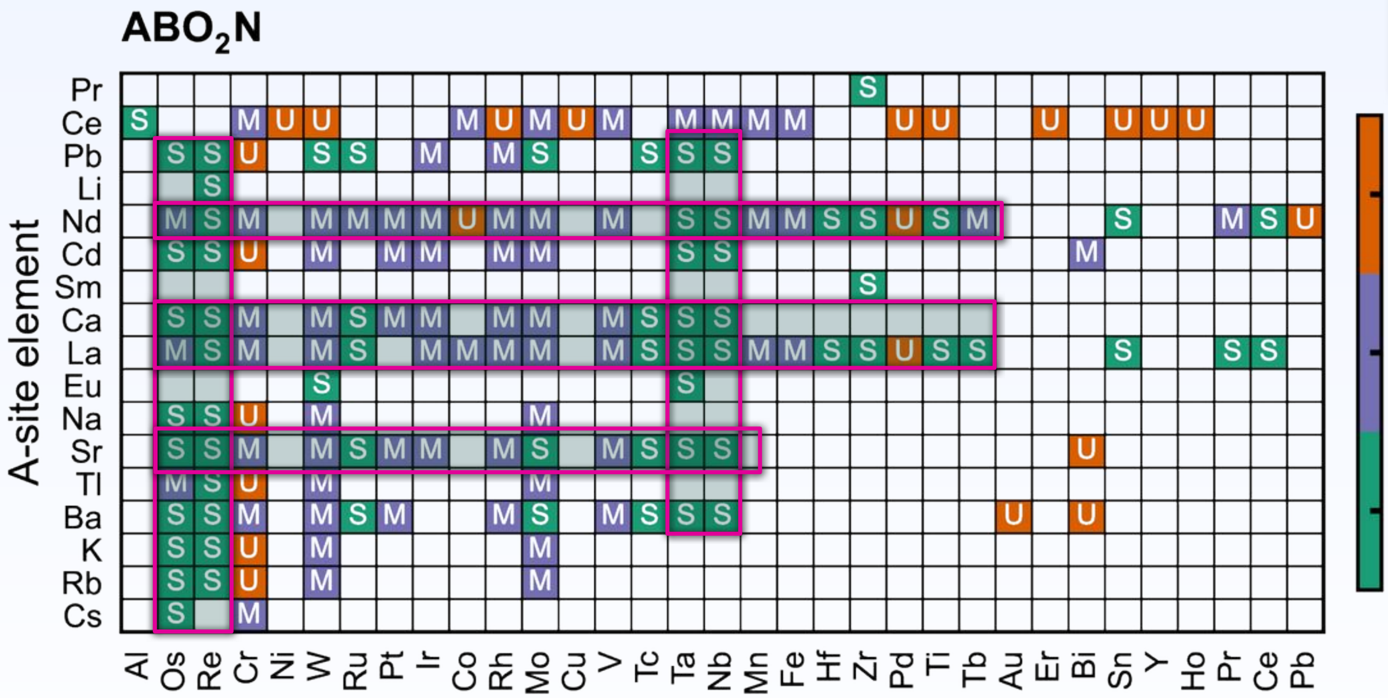
42.3% stable
43.0% metastable
14.7% unstable



Unstable
≥ 25 meV/atom

Metastable
$10 \leq E < 25$ meV/atom

Stable
< 10 meV/atom

A = {Nd, Ca, La, Sr, Ba}

B = {Os, Re,[1] W, Mo, Ta, Nb}

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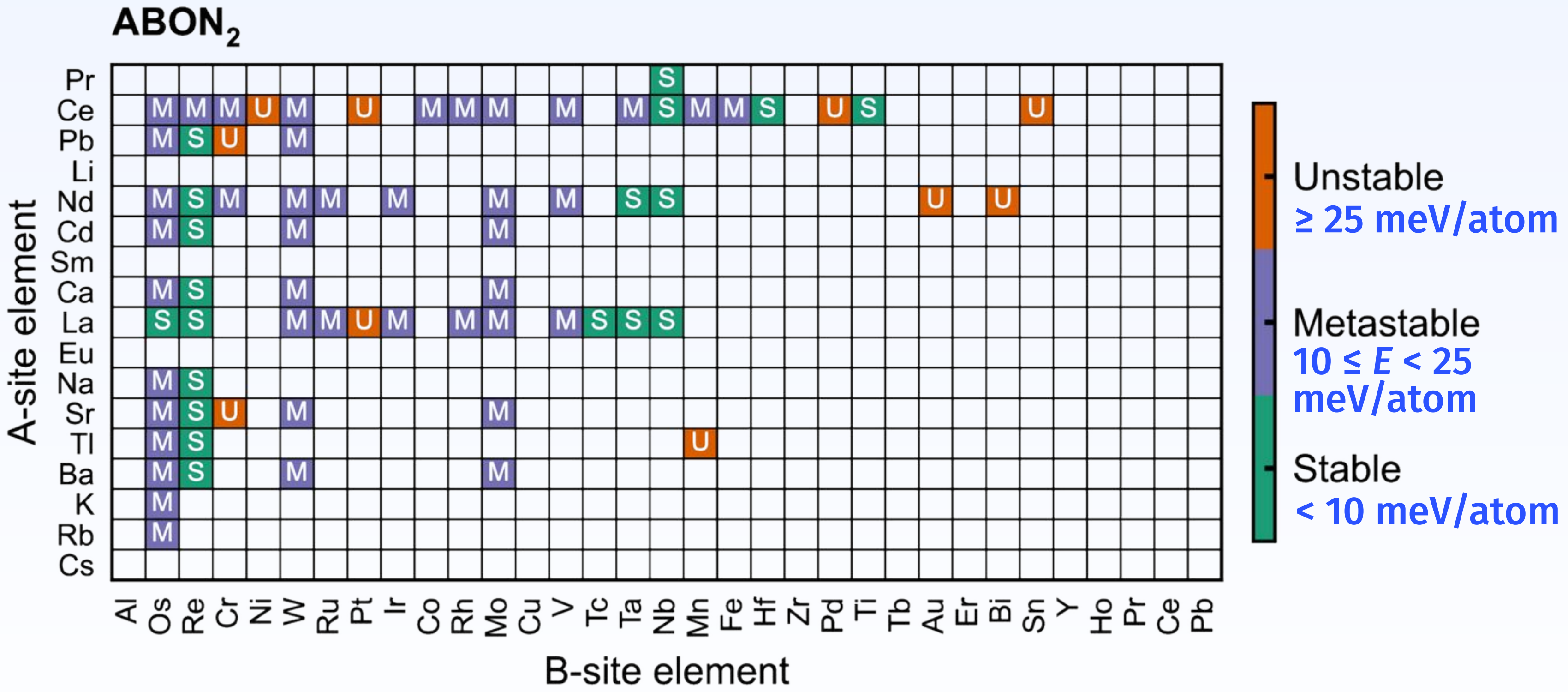
We identify 19 stable ABO_2N PON materials



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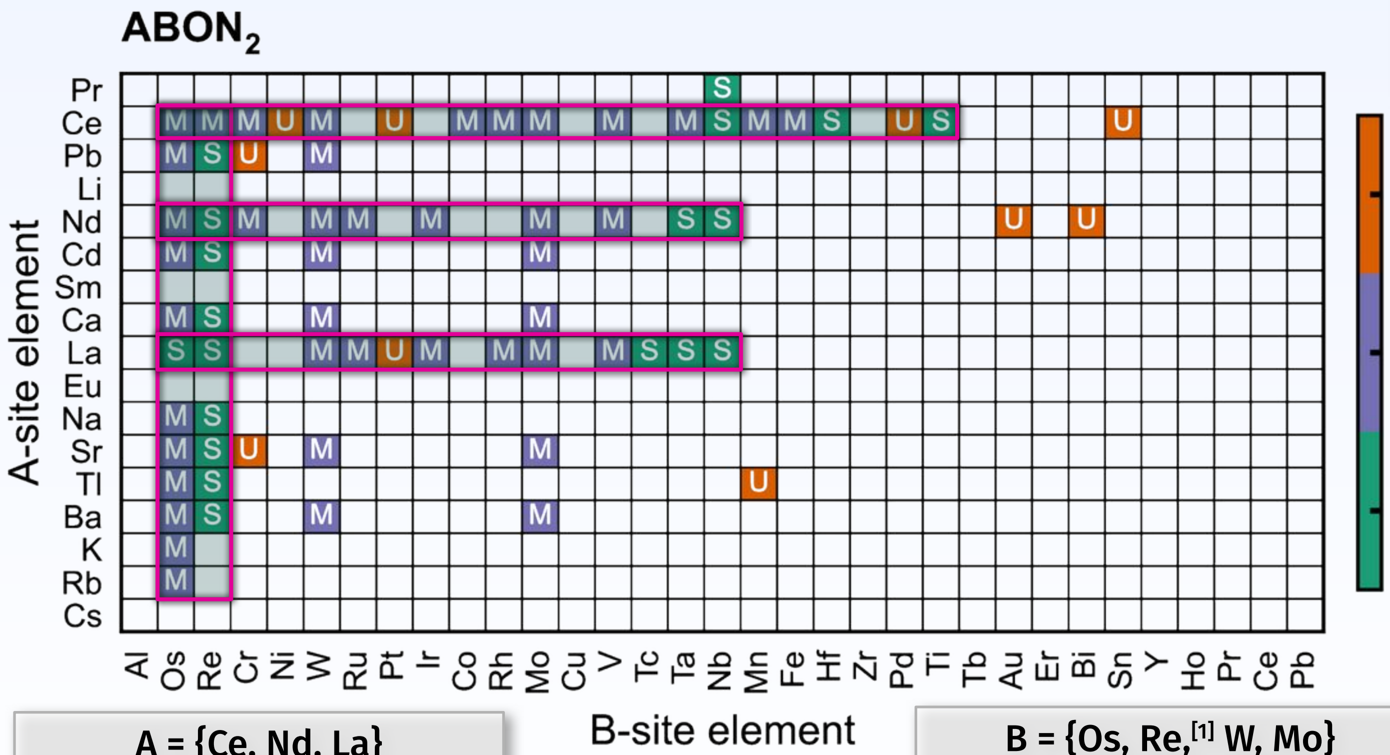

26.8% stable
59.2% metastable
14.1% unstable

Unstable
≥ 25 meV/atom

Metastable
$10 \le E < 25$ meV/atom

Stable
< 10 meV/atom

A = {Ce, Nd, La}

B = {Os, Re,[1] W, Mo}

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We generate a Pourbaix diagram for $LaTaO_2N$

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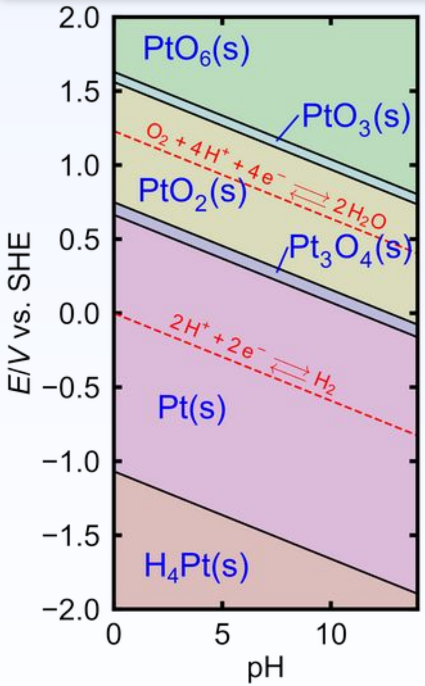
Pourbaix diagram, Pt-O-H system



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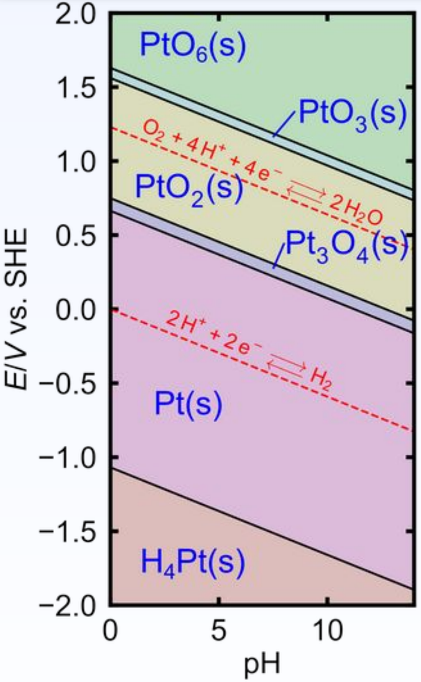
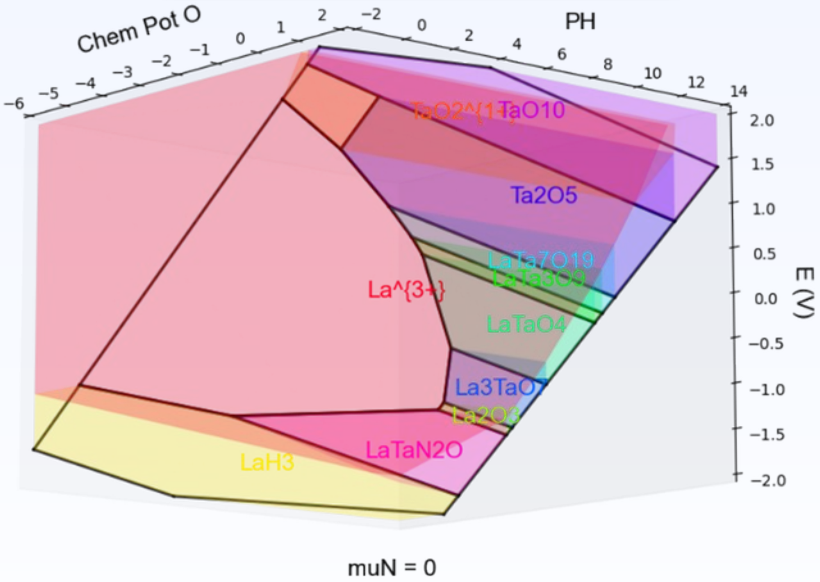


Pourbaix diagram, La-Ta-O-N-H system, $\mu_{La} = \mu_{Ta} = 0$

Animation



Jiadong Chen
Sun Research Group
Materials Science
University of Michigan

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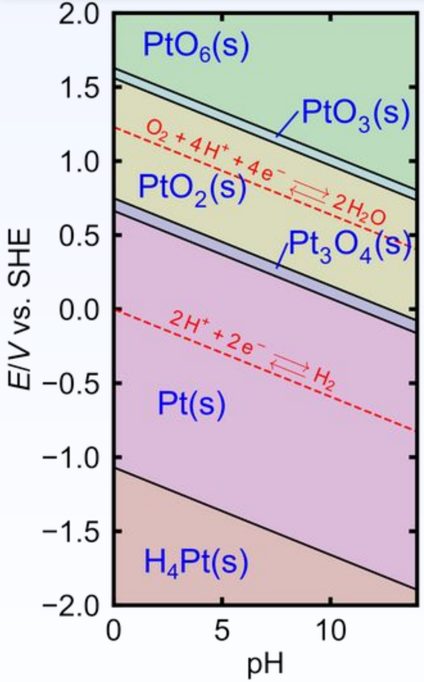

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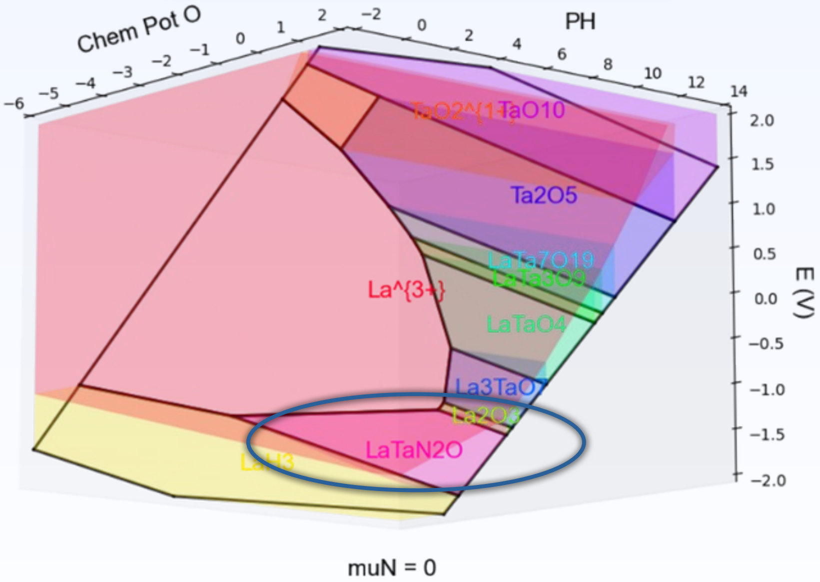

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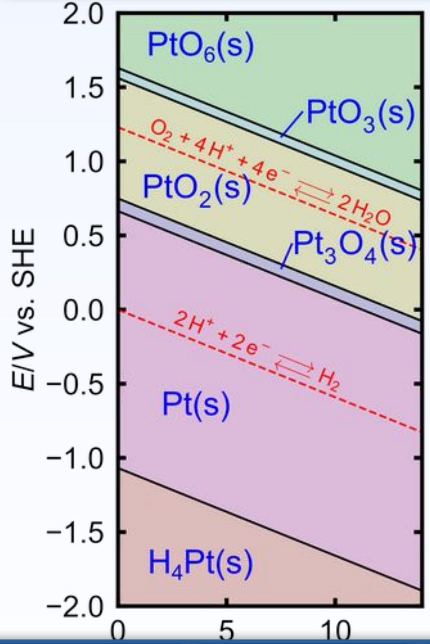

Pourbaix diagram, La-Ta-O-N-H system, $\mu_{La} = \mu_{Ta} = 0$

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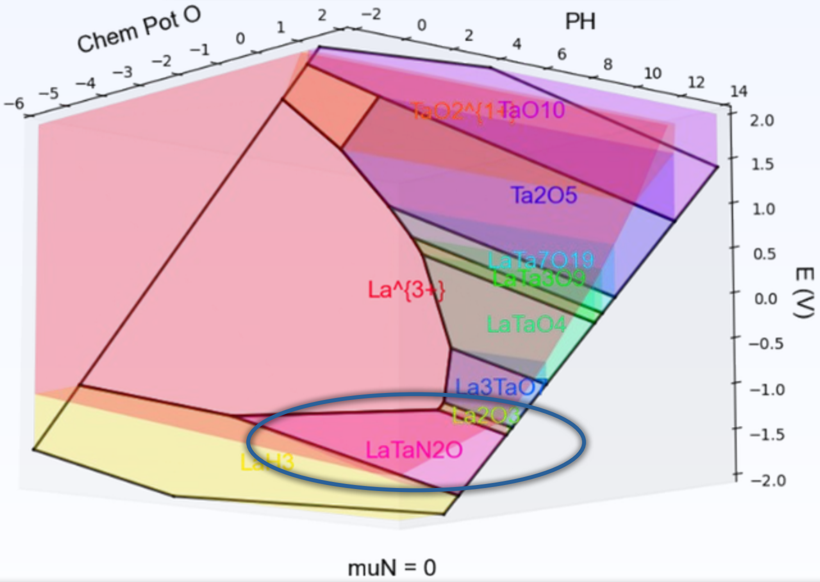

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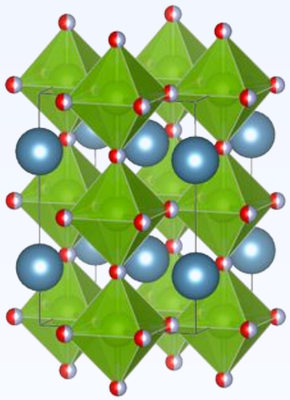
$LaTaO_2N$ appears to be synthesizable with relative low NH_3, N_2 pressures and flowrates.

Found 85 stable PONs and that *cis* ordering is preferred in PON structures



PON compound

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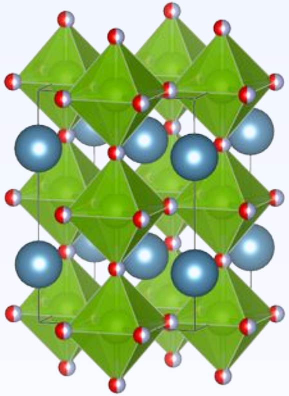

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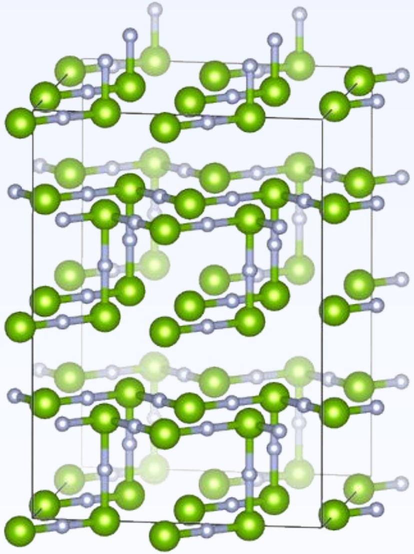

Anion ordering with
cis M—B—M bonds

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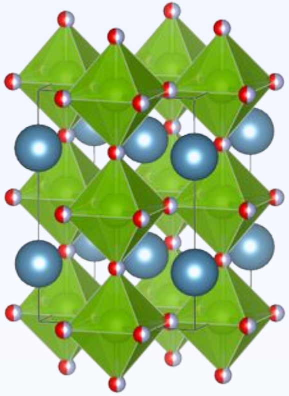

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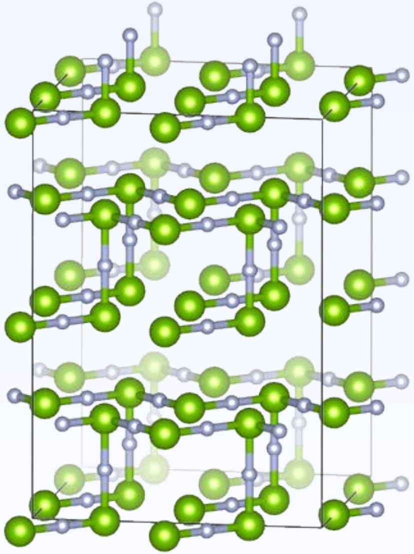

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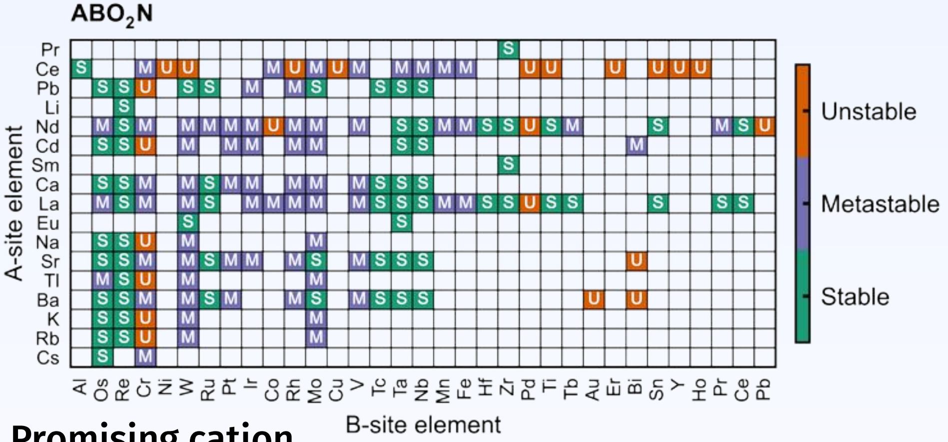

Promising cation
chemistries

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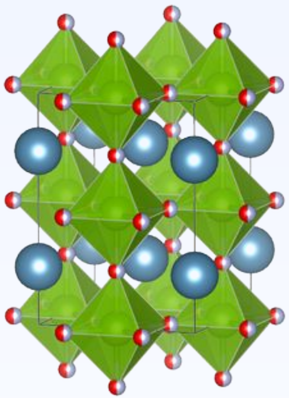

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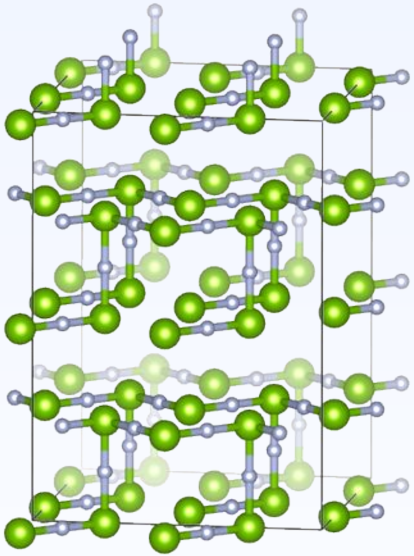

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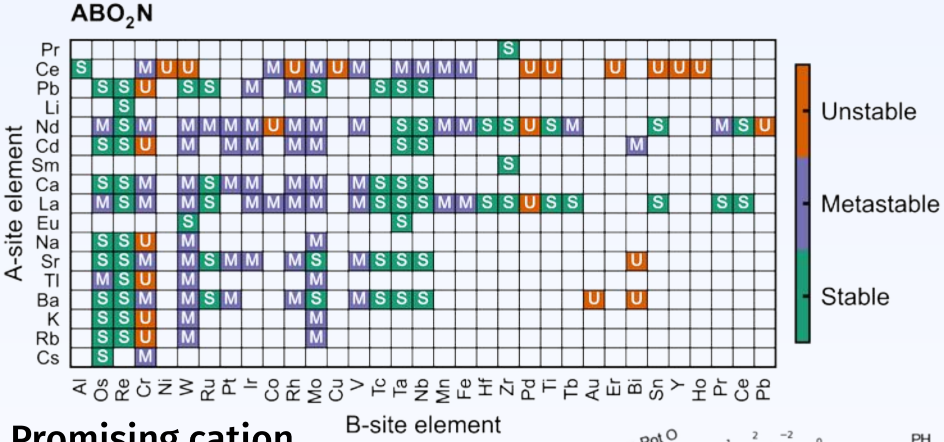

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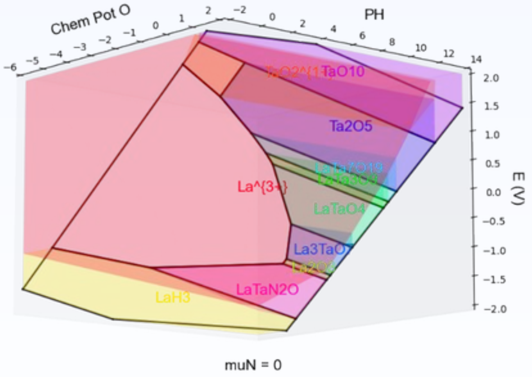
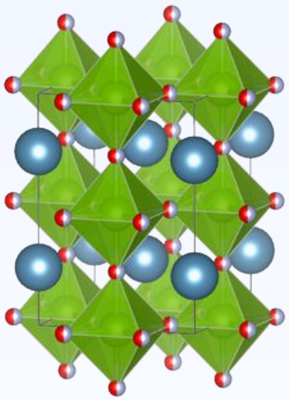


Developing electrochemical stability screening

Found 85 stable PONs and that *cis* ordering is preferred in PON structures



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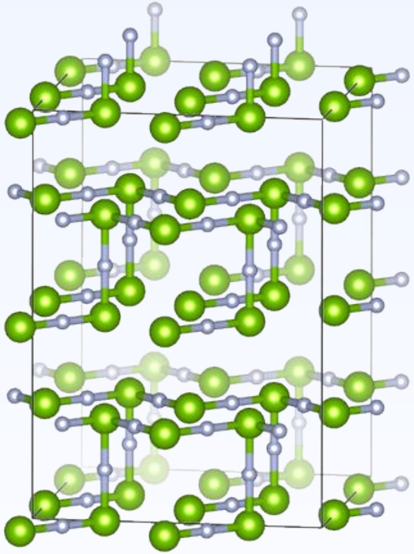

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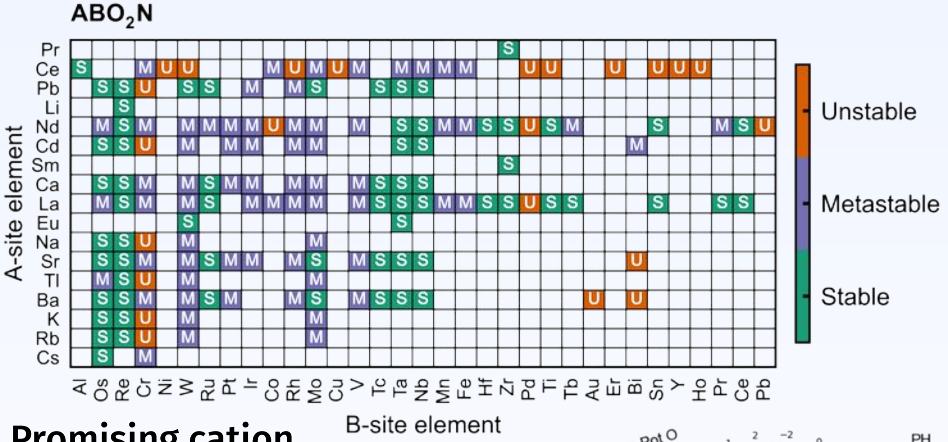

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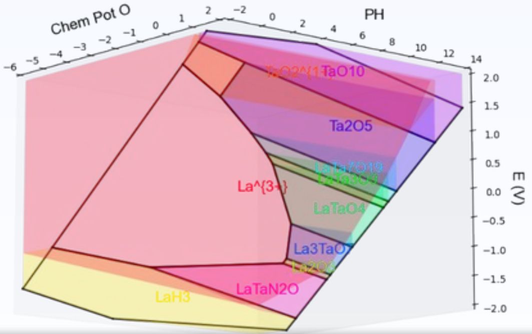

Developing electrochemical stability screening

Next steps: synthesis!! Collaborating with LANL experimentalists to make stable candidates.

Acknowledgments

Bryan Goldsmith
Chemical Engineering
University of Michigan

Bianca Ceballos
Materials Physics and Applications
Los Alamos National Laboratory

Ranganchary Mukundan
Materials Physics and Applications
Los Alamos National Laboratory

Jiadong Chen
Materials Science
University of Michigan

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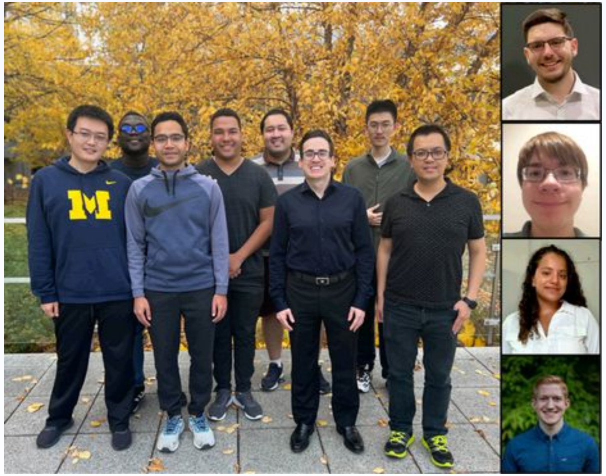

Amitava Banerjee
Metallurgical & Materials Engineering
IIT-Jodhpur

Ghanshyam Pilania
Materials Science and Technology
Los Alamos National Laboratory

Wenhao Sun
Materials Science
University of Michigan

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J. Robert Beyster Computational Innovation Graduate Fellows Program

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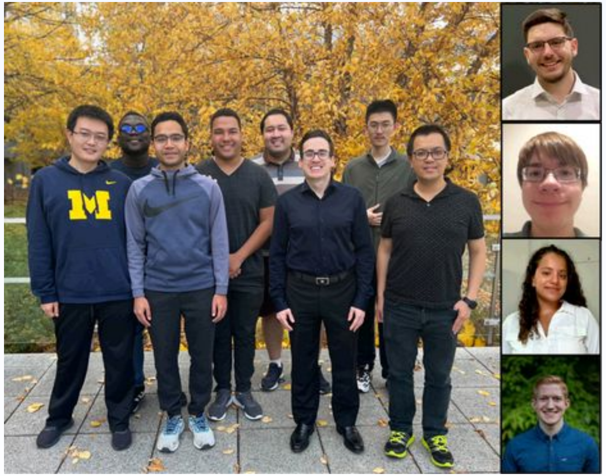

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Questions?

Backup Slides

Low-energy orderings have a high degree of *cis* bonding

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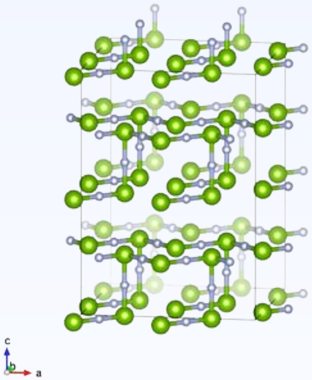
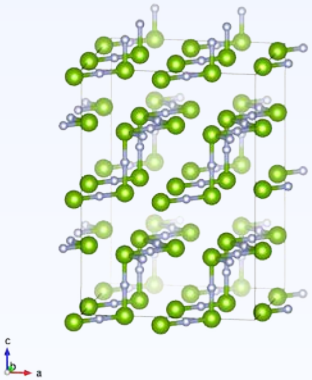
B M



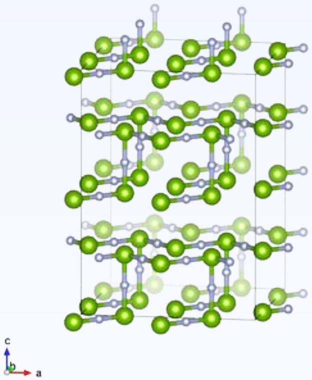
ordering-0
100% global cis bonding
Cis counts: 1, 0, 3, 1
3/4 octahedra with cis bonds



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

Low-energy orderings have a high degree of *cis* bonding

B M



ordering-0
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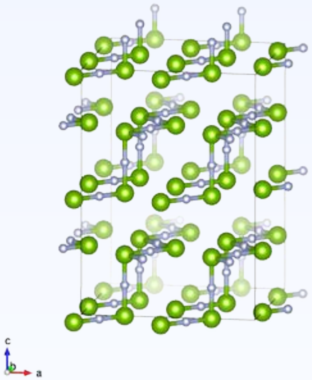
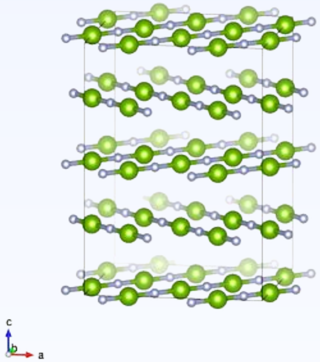
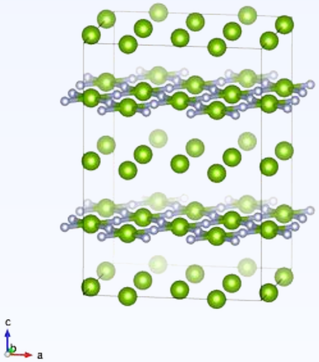


ordering-1
100% global cis bonding
Cis counts: 1, 0, 3, 1
3/4 octahedra with cis bonds

…



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**

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).

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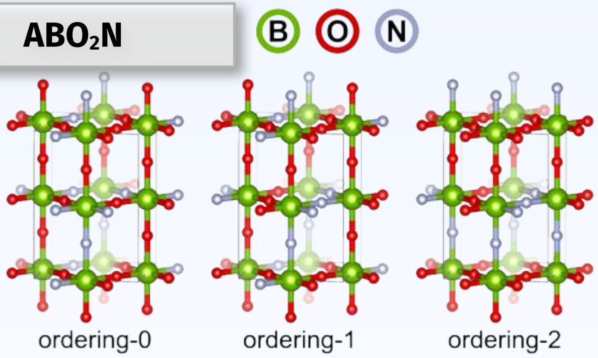
ABO_2N



... (29 more)

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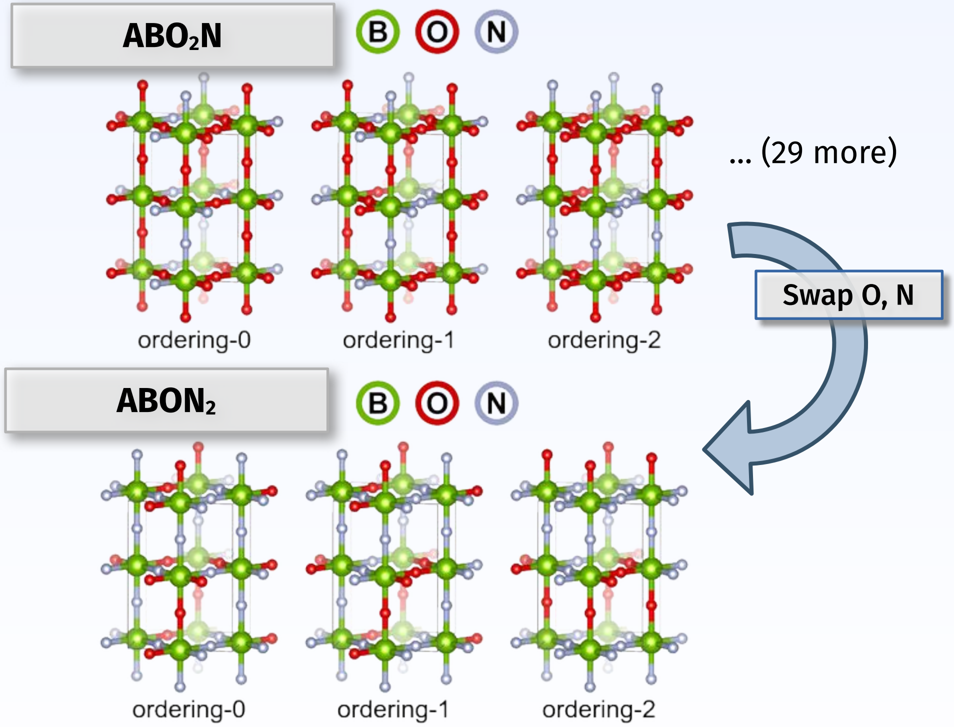

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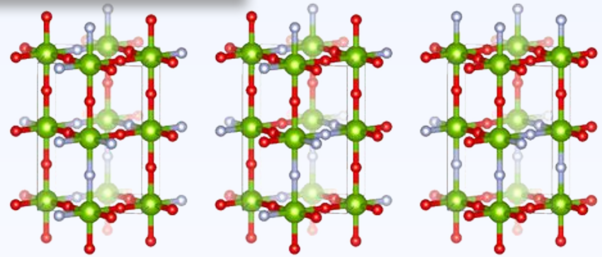
ABO_2N

B O N

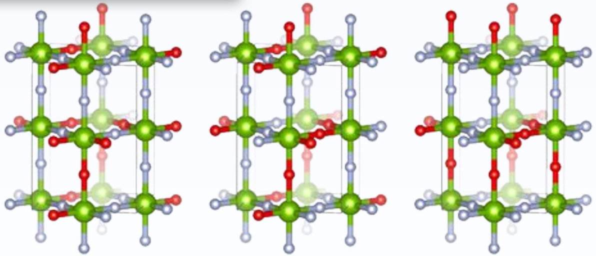


... (29 more)

Swap O, N

$ABON_2$

B O N

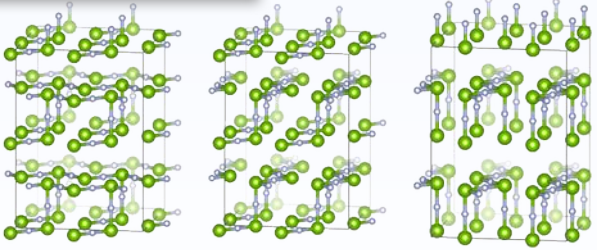


Look at M-B-M bonds only

Topology

B M

M = minority composition anion



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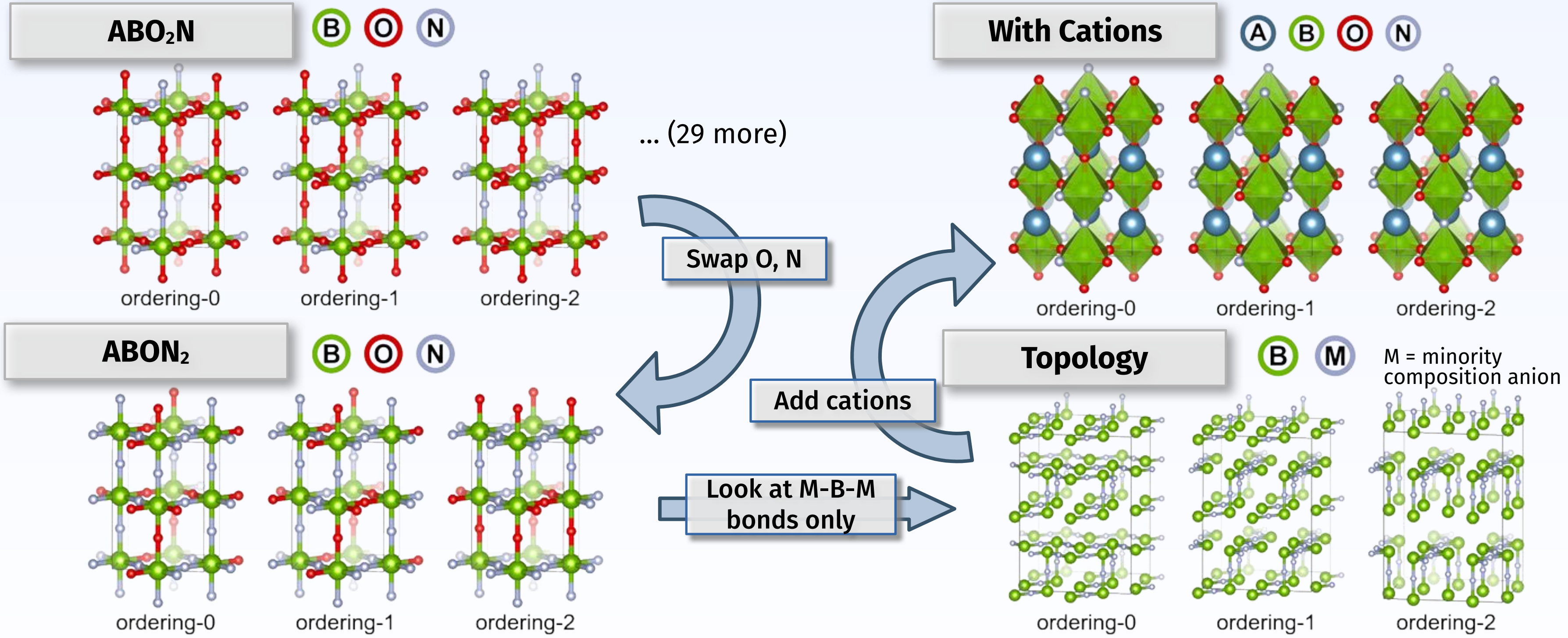

We screen 295 PON compounds and group by stability above convex hull

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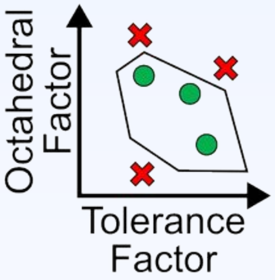
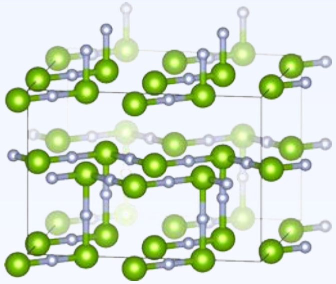


Cation pairs

+



Optimal anion ordering

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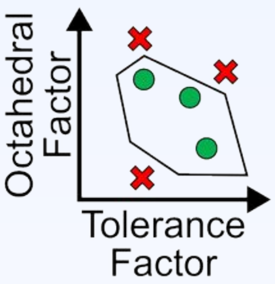

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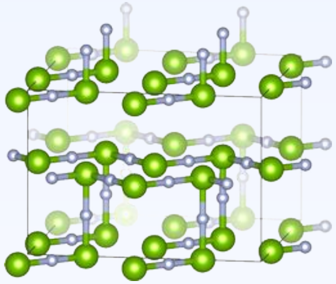
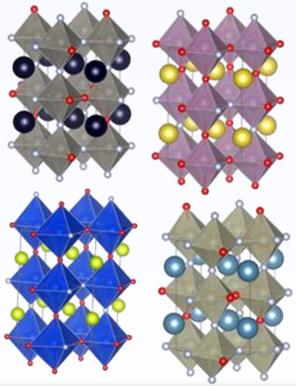


Cation pairs **Optimal anion ordering**



... 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).

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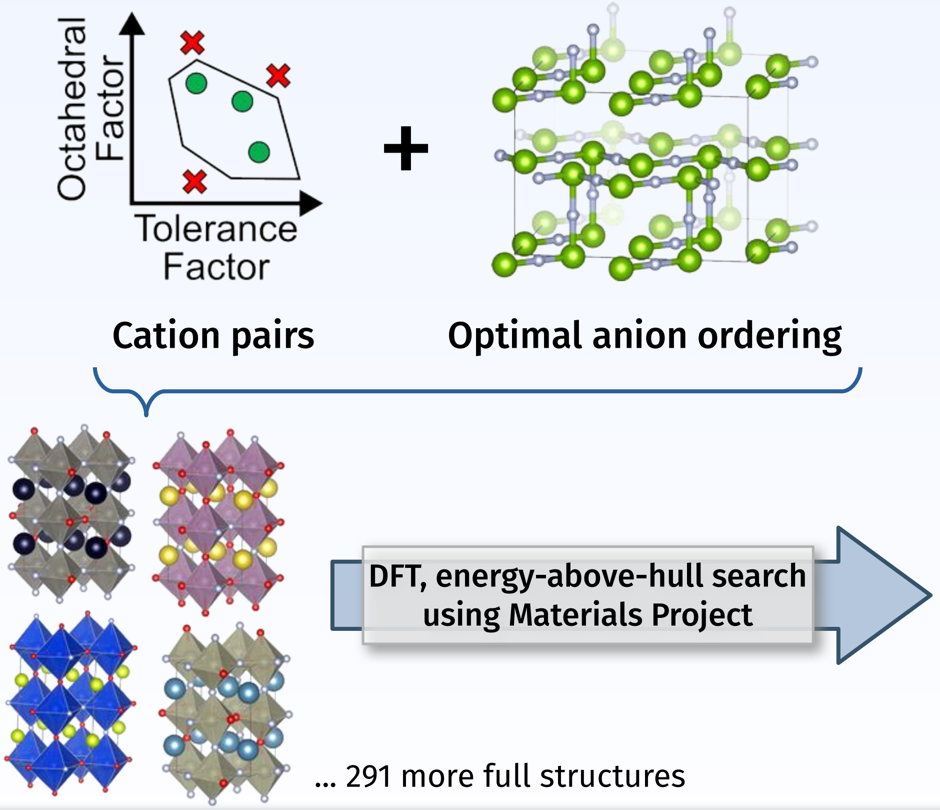

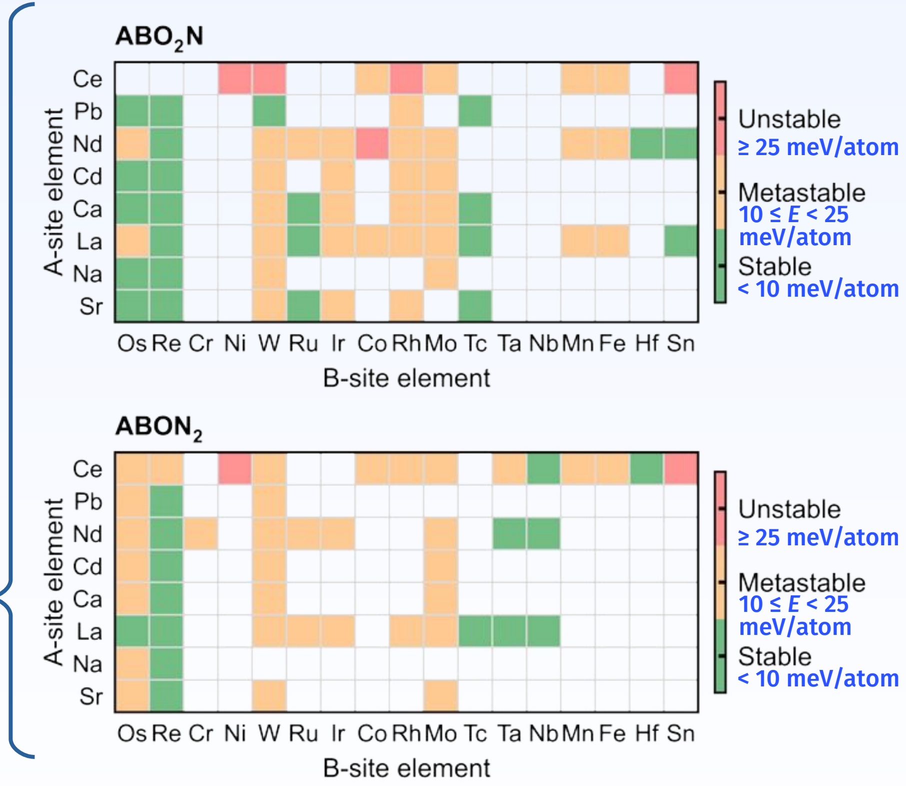

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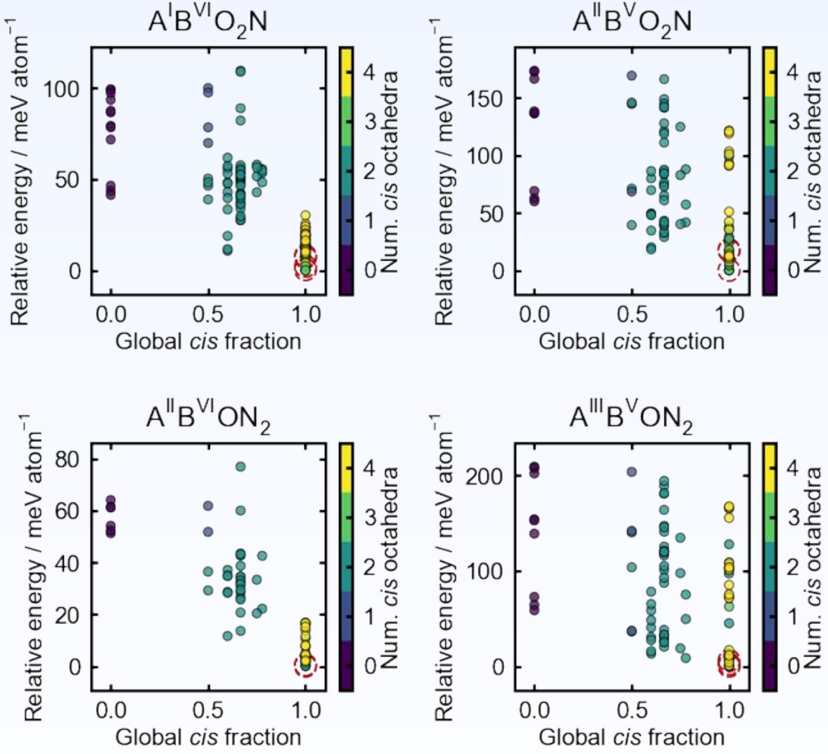
A global *cis* fraction of 1 leads to the most stable anion ordering, for all cation pairs



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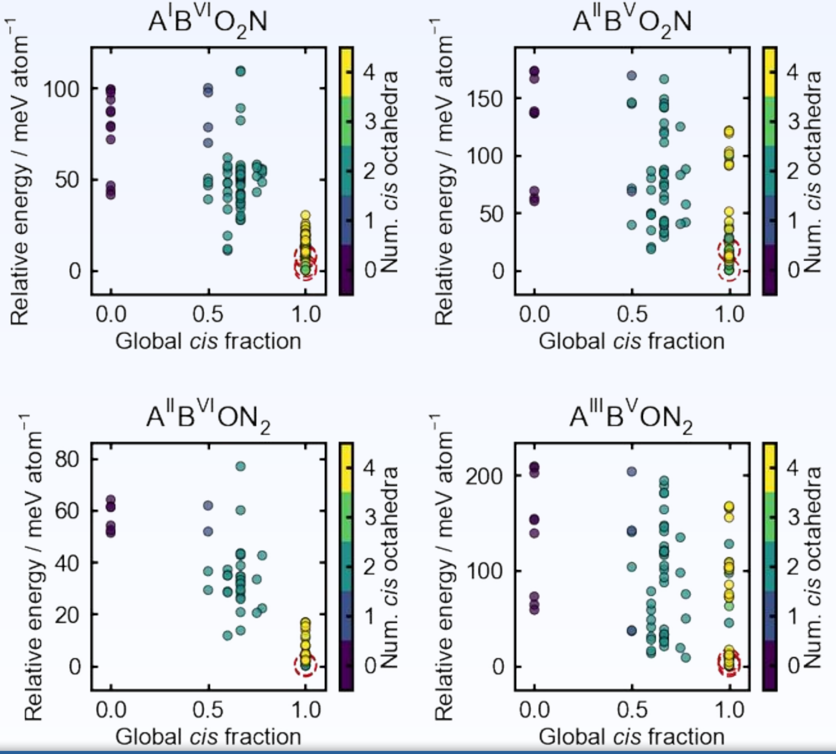
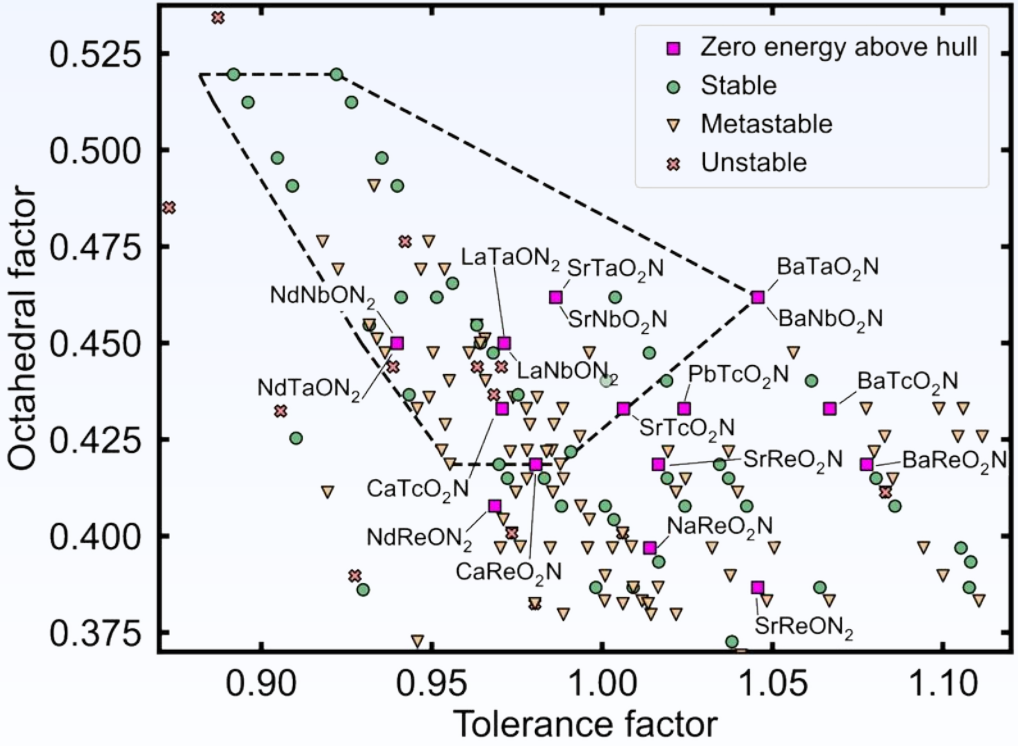


Correlations not strong across all cation pairs, but high fraction of global *cis* ordering is important.

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 $CaReO_2N$

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Sun Research Group
Materials Science
University of Michigan

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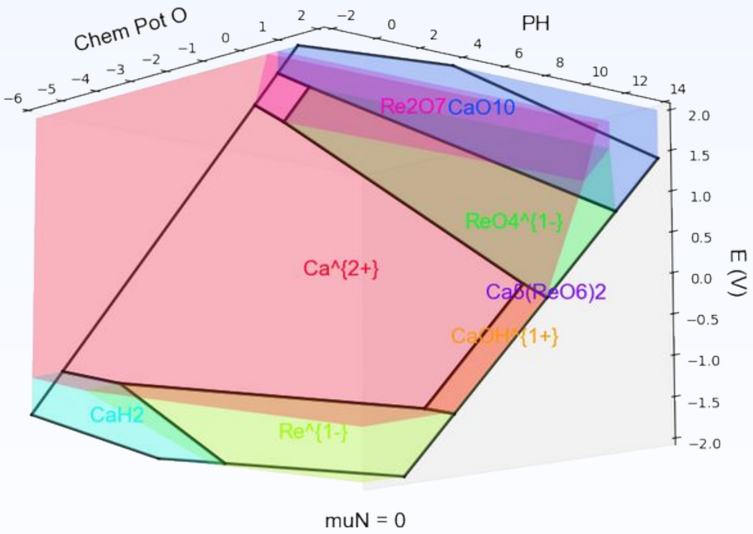
Pourbaix diagram, $\mu_{Ca} = \mu_{Re} = 0$



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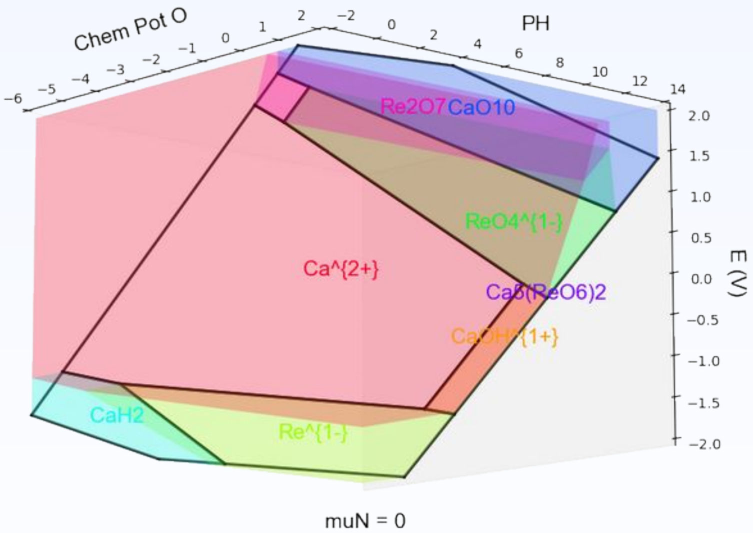
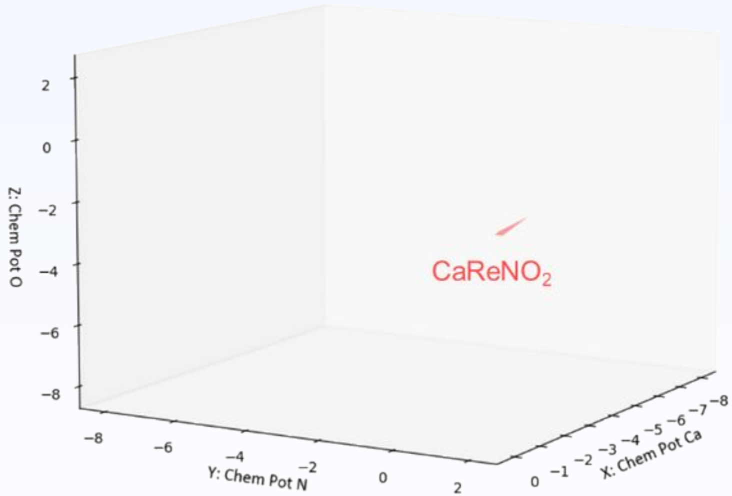


Stability region for solid PON



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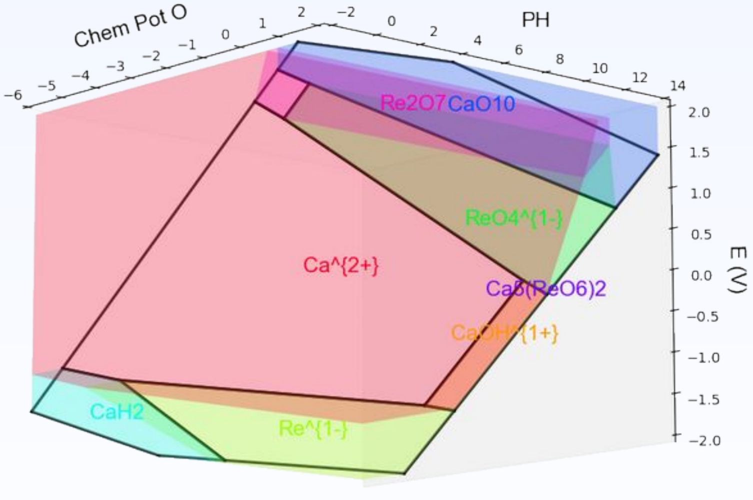
We generate a Pourbaix diagram for $CaReO_2N$

Pourbaix diagram, μ_{Ca} = μ_{Re} = 0

Animation



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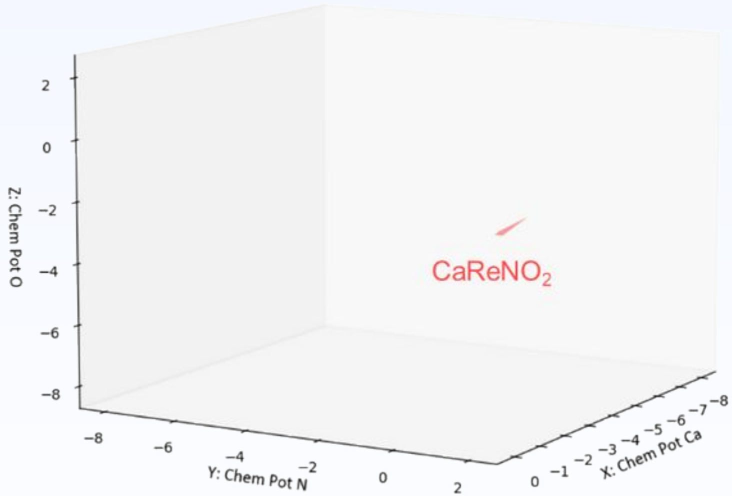

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Synthesis could require very high partial pressures of NH_3 or N_2 precursor.

MvK mechanism for perovskite oxynitrides

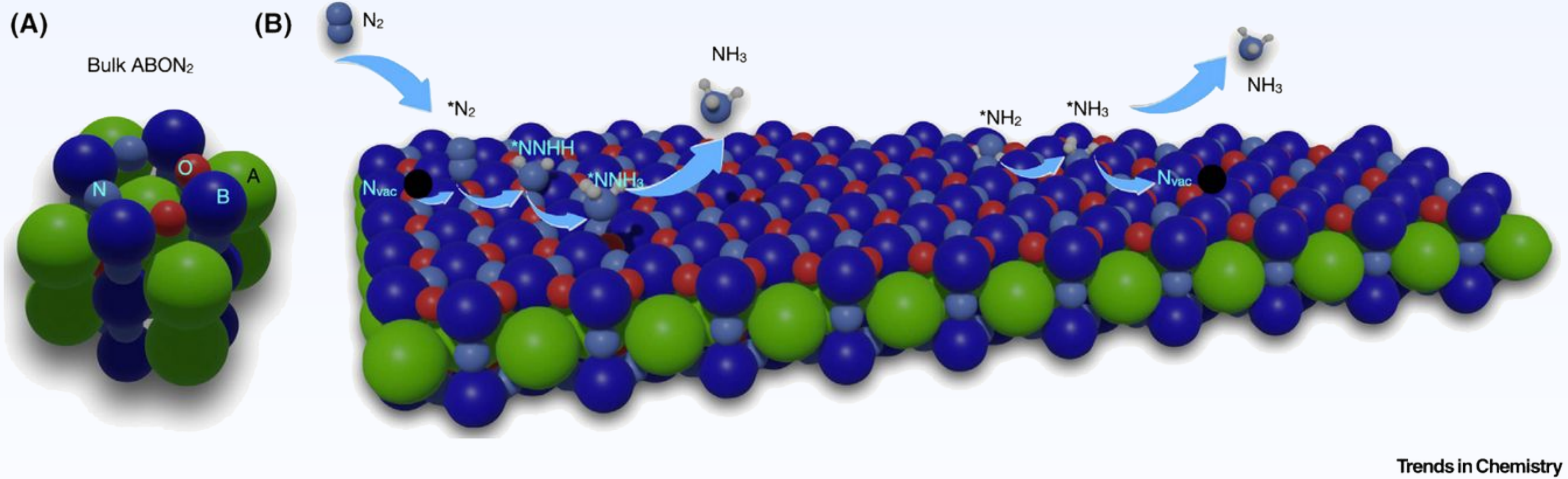

Figure 1. Overview of the electrocatalytic nitrogen reduction reaction (ENRR) on an $ABON_2$ perovskite oxynitride. (A) Bulk unit cell of an $ABON_2$ perovskite oxynitride. (B) Illustration of an associative distal Mars-van-Krevelen mechanism, with N vacancies (N_{vac}, ●) facilitating associative adsorption and stepwise hydrogenation of N_2 to NH_3. Atom key: light blue = N, red = O, green = A, dark blue = B, gray = H.

Young, S. D., Banerjee, A., Pilania, G. & Goldsmith, B. R. Perovskite oxynitrides as tunable materials for electrocatalytic nitrogen reduction to ammonia. *Trends in Chemistry* **3**, 694–696 (2021).