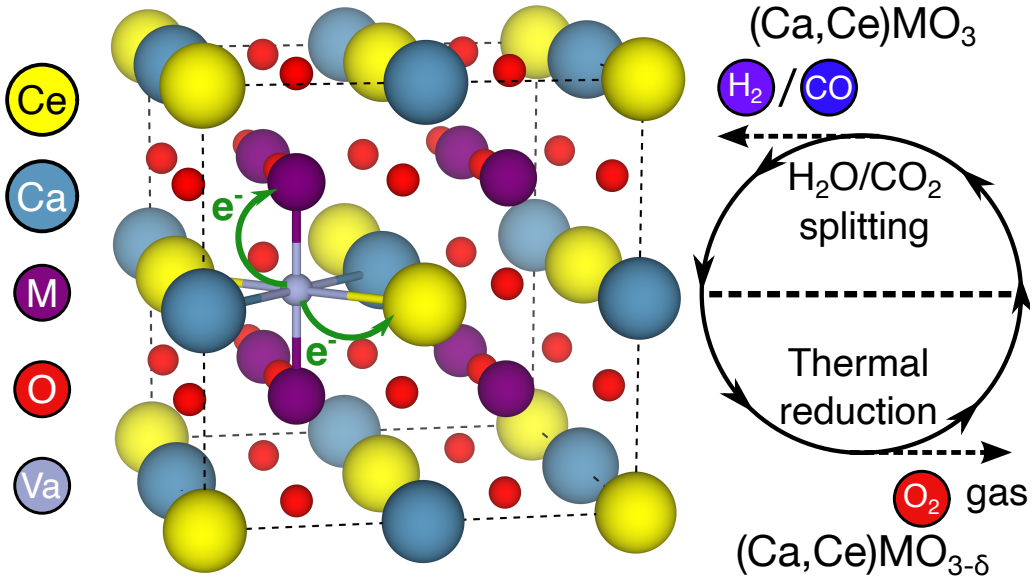


Discovering oxide perovskites with simultaneous cation redox-activity using first-principles for solar thermochemical applications

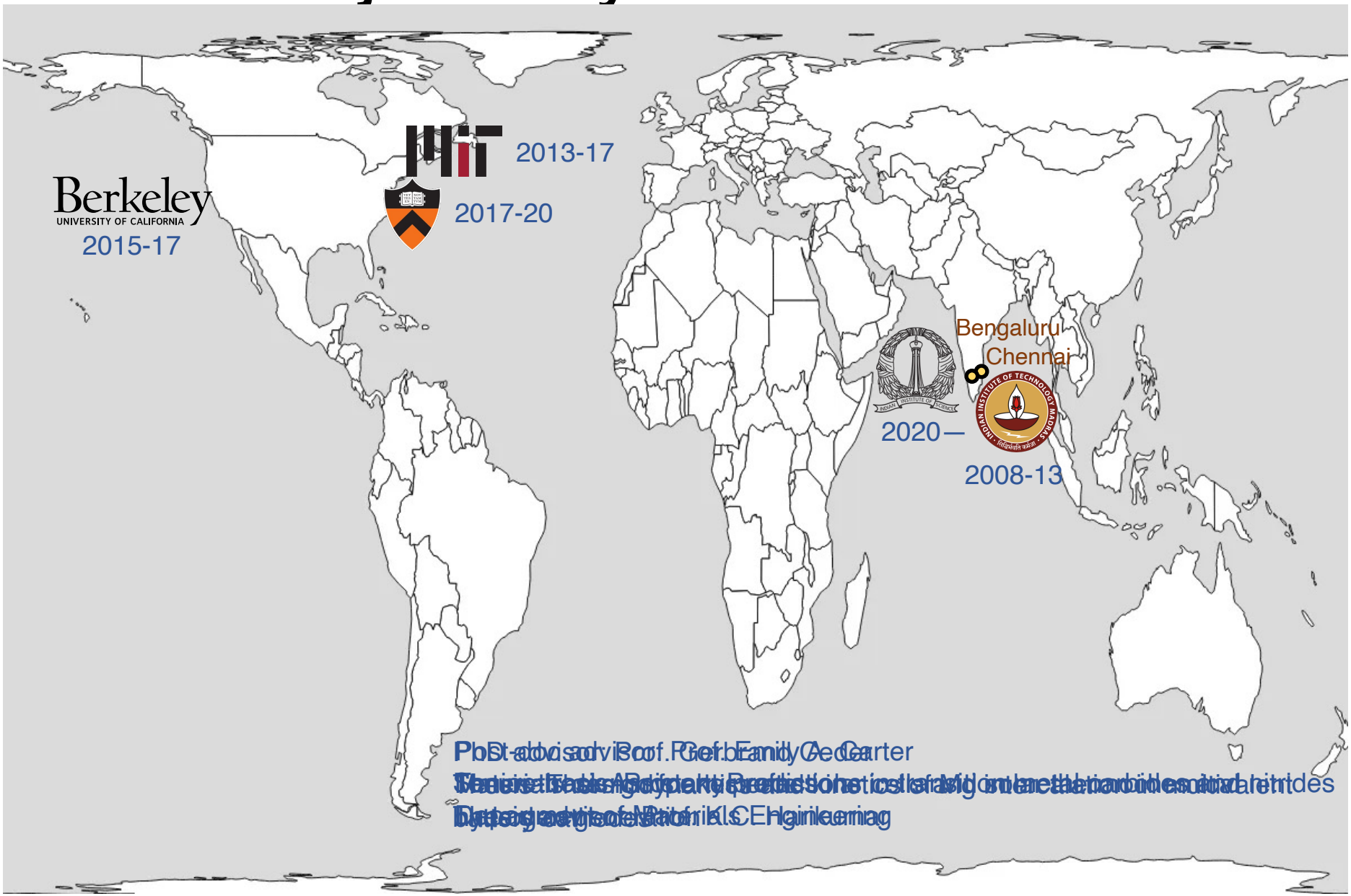
Sai Gautam Gopalakrishnan, Ellen B. Stechel, Emily A. Carter

Indian Institute of Science & Princeton University

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

Pratidhwani, Indian Institute of Technology Delhi
Nov 12, 2020

Scientific journey so far…



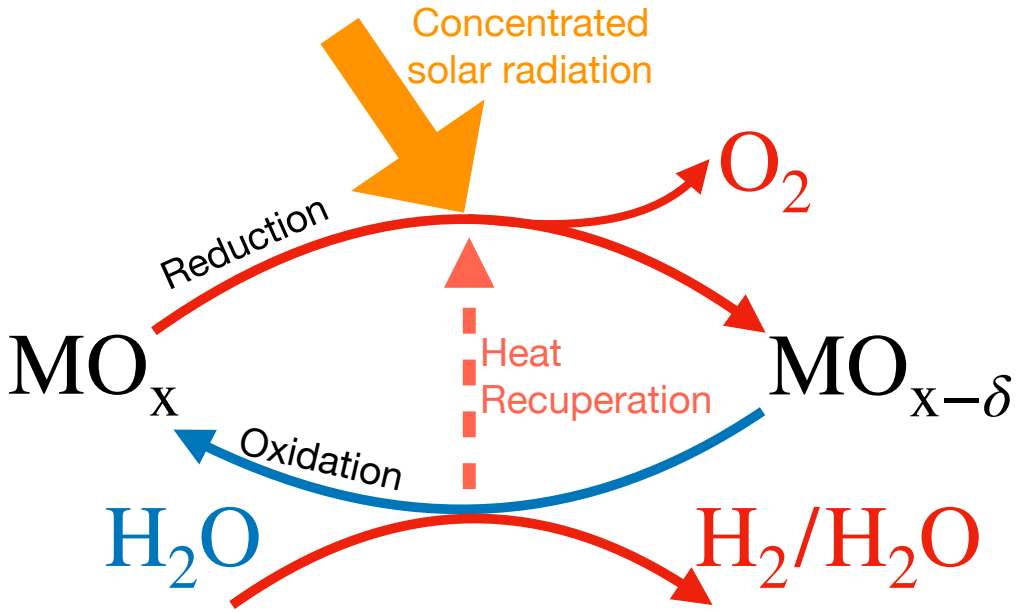
https://en.wikipedia.org/wiki/Gall%E2%80%93Peters_projection

Solar thermochemical (STC) production of H_2 and/or CO

Candidates so far:

- CeO_2
- $Fe(Fe,X)_2O_4$
- $(A,A')BO_3$

$$\frac{1}{\delta} MO_x \rightarrow \frac{1}{\delta} MO_{x-\delta} + \frac{1}{2} O_2$$



Thermal reduction (TR)
High T (> 1473 K)
~vacuum ($p_{O_2} < 100$ Pa)

Water splitting (WS)
Low T (873-1073 K)
High H_2 yield $\left(\frac{p_{H_2O}}{p_{H_2}} = 9\right)$

State-of-the-art:
Pure and doped fluorite-CeO_2

$$\frac{1}{\delta} MO_{x-\delta} + H_2O \rightarrow \frac{1}{\delta} MO_x + H_2$$

Needs "good" materials!

- Durability (withstand high TR and low WS temperatures)
- Capacity (tolerate high degrees of oxygen off-stoichiometry)
- Stability (no undesired phase transformations)

New candidates?

Siegel *et al.*, **Ind. Eng. Chem. Res. 2013**, *52*, 3276
Carillo and Scheffe, **Sol. Energy 2017**, *156*, 3

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Candidates so far:

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Image: https://www.solarpaces.org/csp-efficient-solar-split-h2o-hydrogen/

German research center (DLR), 2017

State-of-the-art: Pure and doped fluorite-CeO_2

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Enthalpy of reduction = spontaneity

$$\frac{1}{\delta} MO_x \rightarrow \frac{1}{\delta} MO_{x-\delta} + \left(\frac{1}{2}\right) O_2(g)$$ Reducing conditions

Enthalpy of reduction for the induced off-stoichiometry, δ

$$\Delta H_{reduction} = \frac{H_{MO_{x-\delta}} - H_{MO_x}}{\delta} + \left(\frac{1}{2}\right) H_{O_2}(g)$$

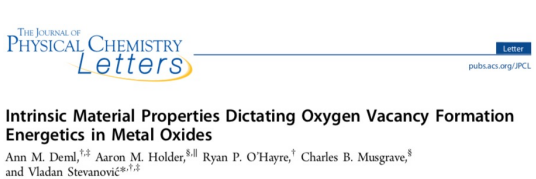
If $\delta \rightarrow 0$, then

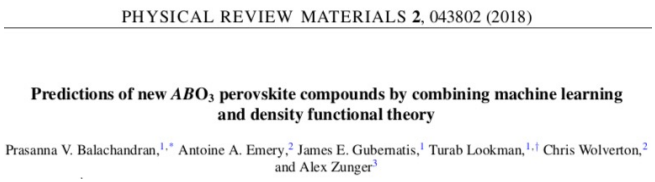
$$\Delta H_{reduction} = -\frac{dH_{MO_x}}{dx}\Big|_x + \left(\frac{1}{2}\right) H_{O_2}(g) \equiv \Delta H_{formation}^{Va_O}$$

Oxygen vacancy formation energy (Calculable)

Low $\Delta H_{reduction}$ = large δ
But induced δ needs to be recovered during water-splitting (re-oxidation) →optimal $\Delta H_{reduction}$

Thermodynamic models[1] point to optimal $\Delta H_{reduction}$ or $\Delta H_{formation}^{Va_O}$ ~ 3.4-3.9 eV (CeO_2 is ~4 eV)
Theoretical screening purposes: 3.2-4.1 eV ($\pm$0.2 eV error)





1.Stechel, Ermanoski, and Miller, in preparation

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$$\Delta H_{reduction} = \frac{H_{MO_{x-\delta}} - H_{MO_x}}{\delta} + \left(\frac{1}{2}\right) H_{O_2}(g)$$

Several studies have theoretically screened, high-throughput calculations and/or machine learning, for novel ABO_3 perovskites, based on a $\Delta H_{formation}^{Va_O}$ range

- Candidates either exhibit rare elements (e.g., Eu, Ho) or don't exceed CeO_2's performance in experiments (stability or kinetic limitations or theory error)
- Entropic handles? Beyond ternary ABO_3 candidates?

Thermodynamic models[1] point to optimal $\Delta H_{reduction}$ or $\Delta H_{formation}^{Va_O}$ ~ 3.4-3.9 eV (CeO_2 is ~4 eV)

Theoretical screening purposes: 3.2-4.1 eV ($\pm$0.2 eV error)


CHEMISTRY OF MATERIALS

Article

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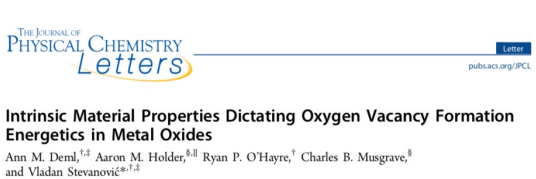
High-Throughput Computational Screening of Perovskites for Thermochemical Water Splitting Applications

Antoine A. Emery, James E. Saal, Scott Kirklin, Vinay I. Hegde, and Chris Wolverton*

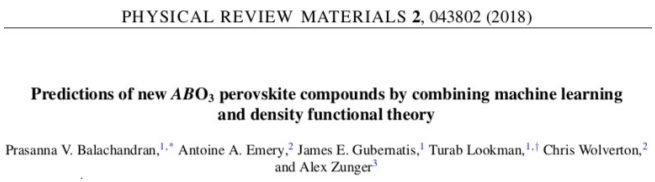

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

Intrinsic Material Properties Dictating Oxygen Vacancy Formation Energetics in Metal Oxides

Ann M. Deml, Aaron M. Holder, Ryan P. O'Hayre, Charles B. Musgrave, and Vladan Stevanović*


PHYSICAL REVIEW MATERIALS 2, 043802 (2018)

Predictions of new ABO_3 perovskite compounds by combining machine learning and density functional theory

Prasanna V. Balachandran, Antoine A. Emery, James E. Gubernatis, Turab Lookman, Chris Wolverton, and Alex Zunger

1.Stechel, Ermanoski, and Miller, in preparation

Higher entropy of reduction = higher productivity

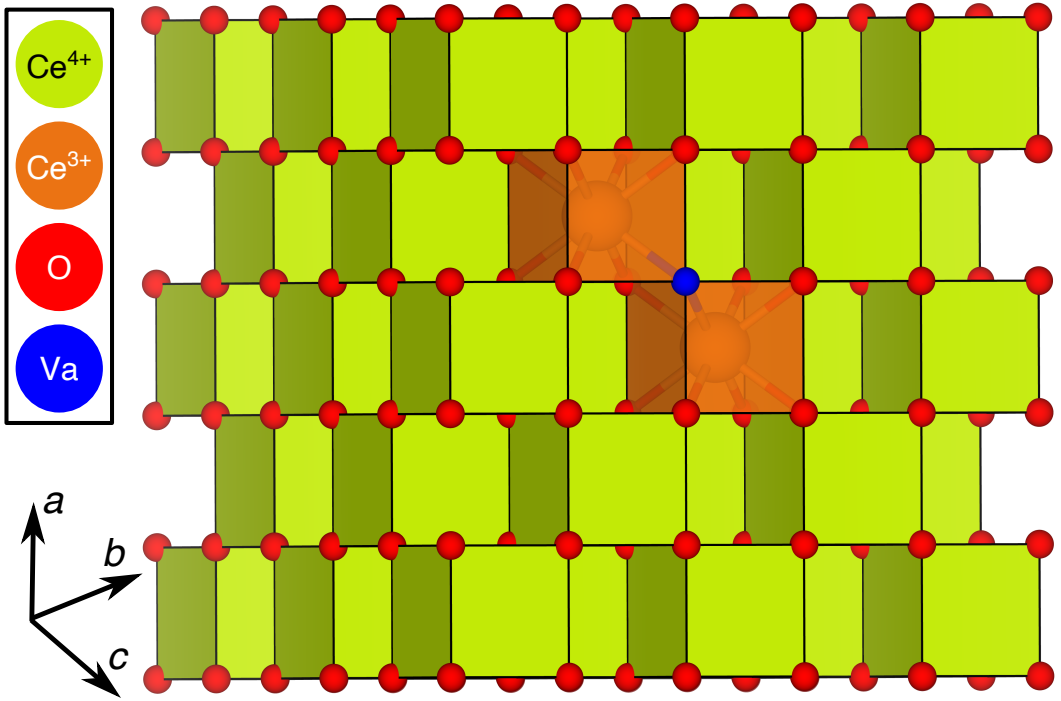
Entropy of reduction for an induced off-stoichiometry, δ, in ABO_3

$$\Delta S_{reduction} = \frac{S_{ABO_{3-\delta}} - S_{ABO_3}}{\delta} + \left(\frac{1}{2}\right) S_{O_2}(g)$$

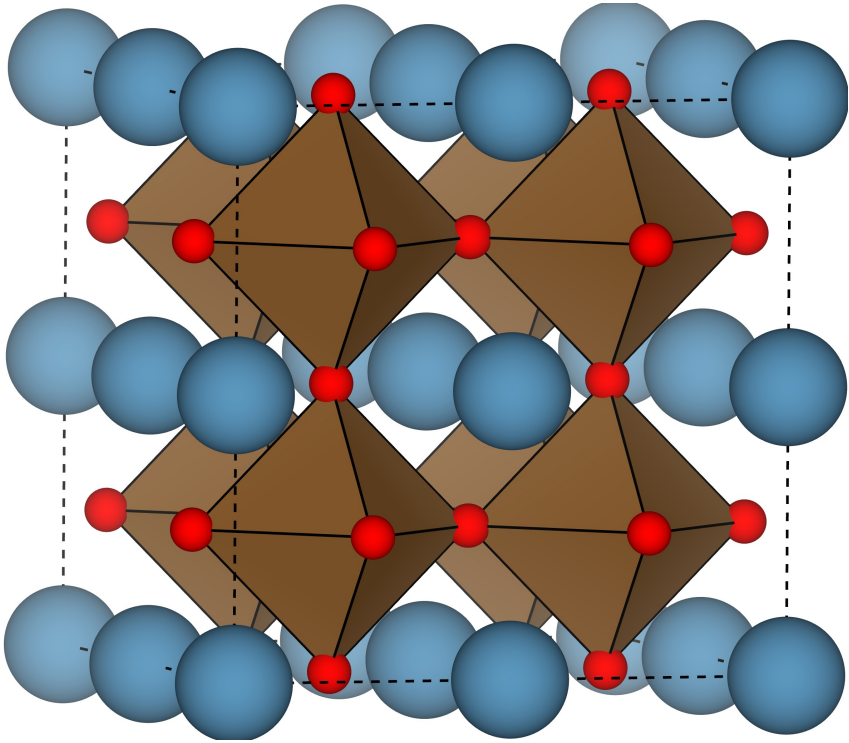
solid gas

Not easily calculable

Higher $\Delta S_{reduction}$ → stabilizes large δ → can result in higher H_2/mol oxide



Ce sub-lattice + O sub-lattice configurational S



B sub-lattice + O sub-lattice

Higher entropy of reduction = higher productivity

Entropy of reduction for an induced off-stoichiometry, δ, in ABO_3

$$\Delta S_{reduction} = \frac{S_{ABO_{3-\delta}} - S_{ABO_3}}{\delta} + \left(\frac{1}{2}\right) S_{O_2}(g)$$

solid gas

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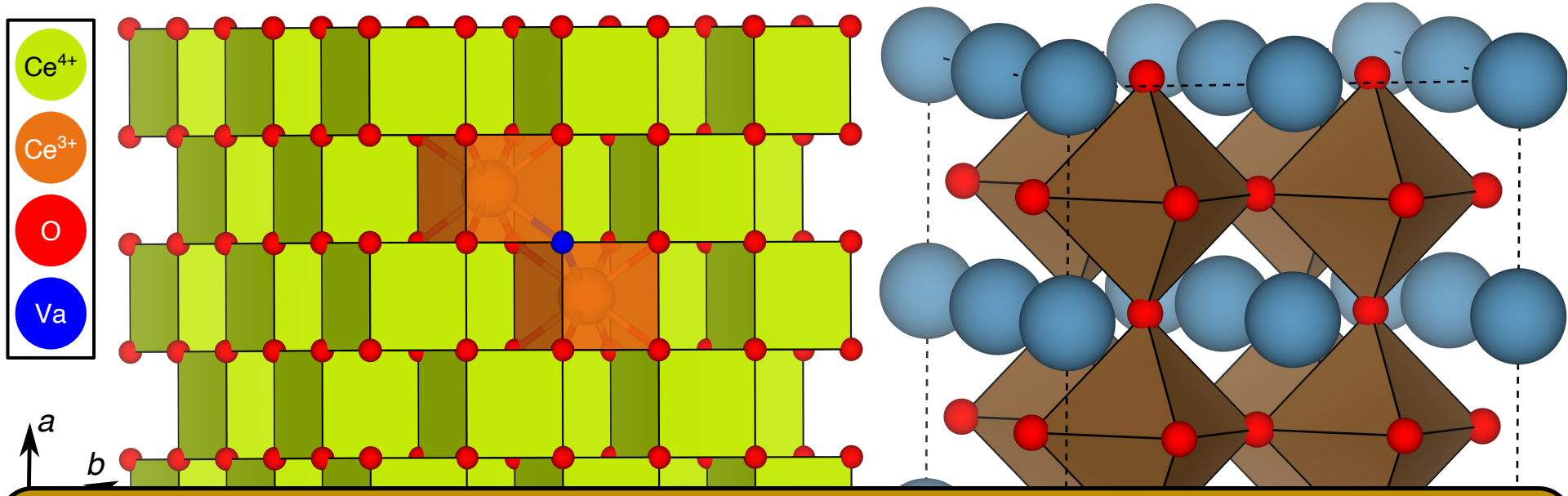


The lack of redox-activity of A in ABO_3 reduces configurational entropy (per O) in ABO_3 vs. CeO_2

- If A is redox-active in addition to B: ABO_3's configurational entropy can increase beyond CeO_2
- Will productivity gains be worth it? How to quantify?

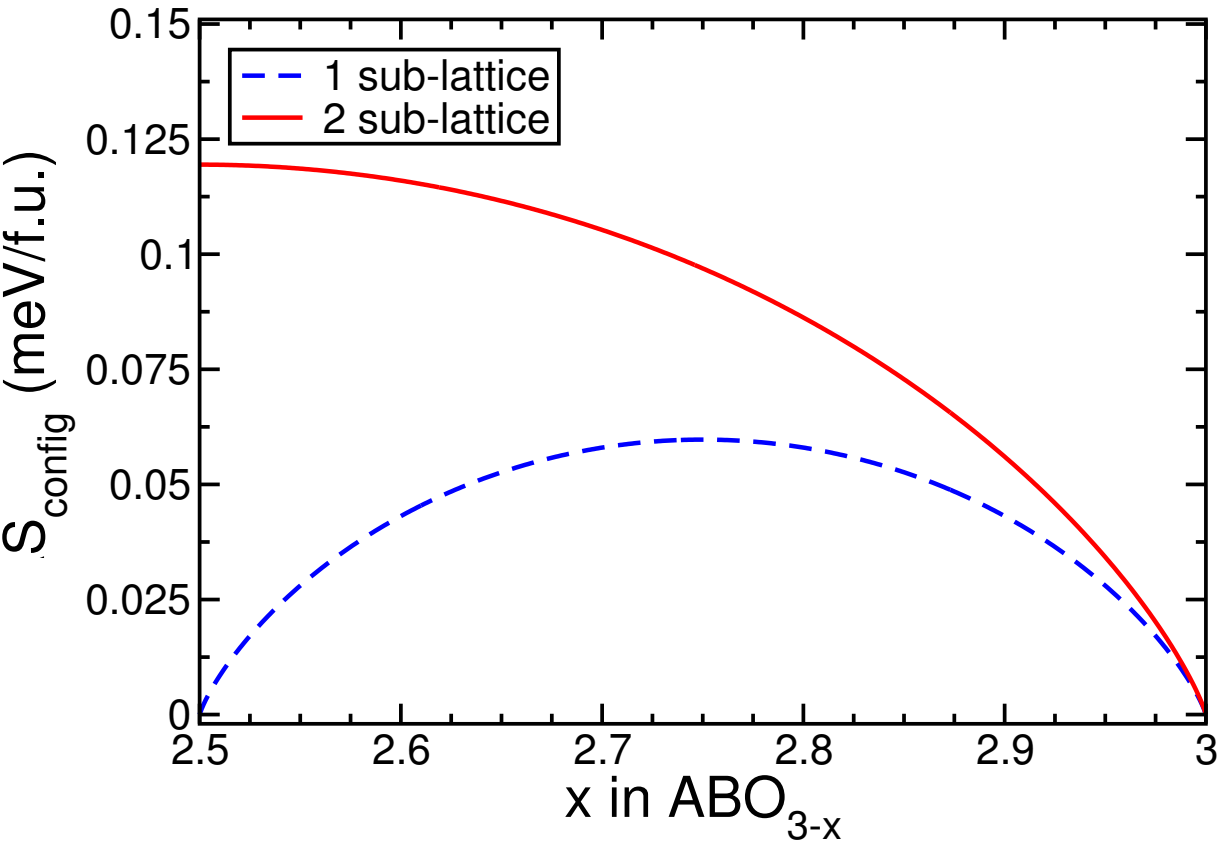
Simultaneous redox-activity = higher productivity

Entropy of reduction for an induced off-stoichiometry, δ, in ABO_3

$$\Delta S_{reduction} = \frac{S_{ABO_{3-\delta}} - S_{ABO_3}}{\delta} + \left(\frac{1}{2}\right) S_{O_2}(g)$$

solid gas

Not easily calculable



Larger configurational entropy of reduction in 2 sub-lattice (simultaneous reduction) than 1 sub-lattice (single reduction) in ABO_3

$$S_{config}\ (1\ sub-lattice, \mathrm{ABO_x}) = -k_B\left((6-2x)\ln(6-2x) + (2x-5)\ln(2x-5)\right)$$

$$S_{config}(2\ sub-lattices, \mathrm{ABO_x}) = -2k_B\left((3-x)\ln(3-x) + (x-2)\ln(x-2)\right)$$

f(x*ln(x))

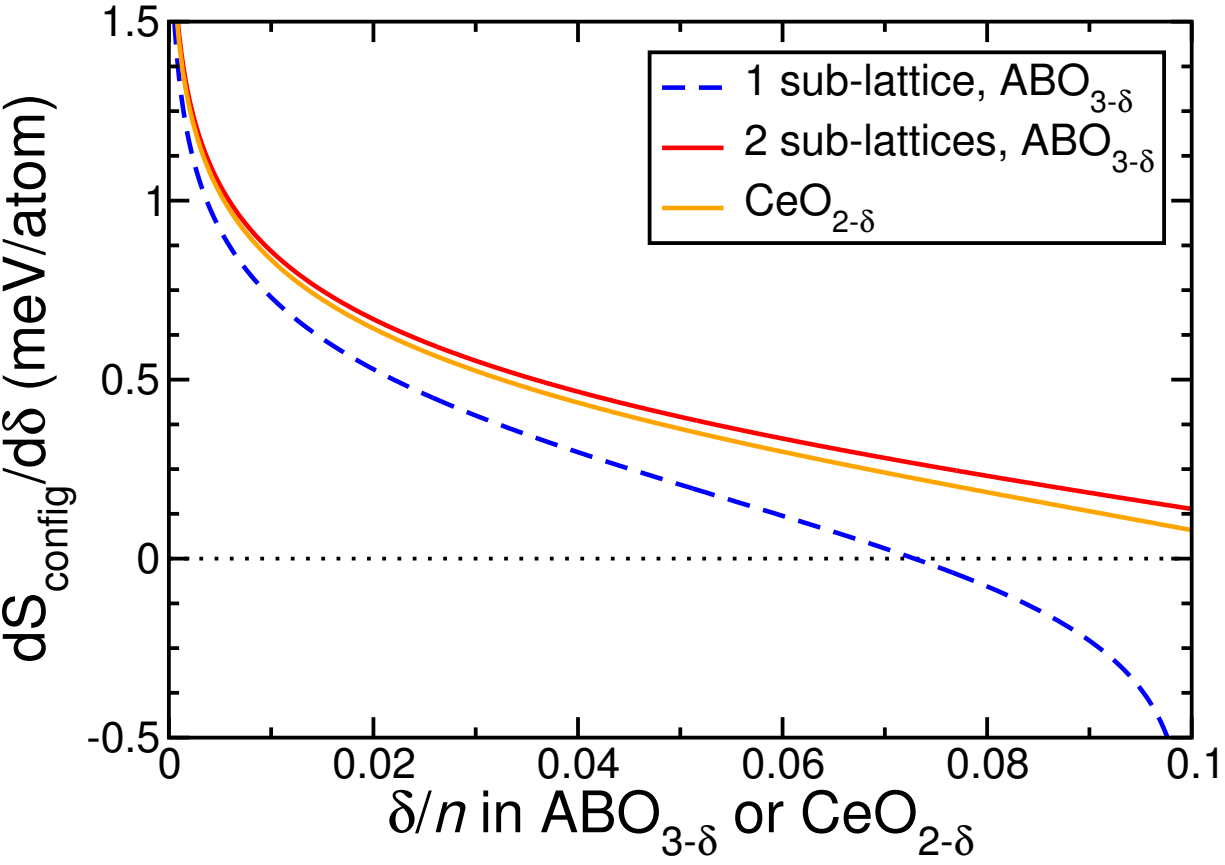
Simultaneous redox-activity = higher productivity

Entropy of reduction for an induced off-stoichiometry, δ, in ABO_3

$$\Delta S_{reduction} = \frac{S_{ABO_{3-\delta}} - S_{ABO_3}}{\delta} + \left(\frac{1}{2}\right) S_{O_2}(g)$$

solid gas

Not easily calculable



Equilibrium oxygen off-stoichiometry (δ_{eq}) is determined by oxygen chemical potential (μ_O) for given reduction/re-oxidation conditions

$$\mu_O \propto \frac{dS_{config}}{d\delta} \approx f[\ln\left(\frac{\delta}{1-\delta}\right)]$$

Differential of configurational entropy in 2 sub-lattice ABO_3 has a less-steep decline than CeO_2

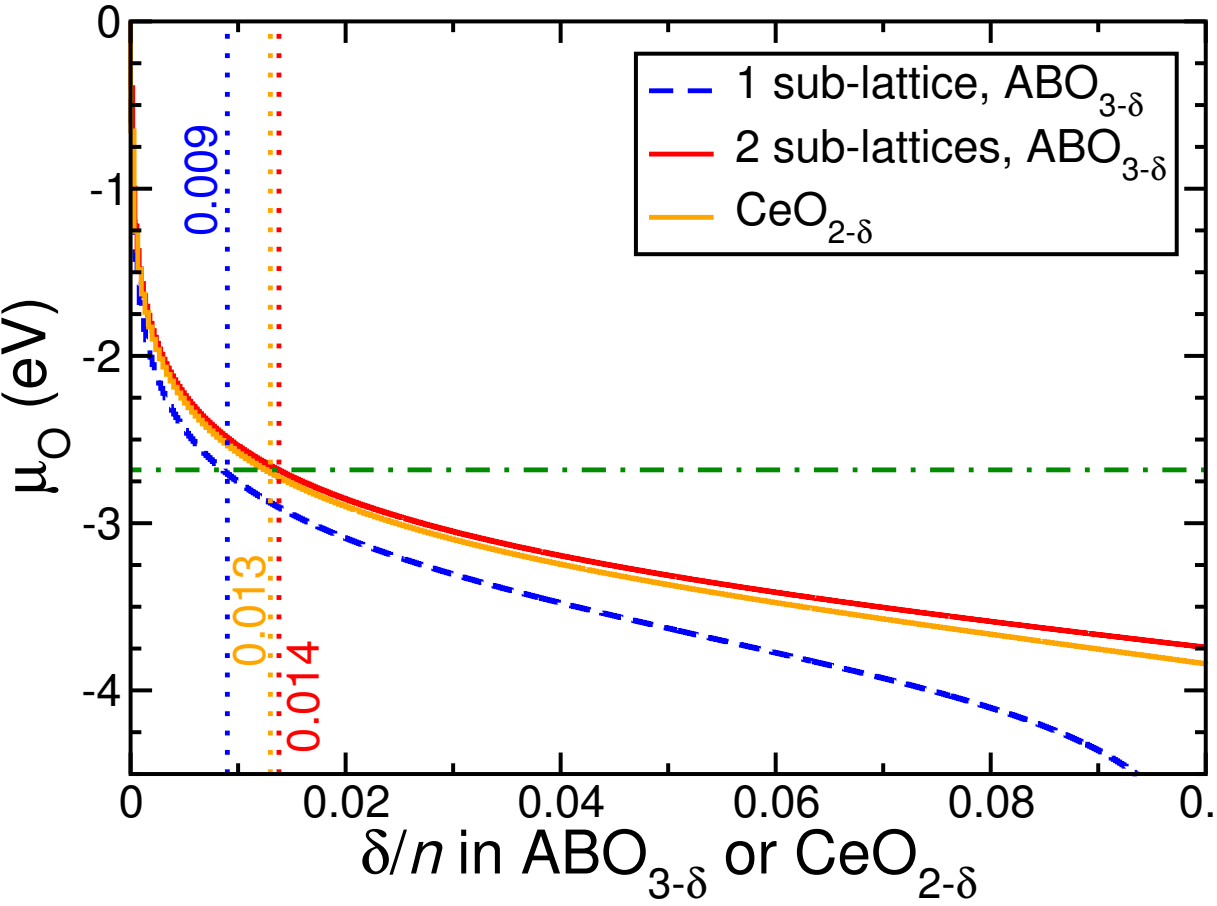
Simultaneous redox-activity = higher productivity

Entropy of reduction for an induced off-stoichiometry, δ, in ABO_3

$$\Delta S_{reduction} = \frac{S_{ABO_{3-\delta}} - S_{ABO_3}}{\delta} + \left(\frac{1}{2}\right) S_{O_2}(g)$$

Not easily calculable

solid gas



$$\mu_O \approx \Delta H_{formation}^{Va_O} + T\frac{dS_{config}}{d\delta}$$

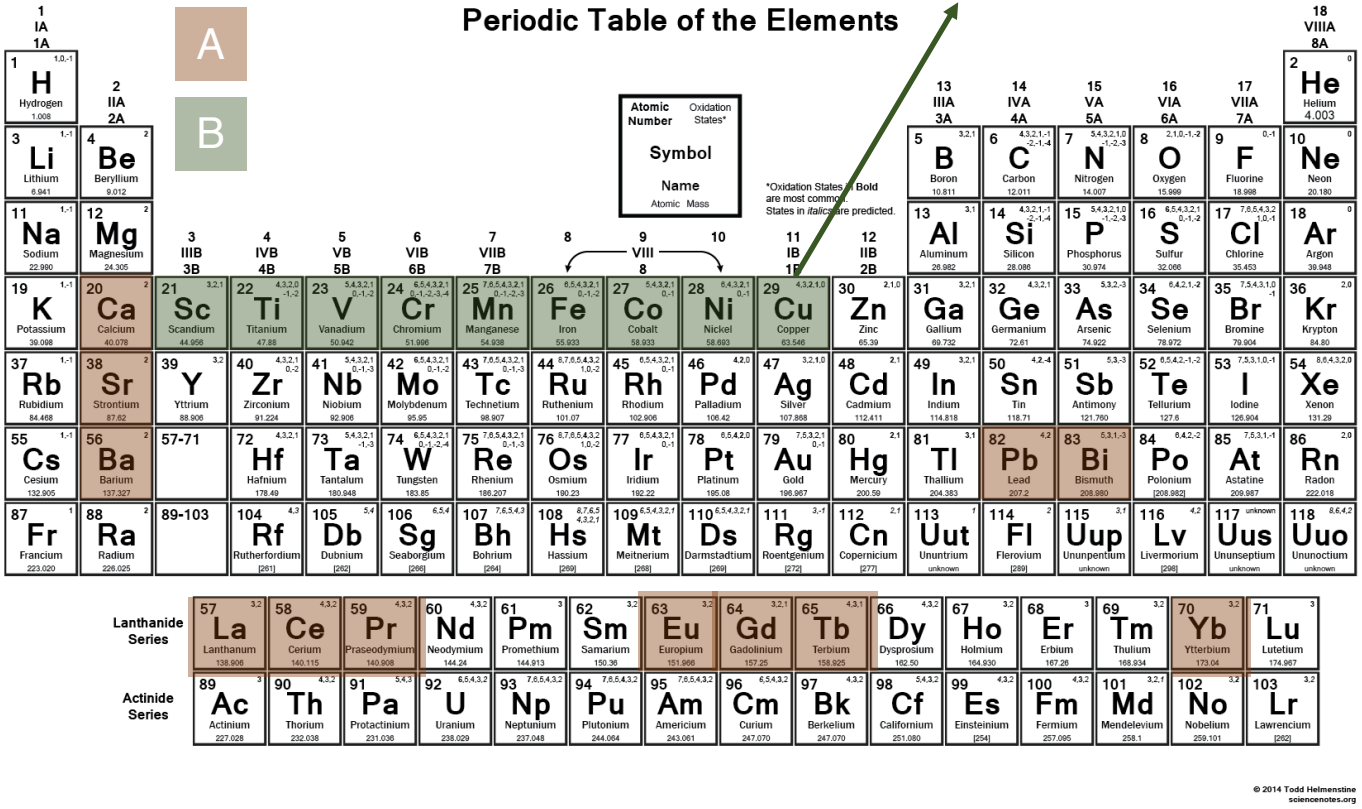
Set same $\Delta H_{formation}^{Va_O} = \mathrm{CeO}_{2-\delta}$

Under given enthalpy of reduction, T and p_{O_2}, 2 sub-lattice can yield 9% and 46% higher productivity than CeO_2 and 1 sub-lattice

Any perovskites with simultaneous redox-activity?

Structural constraints: ABO_3 can allow (A,B) to be redox-active simultaneously, but…

Difficult to describe redox + not common in oxide perovskite



Not as many options for cations on A site that can be redox active (and reasonably abundant)

- Ce (+4/+3)

Ca most compatible with Ce on A (1.12Å ionic radius vs. 0.97-1.14Å)

e.g., $LaFeO_3$

- ABO_3: Perovskite
  - Large A and 3*d* B; need large redox-active A (e.g., Ce)
  - Possible (A,B): (+1,+5), (+2,+4), (+3,+3), (+4, +2), (+5,+1)

Structural constraints: ABO_3 can allow (A,B) to be redox-active simultaneously, but…

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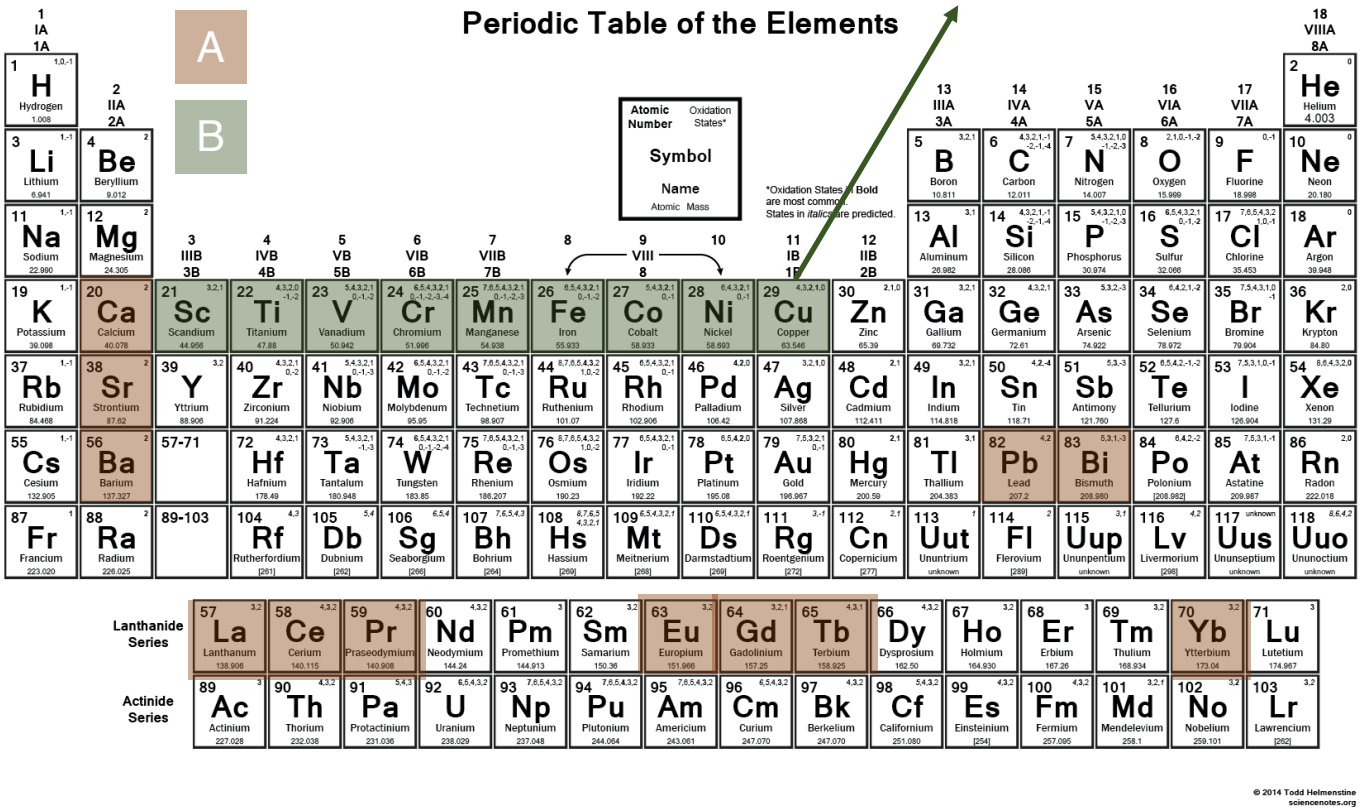

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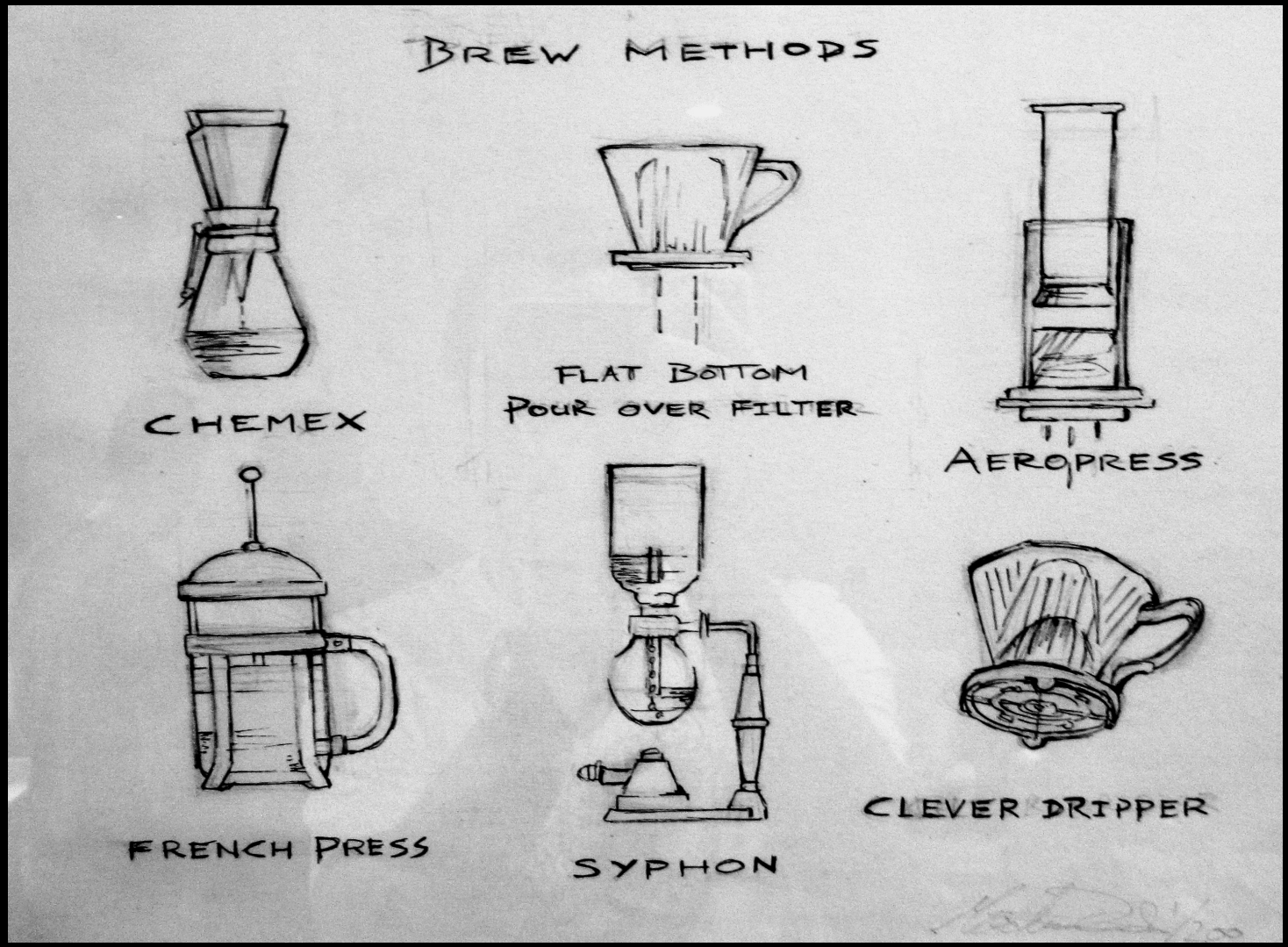
Ca most compatible with Ce on A (1.12Å ionic radius vs. 0.97-1.14Å)

Explore Ca-Ce-M-O perovskites (M = 3*d* except Cu, Zn) for potential simultaneous redox activity

- Specifically, look at $Ca_{0.5}Ce_{0.5}MO_3$ using theoretical calculations
- Still need to have ideal ΔH!
- And be thermodynamically stable



Methods detour: calculation setup, structural input and stability

Density functional theory (DFT): predict material properties

$$H\psi = E\psi$$ → Total energy at 0 K ≈ Gibbs energy → Thermodynamics

Density of states + Band structure → Band gap

Energy to displace atoms → Phonon/vibrational

Barriers for atomic migration → Kinetics

Energy of defective structures → Defect thermodynamics

Density functional theory[1,2]: approximate electronic interactions into a non-interacting mean-field

- Approximation: exchange-correlation (XC) functional

DFT toolkit choice: Vienna ab initio simulation package (https://www.vasp.at/)

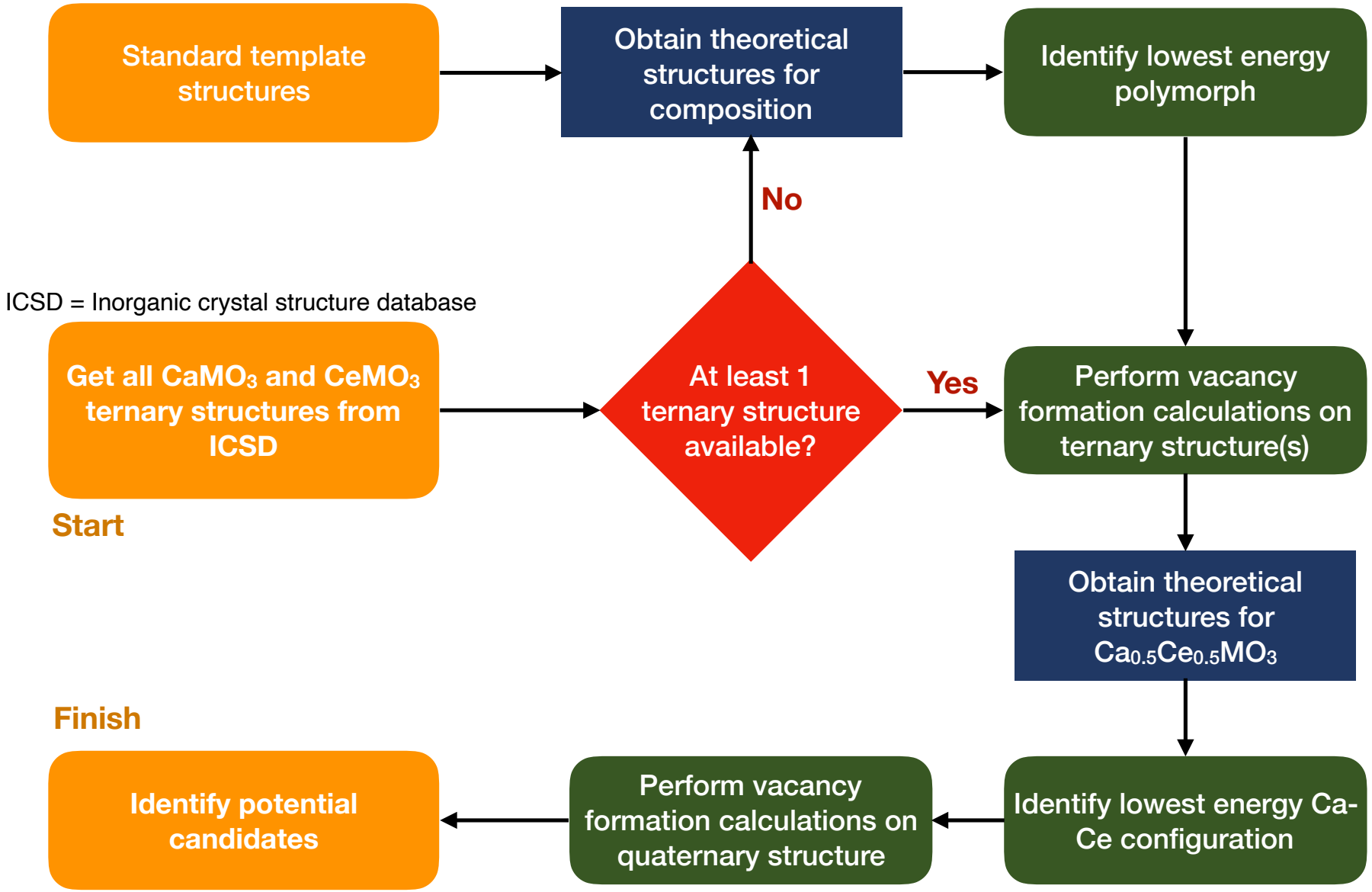
XC functionals: Jacob's ladder of increasing accuracy

- Choice: strongly constrained appropriately normed (SCAN)[3]

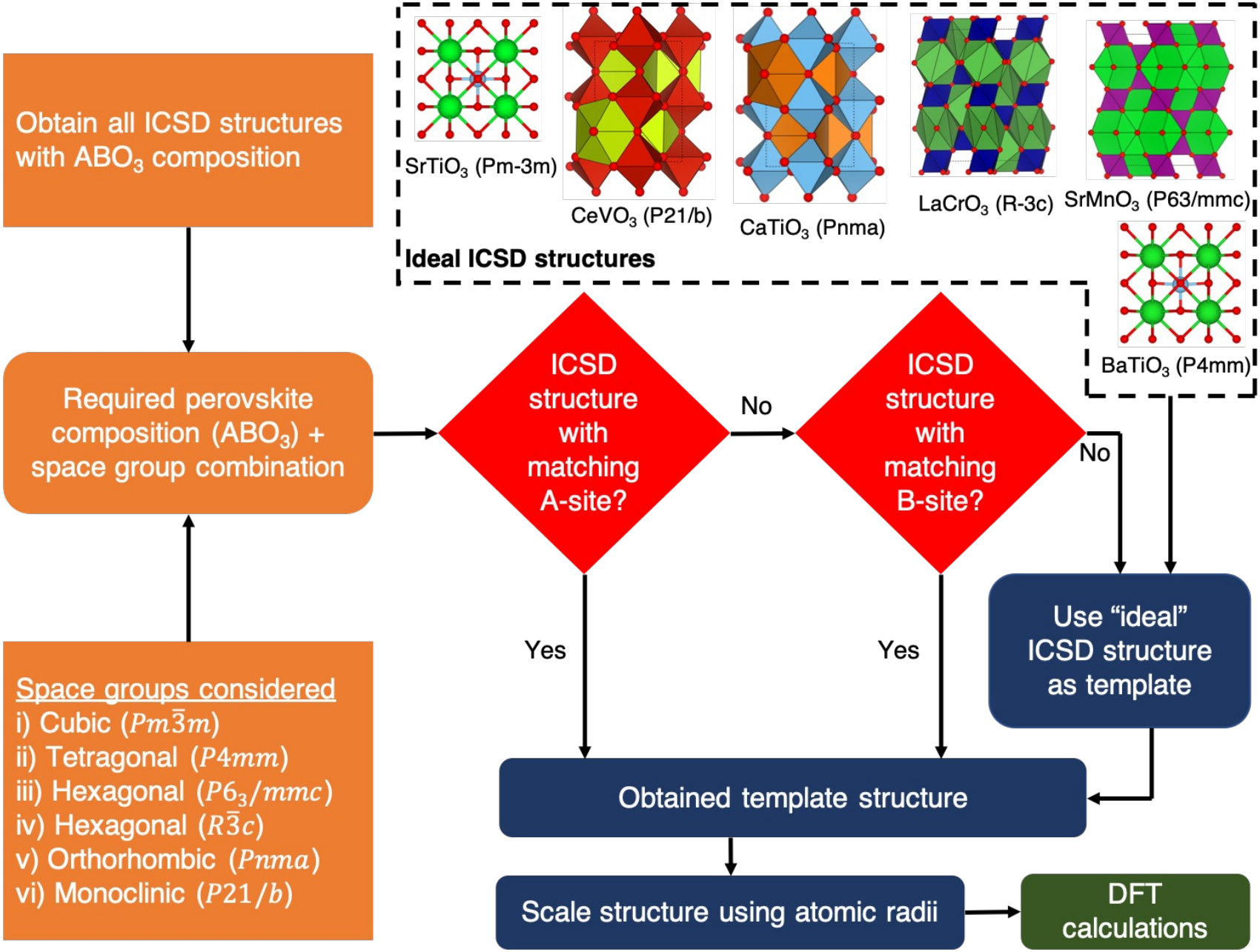
Need structural input!

1. Hohenberg and Kohn, **Phys. Rev. 1964**, *136*, B864
2. Kohn and Sham, **Phys. Rev. 1965**, *140*, A1133
3. Sun et al., **Phys. Rev. Lett. 2015**, *115*, 036402
Figure (above): Car, **Nat. Chem. 2016**, *8*, 820

No experimental $Ca_{0.5}Ce_{0.5}MO_3$ structures available: use $CaMO_3$ or $CeMO_3$

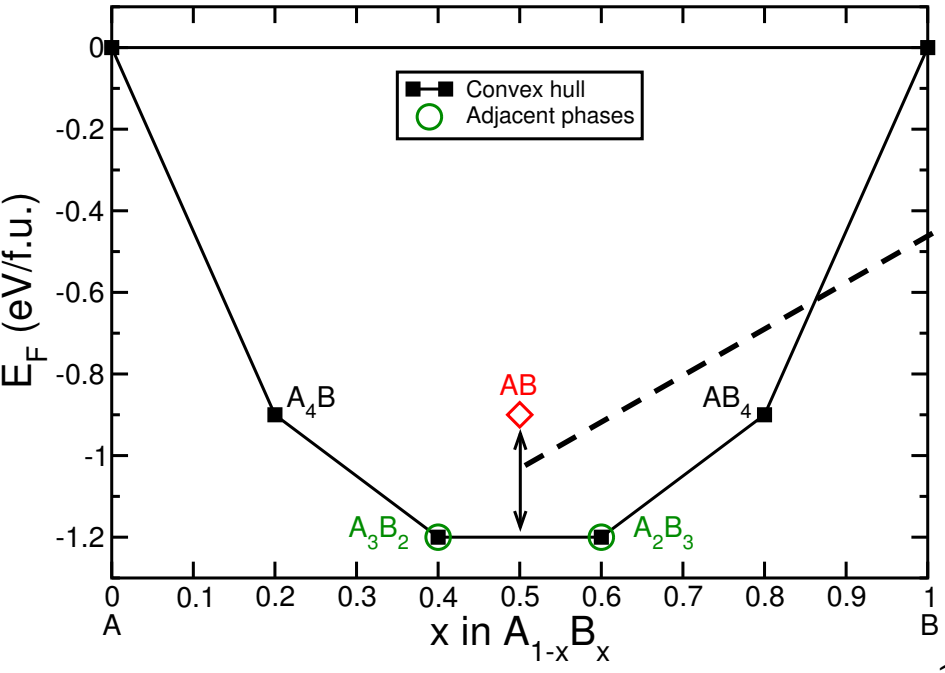


Templating scheme for theoretical (Co & Ni) structures



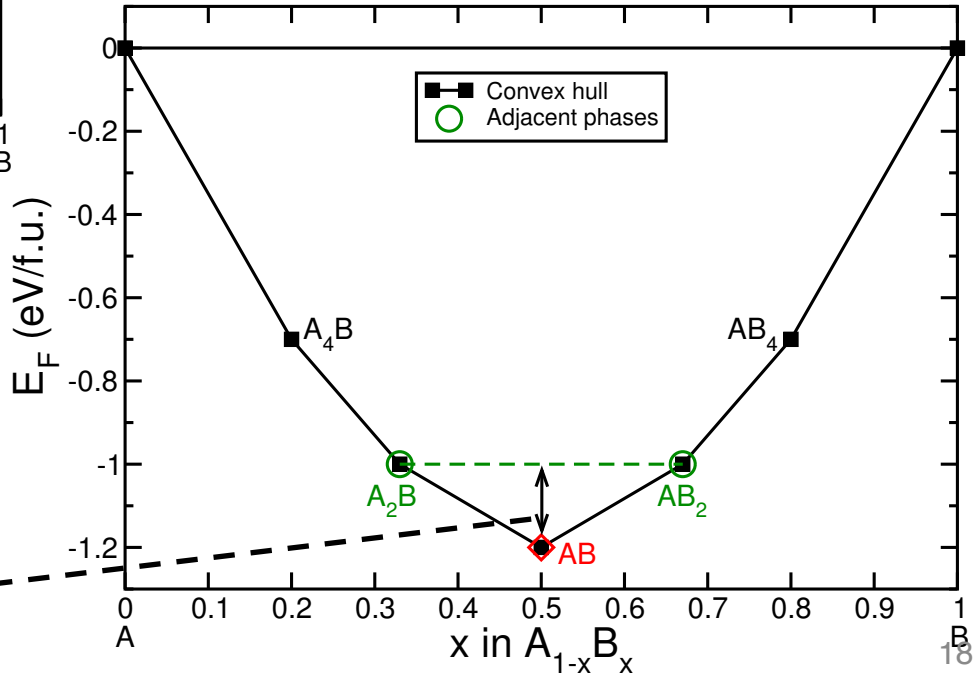
0 K thermodynamics: convex hull

E^{hull}: measure of stability of given structure+composition combination (at 0 K)



Positive E^{hull}: metastable (< 25-50 meV/atom) or unstable (>50 meV/atom)

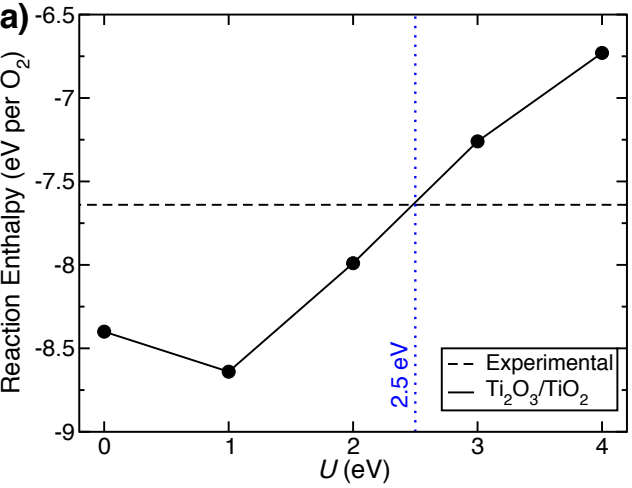
- Largest energy release via decomposition of AB

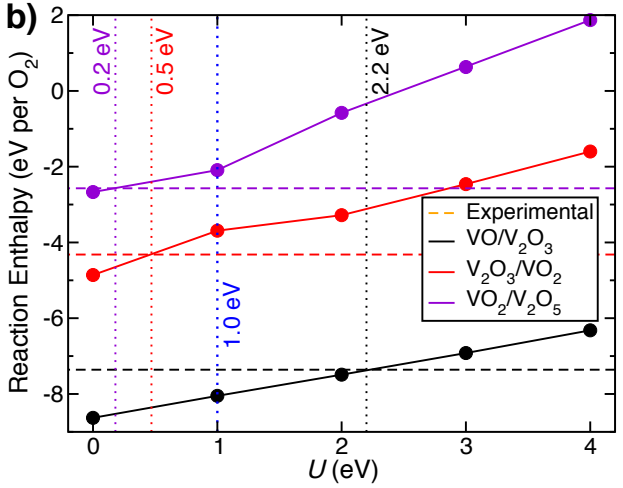


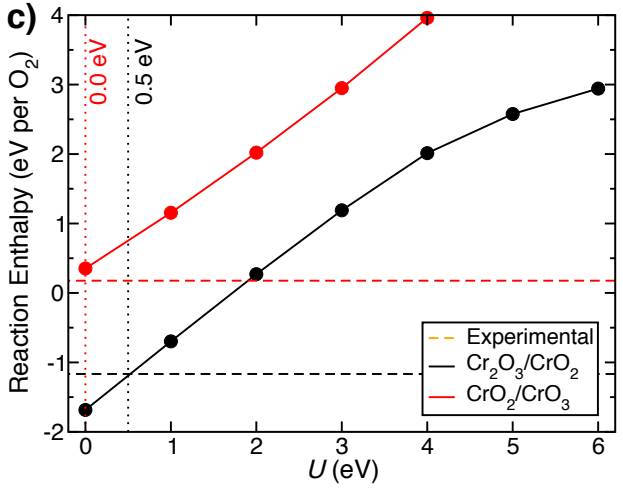
Negative E^{hull}: stable

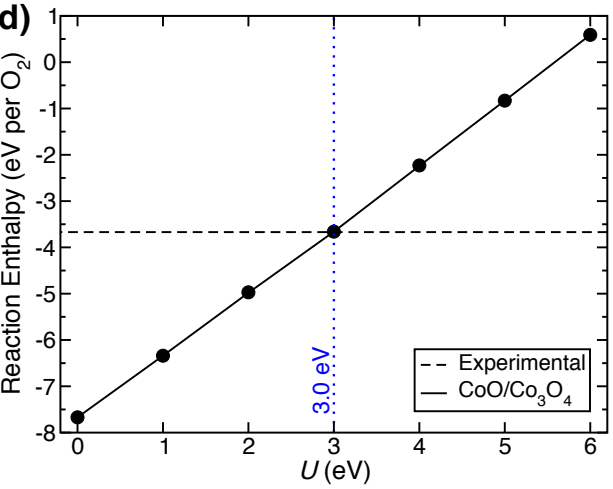
- Lowest energy release via formation of AB

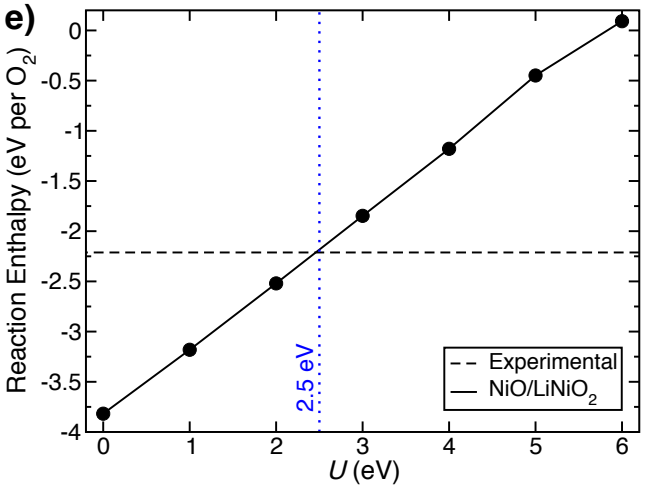
XC functional: a *U* correction to SCAN

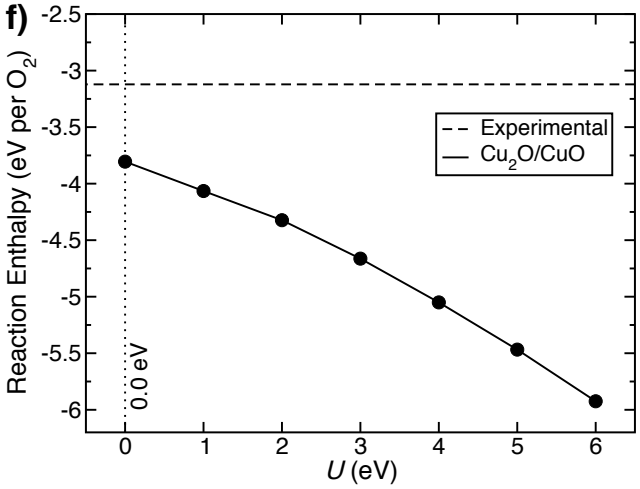










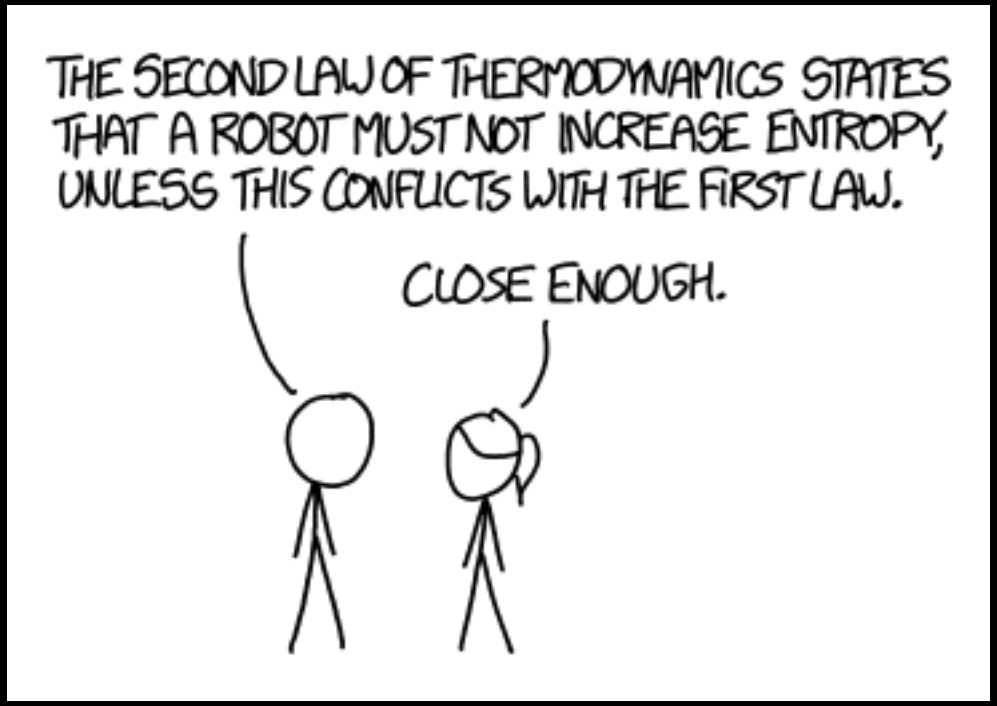


U_{Mn} = 2.7 eV U_{Fe} = 3.1 eV U_{Ce} = 2.0 eV U_{Sc} = 0.0 eV

Convex hull at 0 K: SCAN+*U* including all binary, ternary, and quaternary ICSD structures

$$\Delta H_{reduction} \approx \mathrm{E_F[Va_O]}$$

G.S. Gautam and E.A. Carter, **Phys. Rev. Mater. 2018**, *2*, 095401; O.Y. Long, G.S. Gautam, and E.A. Carter, **Phys. Rev. Mater. 2020**, *4*, 045401



Results

Ternaries

- Structures
- Vacancy formation
- Stability

Quaternaries

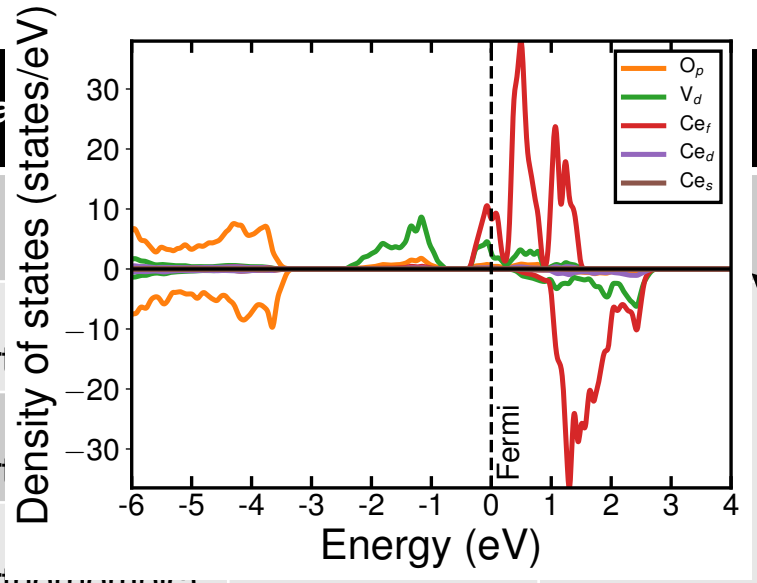
- Vacancy formation
- Stability

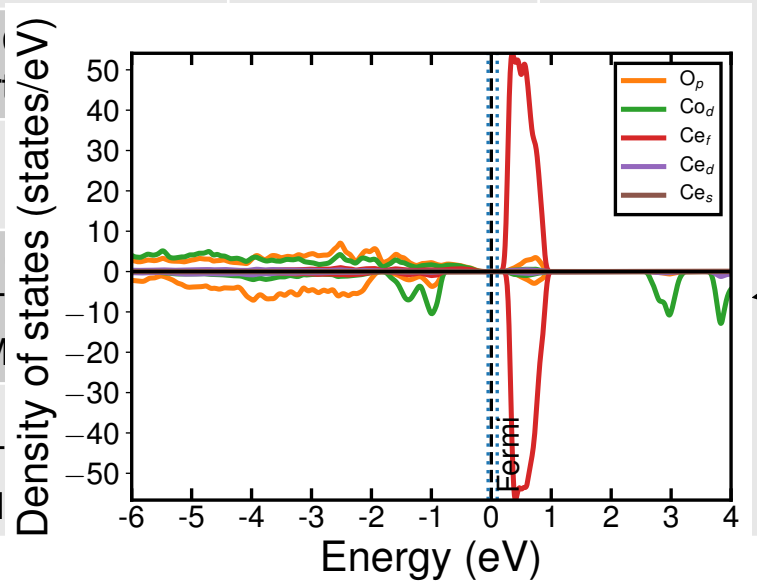
Structures and oxidation states: $CaMO_3$ and $CeMO_3$

Ca-ternaries	Ca	M	Ce-ternaries	Ce	M
$CaScO_3$	–		$CeScO_3$ (Orthorhombic)	+3	+3
$CaTiO_3$ (Orthorhombic)	+2	+4	$CeTiO_3$	–	
$CaVO_3$ (Orthorhombic)			$CeVO_3$ (Monoclinic)	+3	+3
$CaCrO_3$ (Orthorhombic)			$CeCrO_3$ (Cubic)		
$CaMnO_3$ (Orthorhombic)			$CeMnO_3$	–	
$CaFeO_3$			$CeFeO_3$		
$CaCoO_3$ (Theoretical, Monoclinic)			$CeCoO_3$ (Theoretical, Orthorhombic)	+4	+2
$CaNiO_3$ (Theoretical, Hexagonal)			$CeNiO_3$ (Theoretical, Monoclinic)		

Based on on-site magnetic moments and/or density of states

Structures and oxidation states: $CaMO_3$ and $CeMO_3$

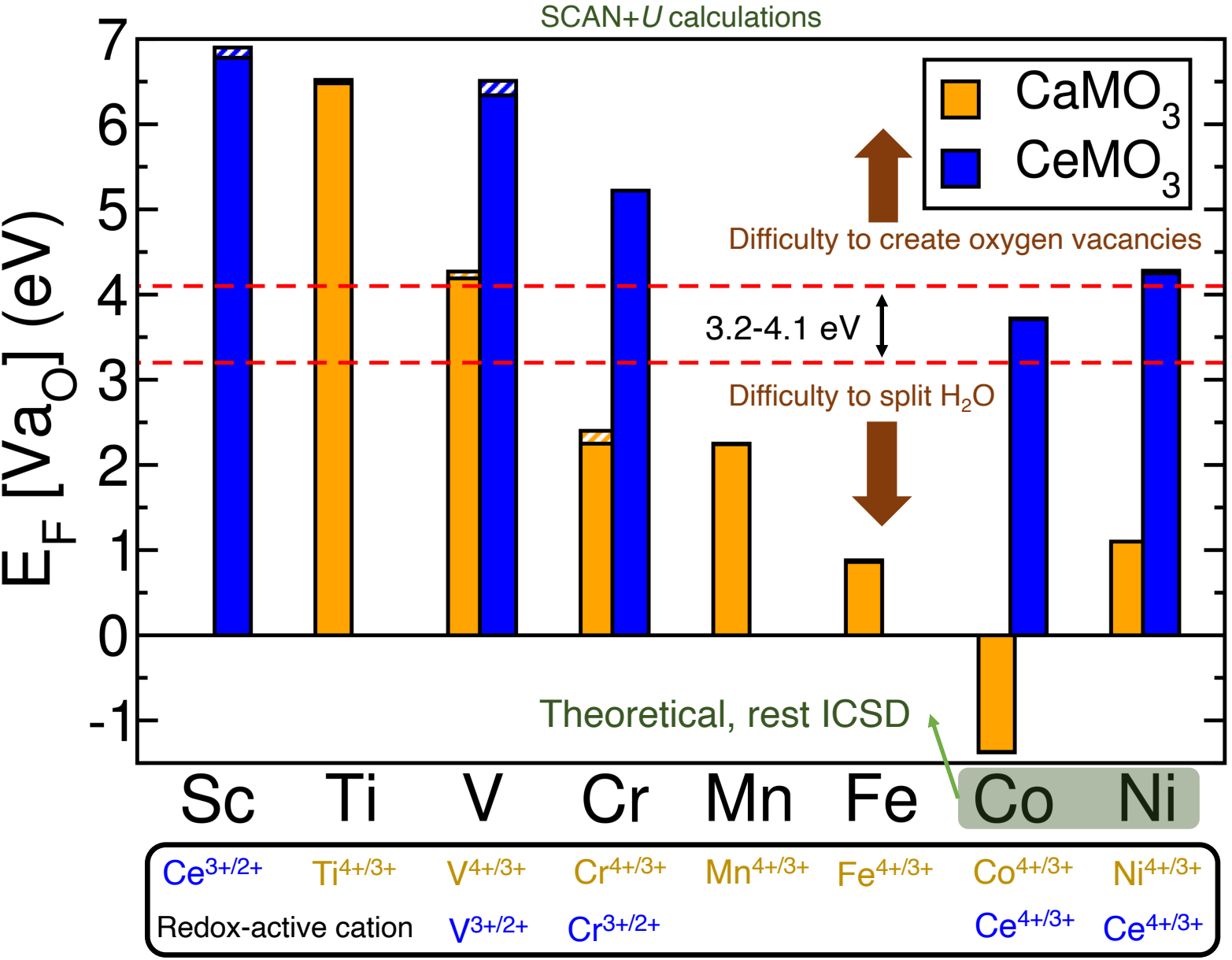




Ce-ternaries	Ce	M
$CeScO_3$ (Orthorhombic)	+3	+3
$CeTiO_3$	–	
$CeVO_3$ (Monoclinic)	+3	+3
$CeCrO_3$ (Cubic)		
$CeMnO_3$	–	
$CeFeO_3$		
$CeCoO_3$ (Theoretical, Orthorhombic)	+4	+2
$CeNiO_3$ (Theoretical, Monoclinic)		

Based on on-site magnetic moments and/or density of states

Oxygen vacancy formation in $CaMO_3$ and $CeMO_3$: no obvious candidate



Vacancy formation energy decreases along 3*d* until Co, increase again in Ni

- Follows inverse standard reduction potentials

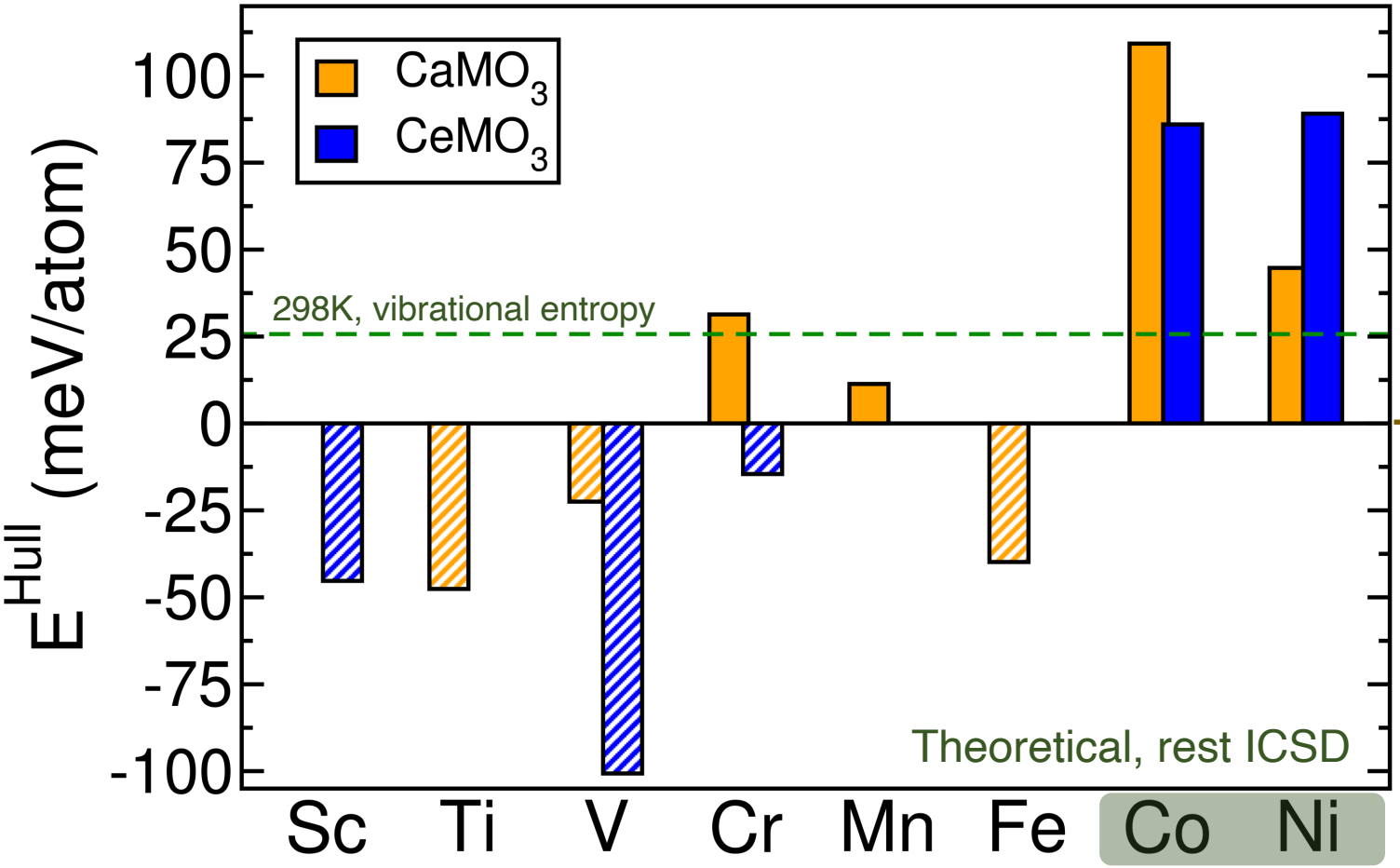
Ce causes higher vacancy formation energy vs. Ca

- Stronger Ce-O bonds

Only $CeCoO_3$ in optimal ΔH window

- Stability remains to be seen

0 K stability: $CaMO_3$ and $CeMO_3$



Energy gain by decomposition to "adjacent" stable compounds

E.g., $ABO_3 \rightarrow AO_2+BO$

E.g., $AO_2+BO \rightarrow ABO_3$

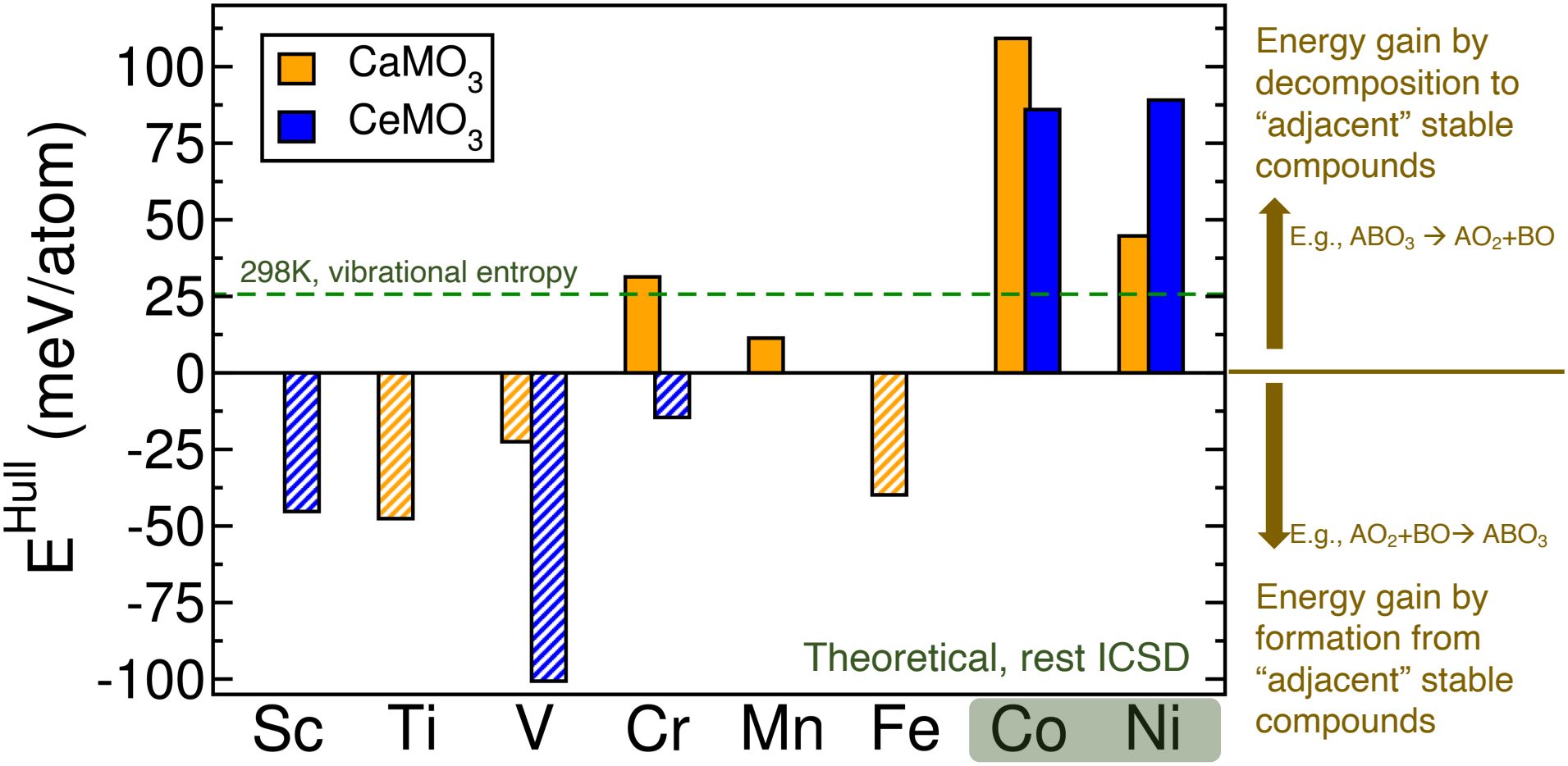
Energy gain by formation from "adjacent" stable compounds

ICSD structures: either negative E^{hull} or small positive E^{hull}
Theoretical structures: large positive E^{hull}

Weak correlation between negative E^{hull} and large vacancy formation energy

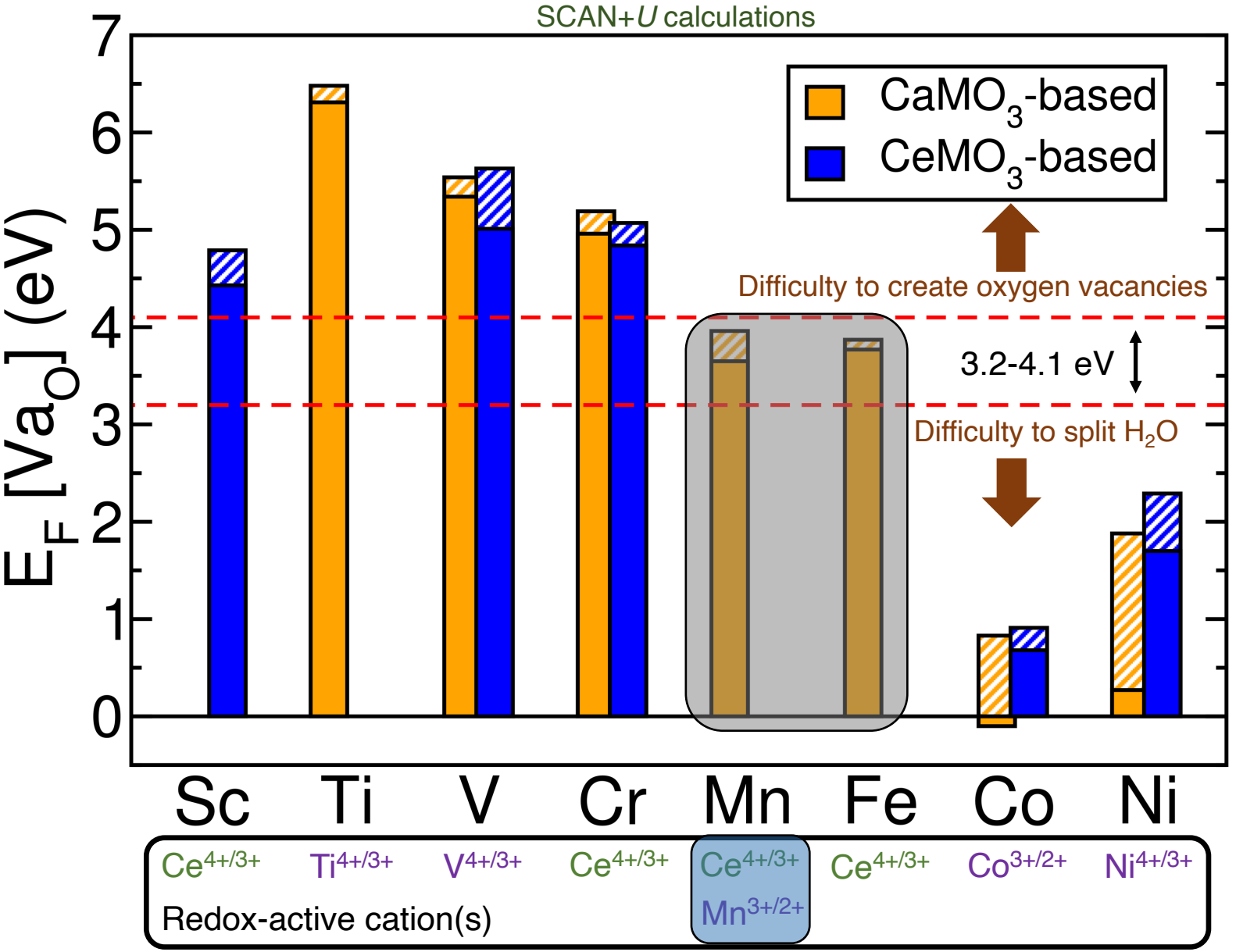
$CeCoO_3$ is highly unstable!

0 K stability: $CaMO_3$ and $CeMO_3$



No candidates among ternaries in terms of simultaneous redox and optimal enthalpy of reduction: what about quaternaries?

Oxygen vacancy formation energy in $Ca_{0.5}Ce_{0.5}MO_3$: $Ca_{0.5}Ce_{0.5}MnO_3$ and $Ca_{0.5}Ce_{0.5}FeO_3$ are promising



$E_F[Va_O]$ decreases along 3*d* from Ti to Co

Redox activity determined by standard reduction potential and structural factors

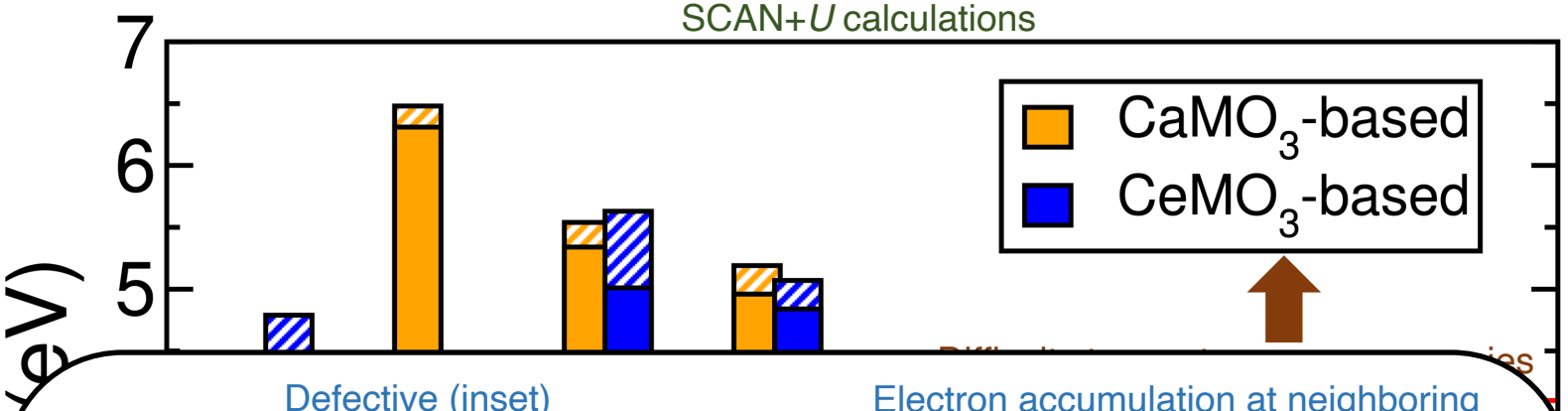
$Ca_{0.5}Ce_{0.5}MnO_3$ and $Ca_{0.5}Ce_{0.5}FeO_3$ show optimal ΔH_{red}

Simultaneous redox

Stability?

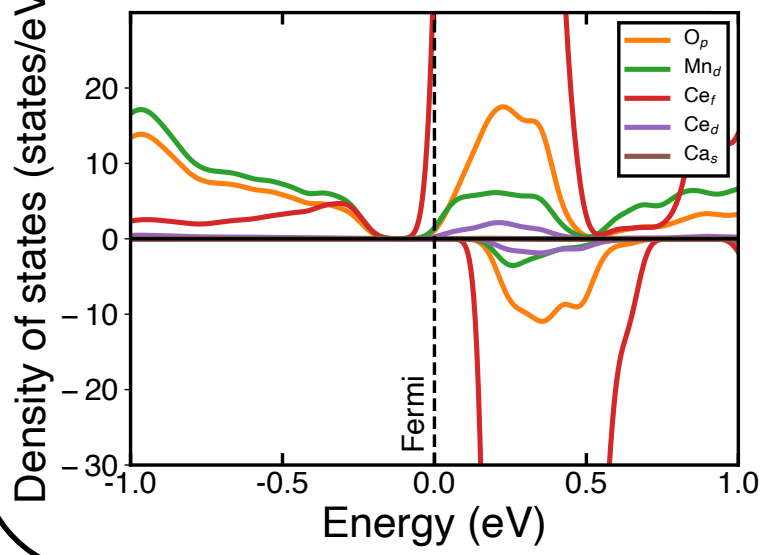
Oxygen vacancy formation energy in $Ca_{0.5}Ce_{0.5}MO_3$: $Ca_{0.5}Ce_{0.5}MnO_3$ and $Ca_{0.5}Ce_{0.5}FeO_3$ are promising

SCAN+*U* calculations

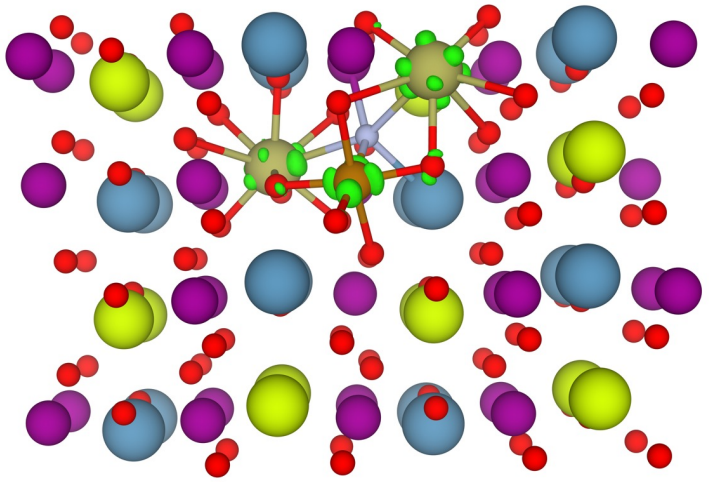


$E_F[Va_O]$ decreases along 3*d* from Ti to Co

Defective (inset)
Ce *f* and Mn *d* below Fermi



Electron accumulation at neighboring Mn and Ce atoms



Lack of Jahn-Teller distortion for reduced Mn

Redox activity determined by standard reduction potential and structural factors

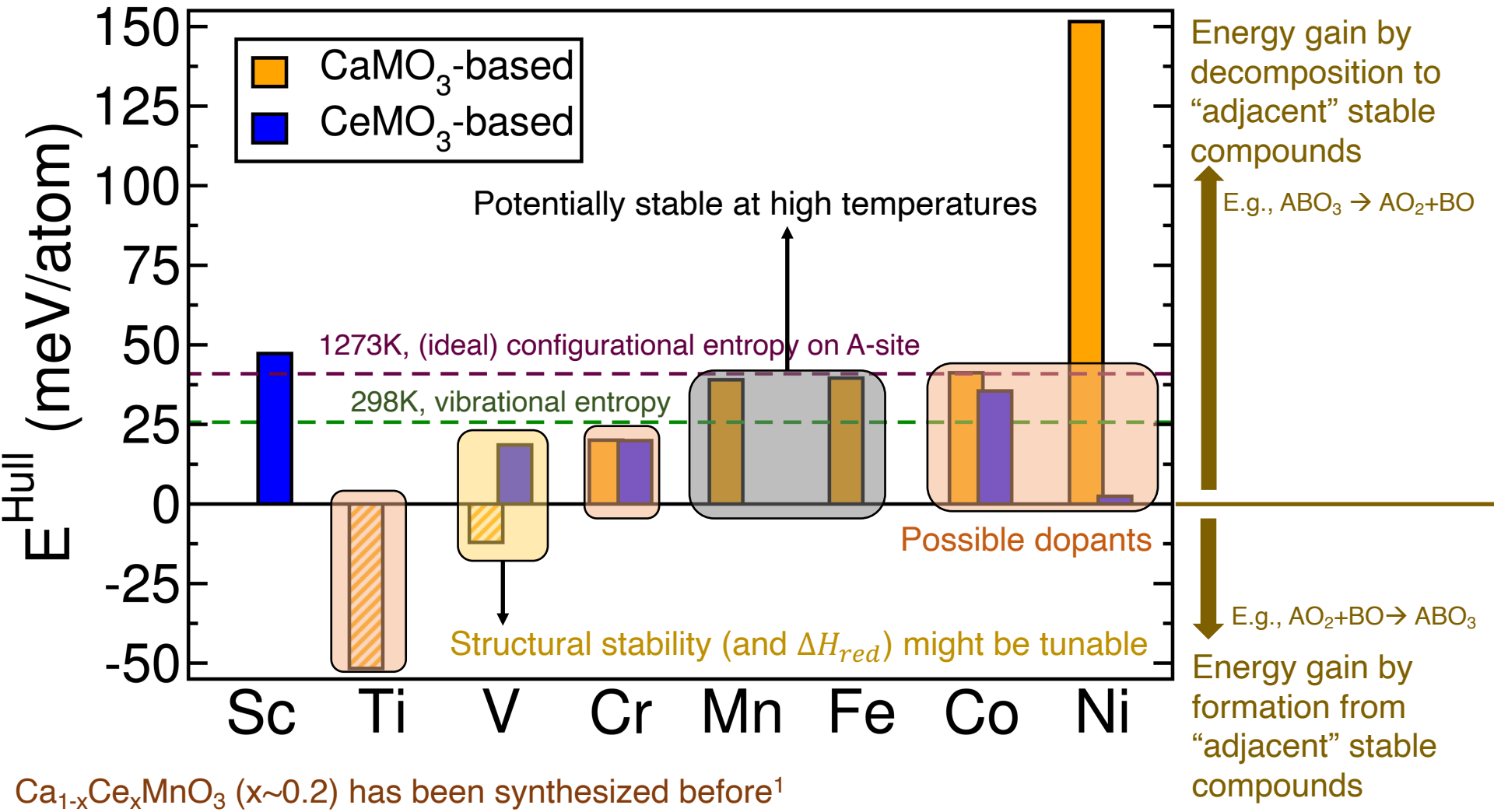
$Ca_{0.5}Ce_{0.5}MnO_3$ and $Ca_{0.5}Ce_{0.5}FeO_3$ show optimal ΔH_{red}

$Ce^{4+/3+}$	$Ti^{4+/3+}$	$V^{4+/3+}$	$Ce^{4+/3+}$	$Ce^{4+/3+}$ $Mn^{3+/2+}$	$Ce^{4+/3+}$	$Co^{3+/2+}$	$Ni^{4+/3+}$
Redox-active cation(s)							

Simultaneous redox

Stability?

0 K stability of $Ca_{0.5}Ce_{0.5}MO_3$
Impact of configurational entropy (of not reduction)



$Ca_{1-x}Ce_xMnO_3$ (x~0.2) has been synthesized before[1]

$Ca_{0.5}Ce_{0.5}MO_3$ perovskites: can be stabilized at higher temperatures via A-site configurational entropy

1. Zeng *et al.*, **Phys. Rev. B 2001**, *63*, 224410

Summary and outlook

- Need better materials for solar thermochemical water splitting
  - Durability, Capacity and Stability
- Search for perovskites with higher entropy of reduction for higher productivity
  - Simultaneous cation redox: $Ca_{0.5}Ce_{0.5}MnO_3$ is a promising candidate
  - Candidates based on optimal enthalpy of reduction: $Ca_{0.5}Ce_{0.5}MnO_3$, $Ca_{0.5}Ce_{0.5}FeO_3$, $Ca_{0.5}Ce_{0.5}VO_3$ (may be), and $CeCoO_3$ (unstable)
- Standard reduction potentials --a strong descriptor of vacancy formation energies
  - Particularly in ternaries, structural factors also dominate
  - Increasing Ca (Ce) concentration introduces weaker (stronger) Ca-O (Ce-O) bonds: decreases (increases) vacancy formation energy
- To do
  - Decouple factors contributing to vacancy formation, find other candidates
  - Quantify productivity and efficiency gains in $Ca_{0.5}Ce_{0.5}MnO_3$ (theory and experiments)

1. G.S. Gautam, E.B. Stechel, and E.A. Carter, "Exploring Ca-Ce-M-O (M = 3*d* transition metal) oxide perovskites for solar thermochemical applications", **Chem. Mater. 2020**, *in press*
2. G.S. Gautam, E.B. Stechel, and E.A. Carter, "A first-principles-based sub-lattice formalism for predicting off-stoichiometry in materials for solar thermochemical applications: the example of ceria", **Adv. Theory Simul**. **2020**, 3, 2000112
3. G.S. Gautam and E.A. Carter, "Evaluating transition metal oxides within DFT-SCAN and SCAN+*U* frameworks for solar thermochemical applications", **Phys. Rev. Mater. 2018**, *2*, 095401
4. O.Y. Long, G.S. Gautam, and E.A. Carter, "Evaluating optimal *U* for 3*d* transition-metal oxides within the SCAN+*U* framework", **Phys. Rev. Mater. 2020**, *4*, 045401

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