

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

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

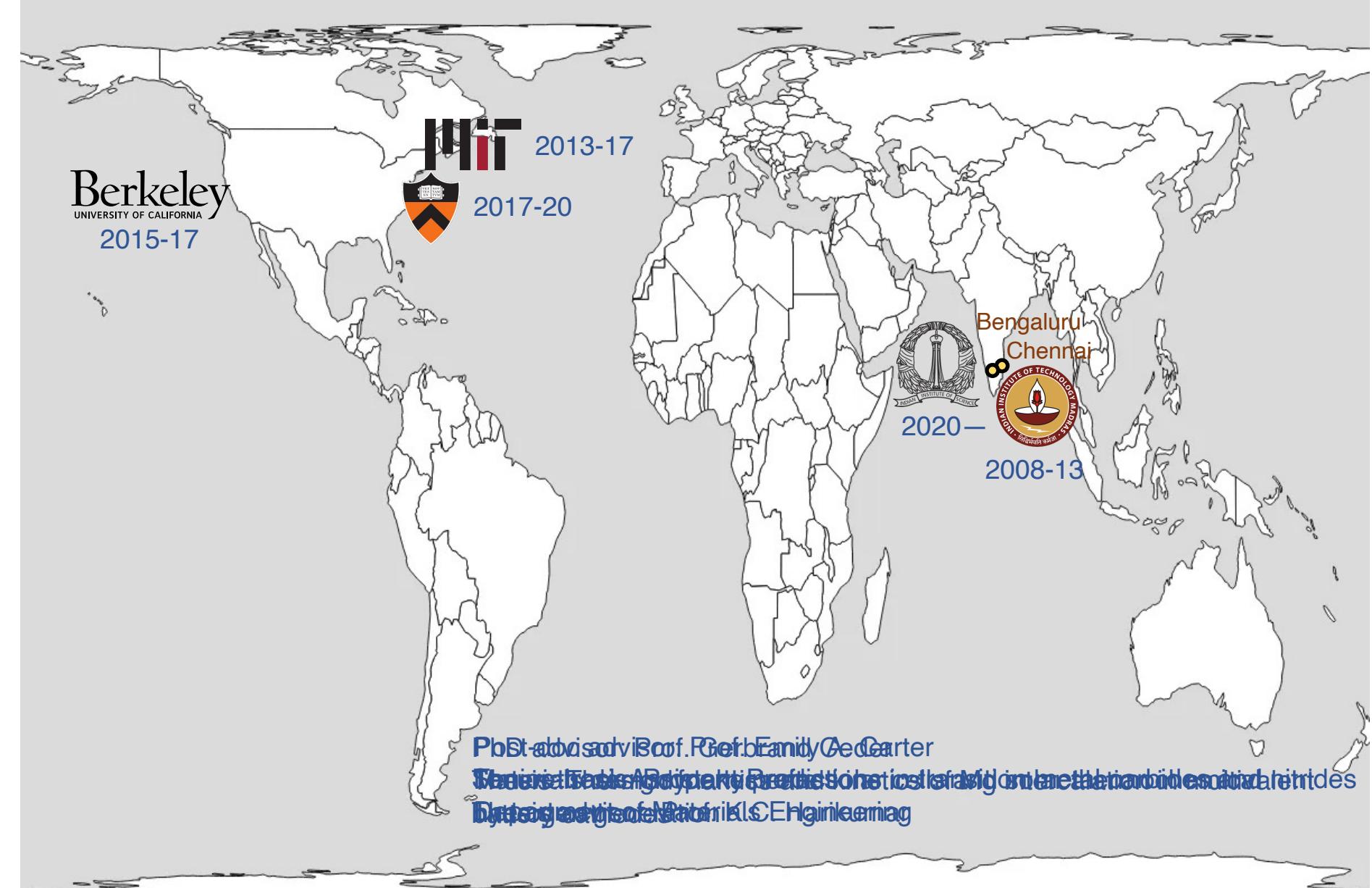
Indian Institute of Science & Princeton University

sraigautamg@iisc.ac.in; <https://sai-mat-group.github.io>

Pratidhwani, Indian Institute of Technology Delhi

Nov 12, 2020

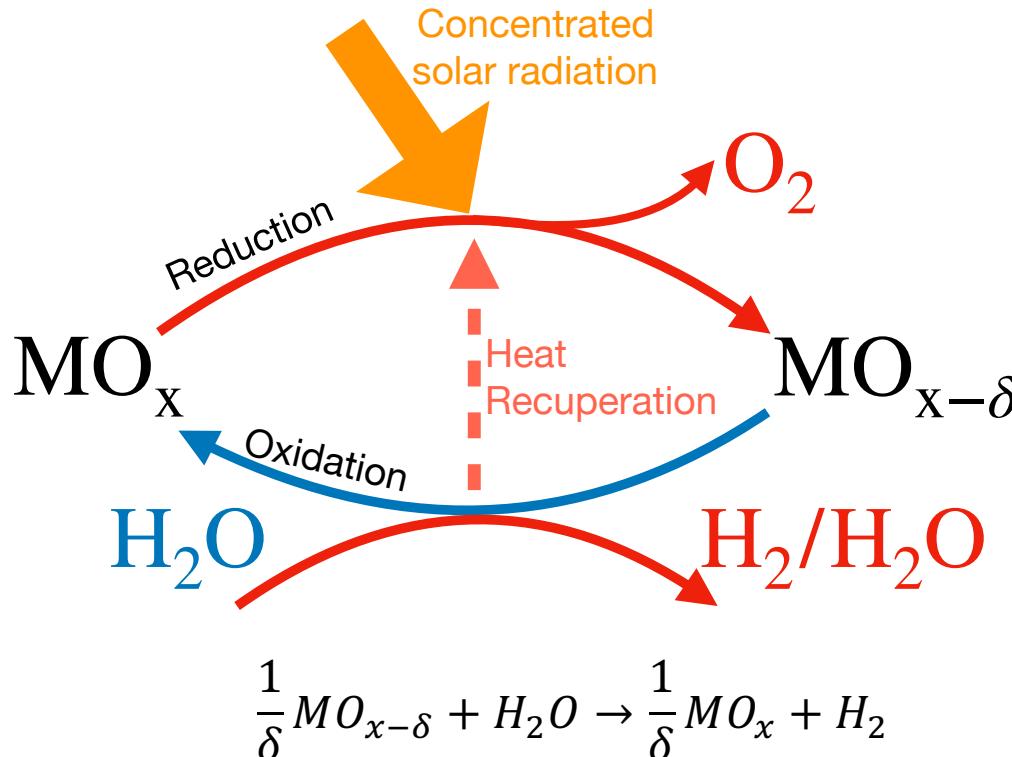
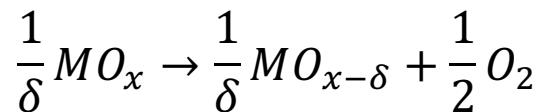
Scientific journey so far...



Solar thermochemical (STC) production of H₂ and/or CO

Candidates so far:

- CeO₂
- Fe(Fe,X)₂O₄
- (A,A')BO₃



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

Water splitting (WS)
Low T (873-1073 K)
High H₂ yield ($\frac{p_{H_2O}}{p_{H_2}} = 9$)

State-of-the-art:
Pure and doped
fluorite-CeO₂

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?

Solar thermochemical (STC) production of H₂ and/or CO

Candidates so far:

- CeO₂
- Fe(Fe,X)₂O₄
- (A,A')BO₃

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

German research center (DLR), 2017

State-of-the-art:
Pure and doped
fluorite-CeO₂



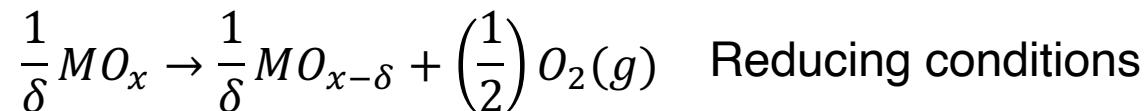
Needs “good” materials!

- 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 Scheifele, Sol. Energy 2017, 156, 3

Enthalpy of reduction = spontaneity



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

$$\Delta H_{reduction} = - \frac{dH_{MO_x}}{dx} \Big|_x + \left(\frac{1}{2}\right) H_{O_2}(g) \equiv \Delta H_{formation}^{Vao} \quad \text{Oxygen vacancy formation energy (Calculable)}$$

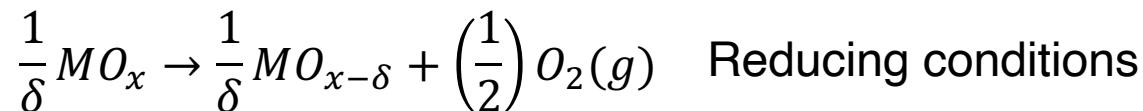
Low $\Delta H_{reduction}$ = large δ

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

Thermodynamic models¹ point to optimal $\Delta H_{reduction}$ or $\Delta H_{formation}^{Vao} \sim 3.4\text{-}3.9$ eV (CeO₂ is ~ 4 eV)

Theoretical screening purposes: 3.2-4.1 eV (± 0.2 eV error)

Enthalpy of reduction = spontaneity



Enthalpy of reduction for the induced off-stoichiometry, δ

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

Several studies have theoretically screened, high-throughput calculations and/or machine learning, for novel ABO_3 perovskites, based on a $\Delta H_{formation}^{Vao}$ 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 models¹ point to optimal $\Delta H_{reduction}$ or $\Delta H_{formation}^{Vao} \sim 3.4\text{-}3.9$ eV (CeO_2 is ~ 4 eV)
Theoretical screening purposes: 3.2-4.1 eV (± 0.2 eV error)

Higher entropy of reduction = higher productivity

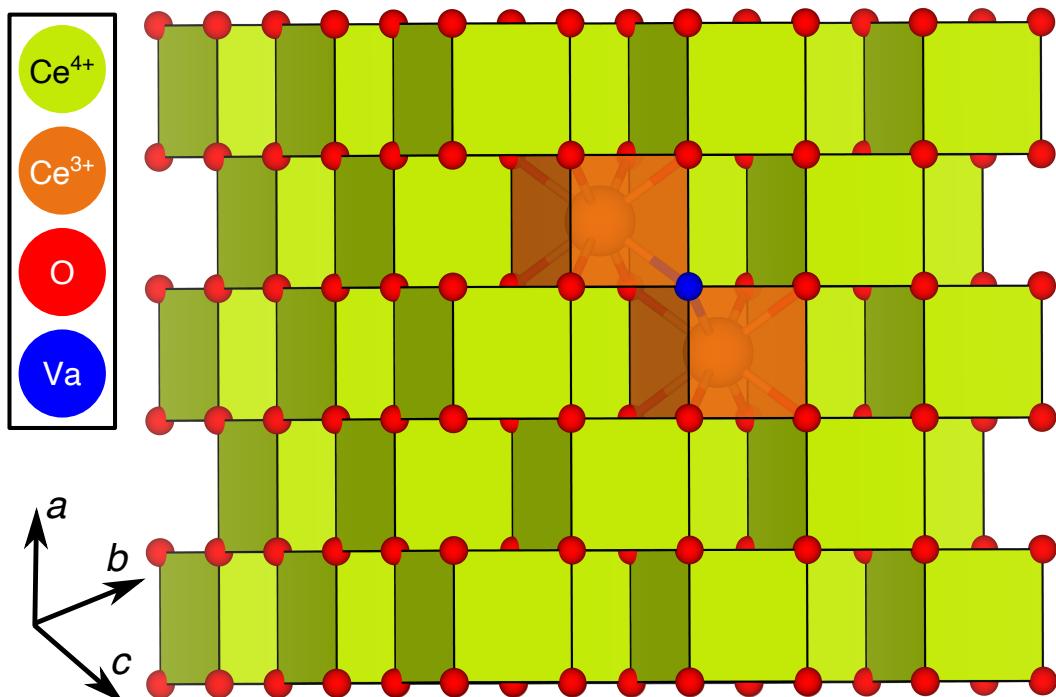
Entropy of reduction for an induced off-stoichiometry, δ , in ABO_3

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

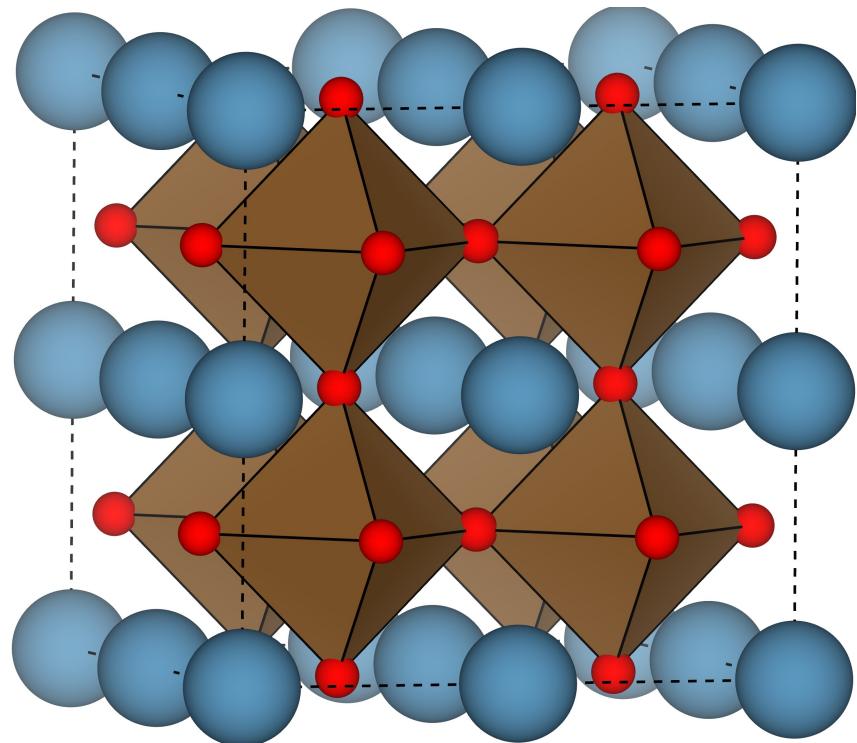
solid gas

Not easily calculable

Higher $\Delta S_{reduction}$ → stabilizes large δ → can result in higher H₂/mol oxide



Ce sub-lattice + O sub-lattice configurational S



B sub-lattice + O sub-lattice

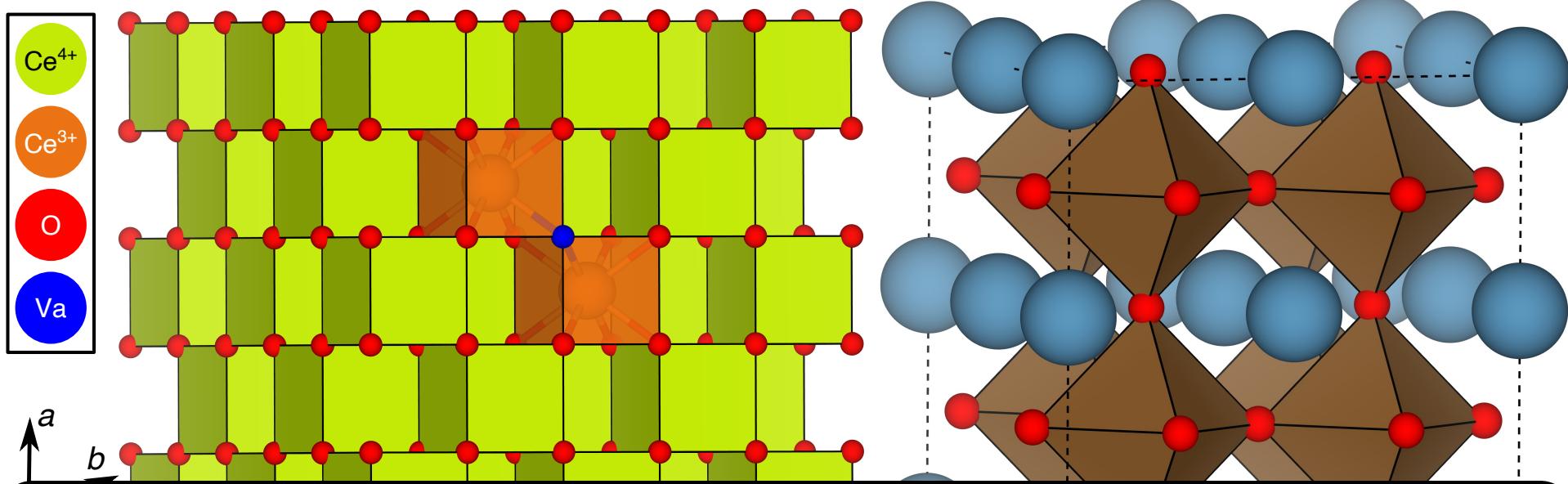
Higher entropy of reduction = higher productivity

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	Not easily calculable
-------	-----	-----------------------

Higher $\Delta S_{reduction}$ → stabilizes large δ → can result in higher H₂/mol oxide



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

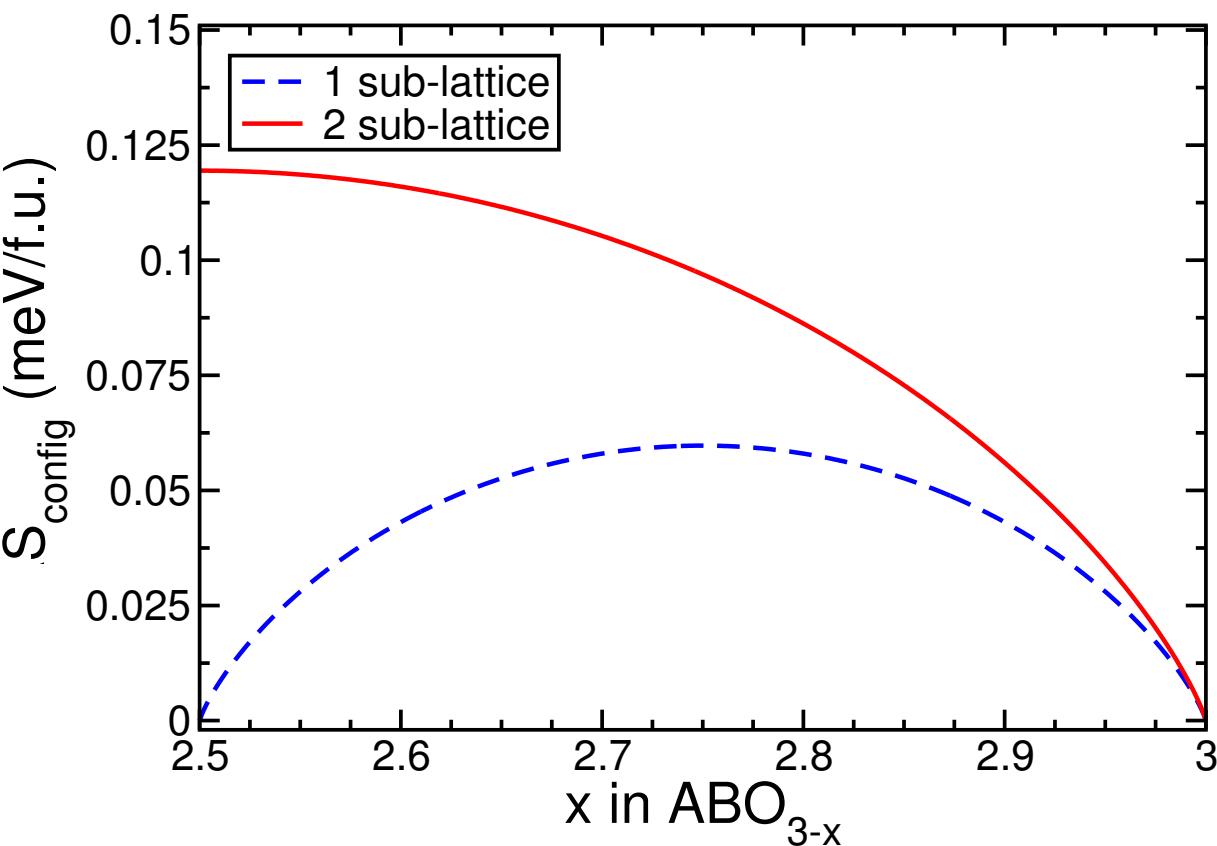
- If A is redox-active in addition to B: ABO_3 's configurational entropy can increase beyond CeO_2
- Will productivity gains be worth it? How to quantify?

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

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

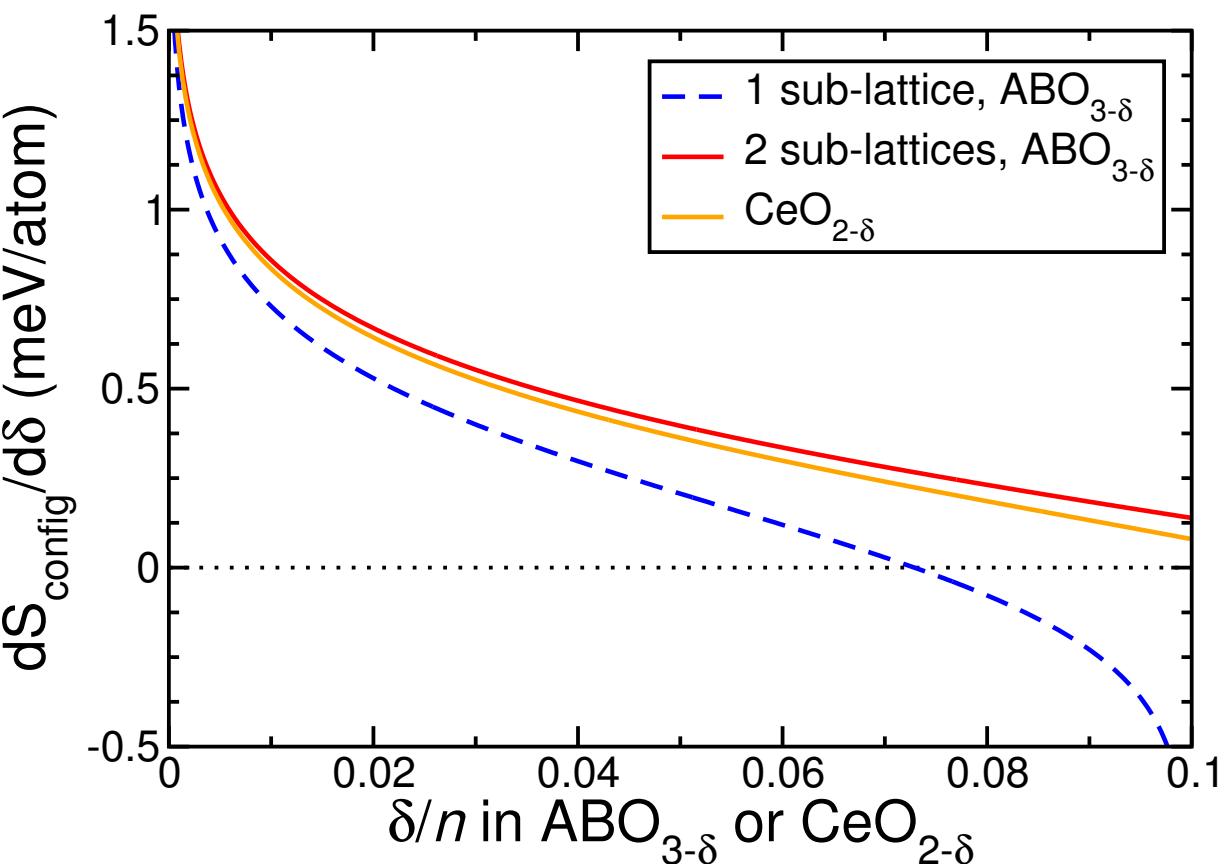
$$S_{config}(2 \text{ sub-lattices}, \text{ABO}_x) = -k_B((3-x) \ln(3-x) + (x-2) \ln(x-2))$$

Simultaneous redox-activity = higher productivity

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

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

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

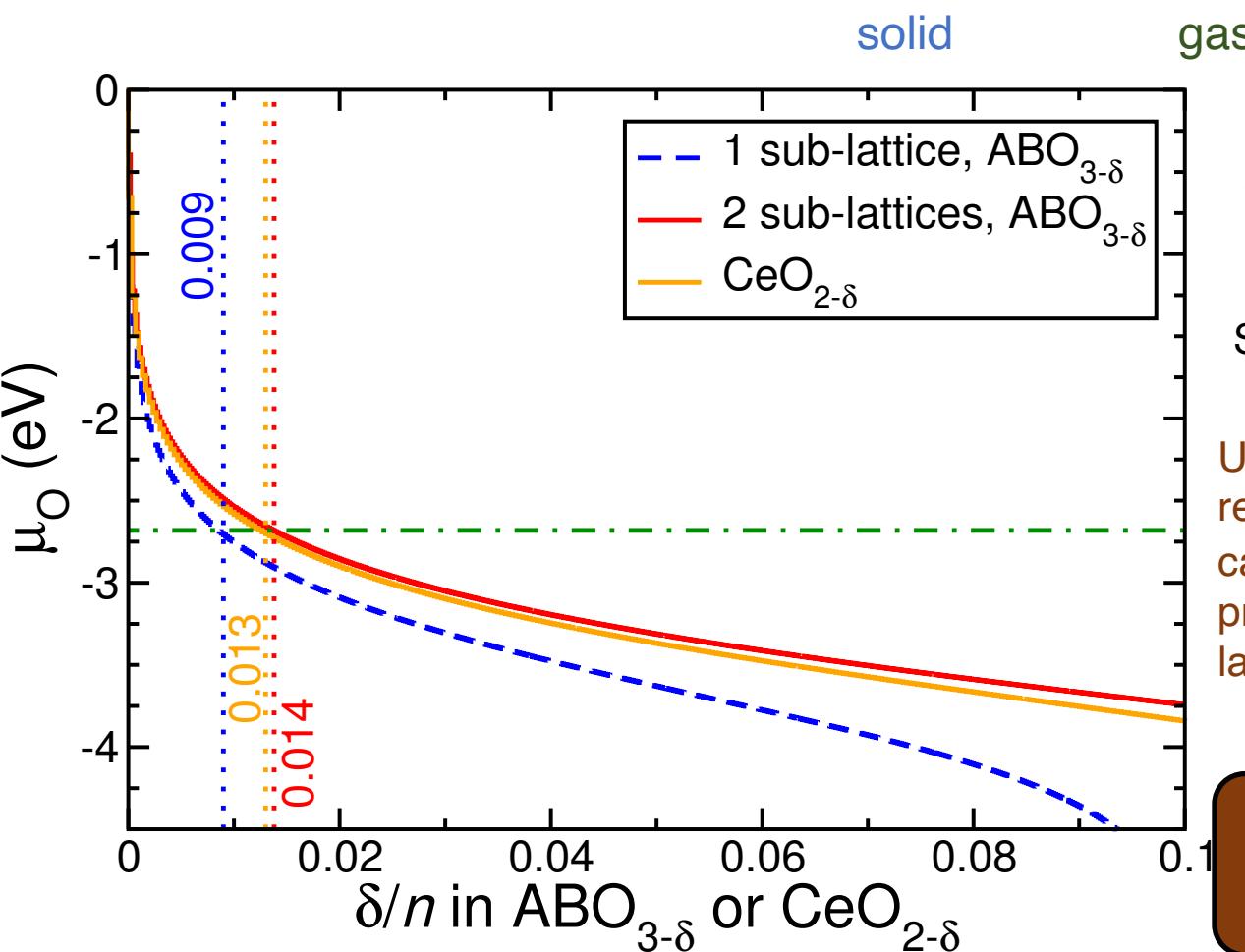
$$\mu_O \propto \frac{dS_{config}}{d\delta} \approx f[\ln\left(\frac{\delta}{1-\delta}\right)]$$

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

$$\Delta S_{reduction} = \frac{S_{ABO_3-\delta} - S_{ABO_3}}{\delta} + \left(\frac{1}{2}\right) S_{O_2}(g) \quad \text{Not easily calculable}$$



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

Set same $\Delta H_{formation}^{Va_0}$ = CeO_{2-δ}

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

Periodic Table of the Elements

Atomic Number Oxidation States*

Symbol Name

Atomic Mass

*Oxidation States in **Bold** are most common. States in *italics* are predicted.

1 IA 1 A 1 H Hydrogen 1.008	2 IIA 2 A 2 Be Beryllium 9.012	A															
3 IA 1 A 3 Li Lithium 6.941	4 IIA 2 A 4 Be Beryllium 9.012	B															
11 IA 1 A 11 Na Sodium 22.990	12 IIIB 3 B 12 Mg Magnesium 24.305	3 IIIB 3 B Sc Scandium 44.956	4 IVB 4 B Ti Titanium 47.88	5 VB 5 B V Vanadium 50.942	6 VIB 6 B Nb Niobium 92.906	7 VIIIB 7 B Cr Chromium 51.996	8 VIII 8 VIIIB 7 B Mn Manganese 54.938	9 VIII 8 VIIIB 7 B Fe Iron 55.933	10 VIII 8 VIIIB 7 B Co Cobalt 58.933	11 IB 1 F Ru Ruthenium 101.07	12 IIB 2 B Rh Rhodium 102.906	13 IIIA 3 A Boron 10.811	14 IVA 4 A C Carbon 12.011	15 VA 5 A N Nitrogen 14.007	16 VIA 6 A O Oxygen 15.999	17 VIIA 7 A F Fluorine 18.998	18 VIIIA 8 A He Helium 4.003
19 IA 1 A 19 K Potassium 39.098	20 IIIB 2 B Ca Calcium 40.078	21 IIIB 3 B Sc Scandium 44.956	22 IVB 4 B Ti Titanium 47.88	23 V Vanadium 50.942	24 VI 5 B Nb Niobium 92.906	25 VI 6 B Cr Chromium 51.996	26 VI 7 B Mn Manganese 54.938	27 VI 8 VIIIB 7 B Fe Iron 55.933	28 VI 8 VIIIB 7 B Ni Nickel 58.933	29 VI 8 VIIIB 7 B Cu Copper 63.546	30 VIIIB 8 VIIIB 7 B Zn Zinc 65.39	31 VIIIB 8 VIIIB 7 B Ga Gallium 69.712	32 VIIIB 8 VIIIB 7 B Ge Germanium 72.61	33 VIIIB 8 VIIIB 7 B As Arsenic 74.922	34 VIIIB 8 VIIIB 7 B Se Selenium 78.972	35 VIIIB 8 VIIIB 7 B Br Bromine 79.904	36 VIIIB 8 VIIIB 7 B Kr Krypton 84.98
37 IA 1 A 37 Rb Rubidium 84.468	38 IIIB 2 B Sr Strontium 87.62	39 IIIA 3 A Y Yttrium 88.900	40 IVB 4 B Zr Zirconium 91.224	41 VA 5 A Nb Niobium 92.906	42 VI 6 B Mo Molybdenum 95.95	43 VI 7 B Tc Technetium 98.907	44 VI 8 VIIIB 7 B Ru Ruthenium 101.07	45 VI 8 VIIIB 7 B Rh Rhodium 102.906	46 VI 8 VIIIB 7 B Pd Palladium 106.42	47 VI 8 VIIIB 7 B Ag Silver 107.898	48 VI 8 VIIIB 7 B Cd Cadmium 112.411	49 VI 8 VIIIB 7 B In Indium 114.818	50 VI 8 VIIIB 7 B Sn Tin 118.71	51 VI 8 VIIIB 7 B Sb Antimony 121.790	52 VI 8 VIIIB 7 B Te Tellurium 127.6	53 VI 8 VIIIB 7 B I Iodine 126.904	54 VI 8 VIIIB 7 B Xe Xenon 131.29
55 IA 1 A 55 Cs Cesium 132.905	56 IIIB 2 B Ba Barium 137.327	57-71 VIIIB 8 VIIIB 7 B Hf Hafnium 178.49	72 IVB 4 B Ta Tantalum 180.948	73 V Ta Nb Tungsten 183.85	74 VI 6 B W Re Rhenium 189.207	75 VI 7 B Os Osmium 190.23	76 VI 8 VIIIB 7 B Ir Iridium 192.22	77 VI 8 VIIIB 7 B Pt Platinum 195.08	78 VI 8 VIIIB 7 B Au Gold 196.987	79 VI 8 VIIIB 7 B Hg Mercury 200.59	80 VI 8 VIIIB 7 B Tl Thallium 204.383	81 VI 8 VIIIB 7 B Pb Lead 207.2	82 VI 8 VIIIB 7 B Po Polonium 208.983	83 VI 8 VIIIB 7 B Bi Bismuth 208.980	84 VI 8 VIIIB 7 B At Astatine 209.887	85 VI 8 VIIIB 7 B Rn Radon 222.018	
87 IA 1 A 87 Fr Francium 223.020	88 IIIB 2 B Ra Radium 226.025	89-103 VIIIB 8 VIIIB 7 B Rf Rutherfordium [281]	104 IVB 4 B Db Dubnium [282]	105 V Db Bh Bohrium [284]	106 VI 6 B Sg Seaborgium [286]	107 VI 7 B Nh Nihonium [288]	108 VI 8 VIIIB 7 B Hs Hassium [289]	109 VI 8 VIIIB 7 B Mt Meitnerium [289]	110 VI 8 VIIIB 7 B Ds Darmstadtium [289]	111 VI 8 VIIIB 7 B Rg Roentgenium [272]	112 VI 8 VIIIB 7 B Cn Copernicium [277]	113 VI 8 VIIIB 7 B Uut Ununtrium Unknown	114 VI 8 VIIIB 7 B Fl Florivium [289]	115 VI 8 VIIIB 7 B Up Ununpentium Unknown	116 VI 8 VIIIB 7 B Lv Livermorium [290]	117 VI 8 VIIIB 7 B Uus Ununseptium Unknown	118 VI 8 VIIIB 7 B Uuo Ununoctium Unknown
Lanthanide Series																	
57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.28	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.987			
Actinide Series																	
89 Ac Actinium 227.028	90 Th Thorium 222.036	91 Pa Protactinium 223.036	92 U Uranium 238.029	93 Np Neptunium 237.046	94 Pu Plutonium 244.084	95 Am Americium 243.081	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]			

e.g., LaFeO_3

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 (1.12 Å ionic radius vs. 0.97-1.14 Å)

• ABO_3 : Perovskite

- Large A and 3d 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...

Difficult to describe redox + not common in oxide perovskite

Periodic Table of the Elements																	
IA 1A		IIA 2A		B			VIIA 7A		VIIIA 8A								
1 H Hydrogen 1.008	2 Be Beryllium 9.012	3 Li Lithium 6.941	4 Be Boron 10.811	5 V Carbon 12.011	6 Si Nitrogen 14.007	7 O Oxygen 15.999	8 F Fluorine 18.998	9 Ne Neon 20.180	10 Ar Argon 39.948	11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.068	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.958	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.893	27 Co Cobalt 58.933	28 Ni Nickel 58.993	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.908	40 Zr Zirconium 91.224	41 Nb Niobium 92.908	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 103.82	47 Ag Silver 107.888	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.281
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 203.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 unknown	118 Uuo Ununseptium unknown
Lanthanide Series		57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.38	63 Eu Europium 151.966	64 Gd Gadolinium 158.925	65 Tb Terbium 162.50	66 Dy Dysprosium 164.930	67 Ho Holmium 167.26	68 Er Erbium 166.934	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967	
Actinide Series		89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.028	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Einsteinium [254]	99 Es Fermium 257.095	100 Fm Mendelevium 259.1	101 Md Nobelium 259.101	102 No Lawrencium [262]	103 Lr Ununoctium unknown	

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

- Ce (+4/+3)

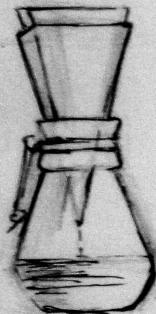
- Ce (+4/+3)

Ca most compatible with Ce on A (1.12\AA ionic radius vs. $0.97\text{-}1.14\text{\AA}$)

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

- Specifically, look at $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MO}_3$ using theoretical calculations
 - Still need to have ideal ΔH !
 - And be thermodynamically stable

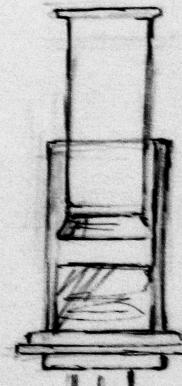
BREW METHODS



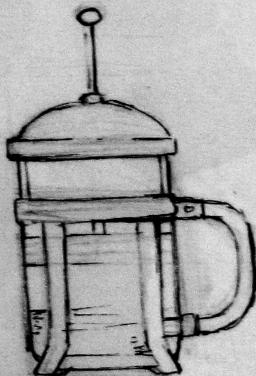
CHEMEX



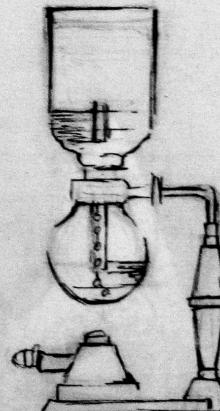
FLAT BOTTOM
POUR OVER FILTER



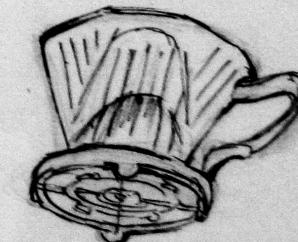
AEROPRESS



FRENCH PRESS



SYPHON



CLEVER DRIPPER

Methods detour: calculation
setup, structural input and stability

Density functional theory (DFT): predict material properties

$$H\psi = E\psi \longrightarrow \begin{array}{l} \text{Total energy at 0 K} \approx \text{Gibbs energy} \rightarrow \text{Thermodynamics} \\ \text{Density of states + Band structure} \rightarrow \text{Band gap} \end{array}$$



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



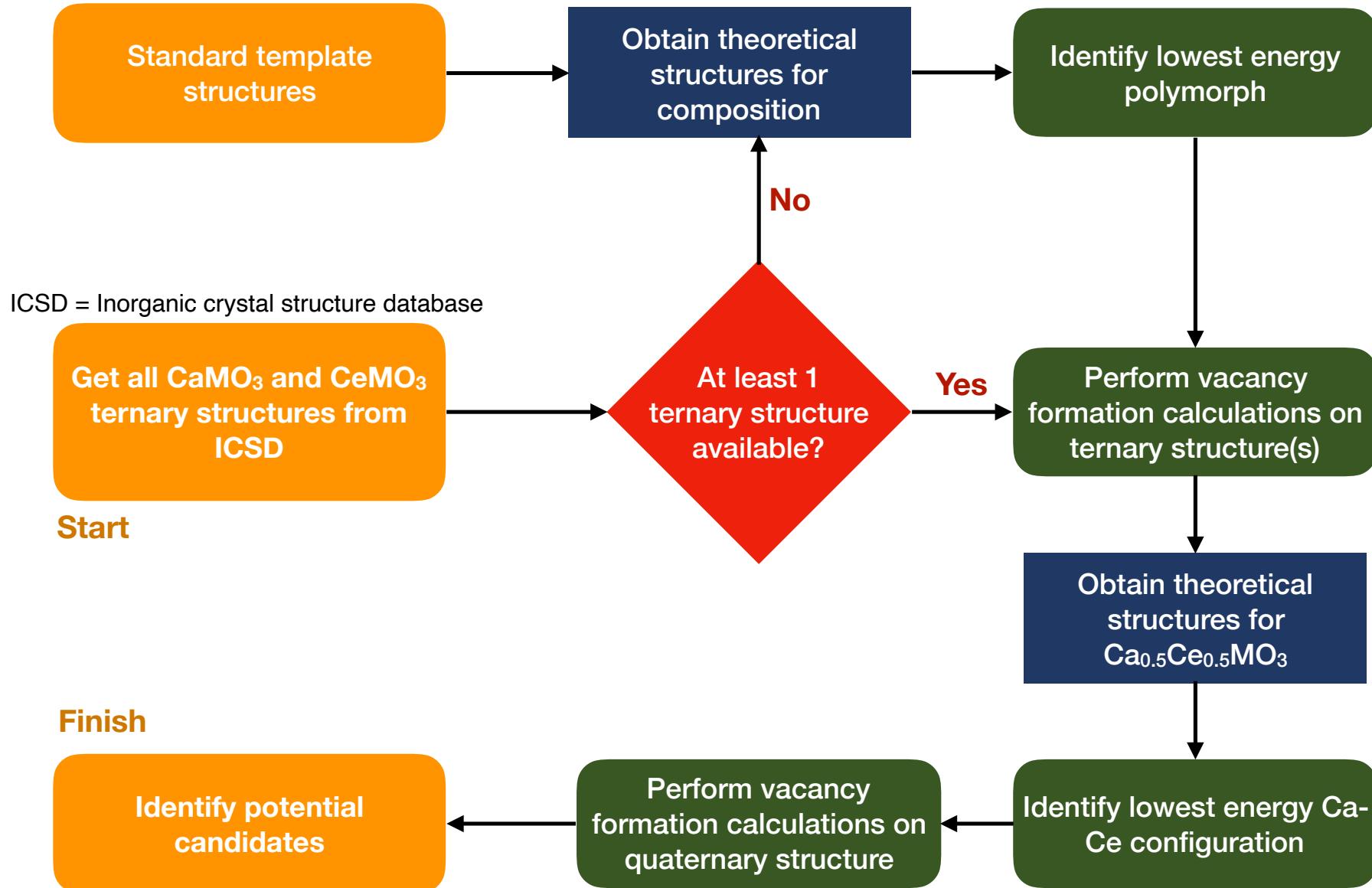
Need structural input!

3. Sun et al., *Phys. Rev. Lett.* 2015, 115, 036402
Figure (above): Car, *Nat. Chem.* 2016, 8, 820

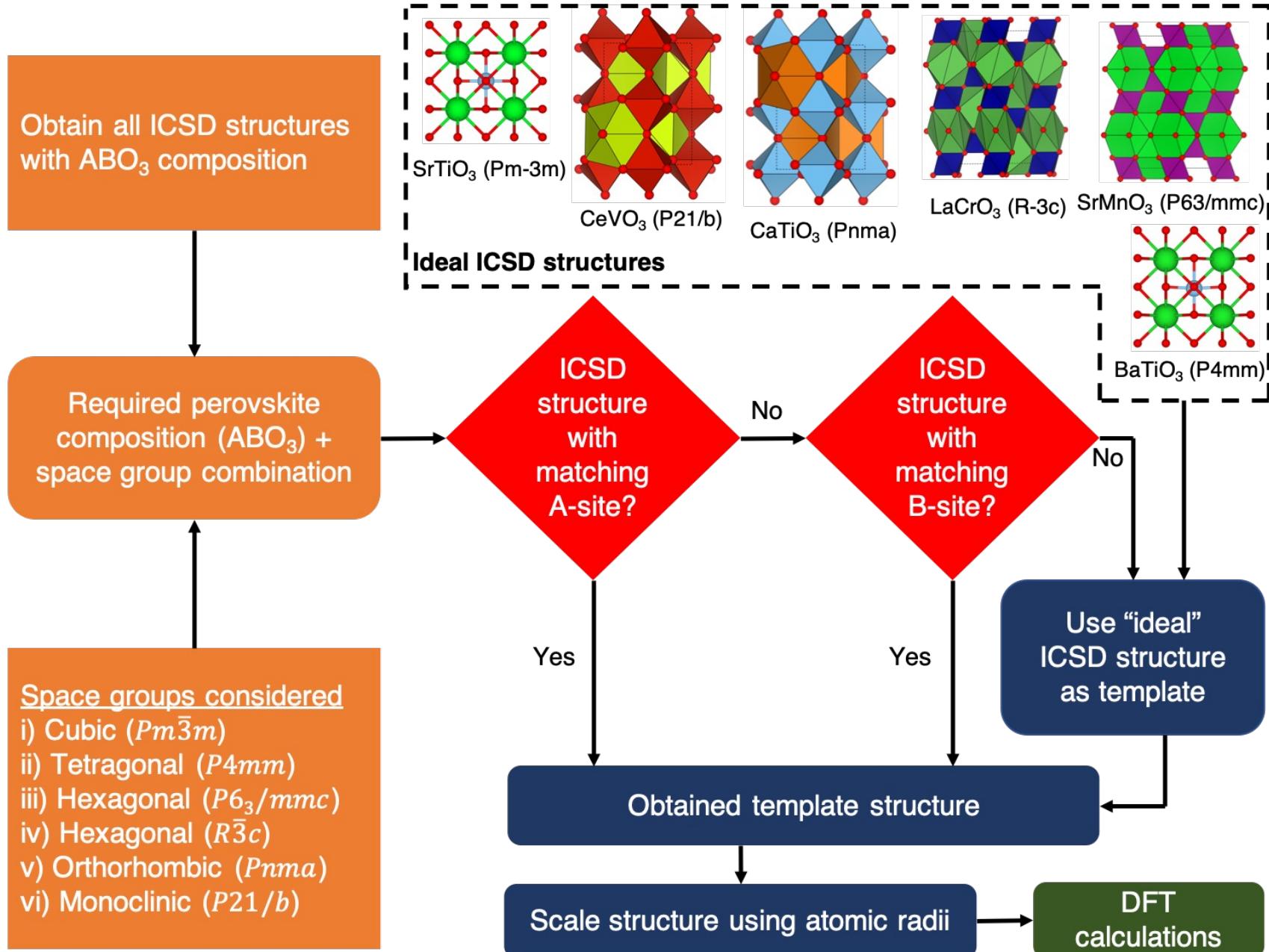
1. Hohenberg and Kohn, *Phys. Rev.* 1964, 136, B864

2. Kohn and Sham, *Phys. Rev.* 1965, 140, A1133

No experimental $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MO}_3$ structures available: use CaMO_3 or CeMO_3

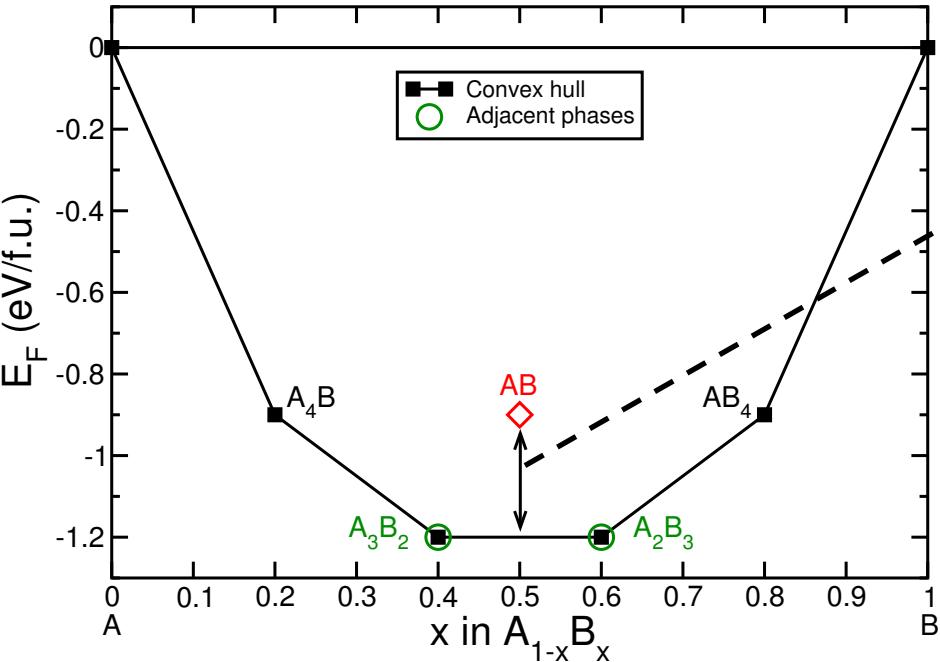


Templating scheme for theoretical (Co & Ni) structures



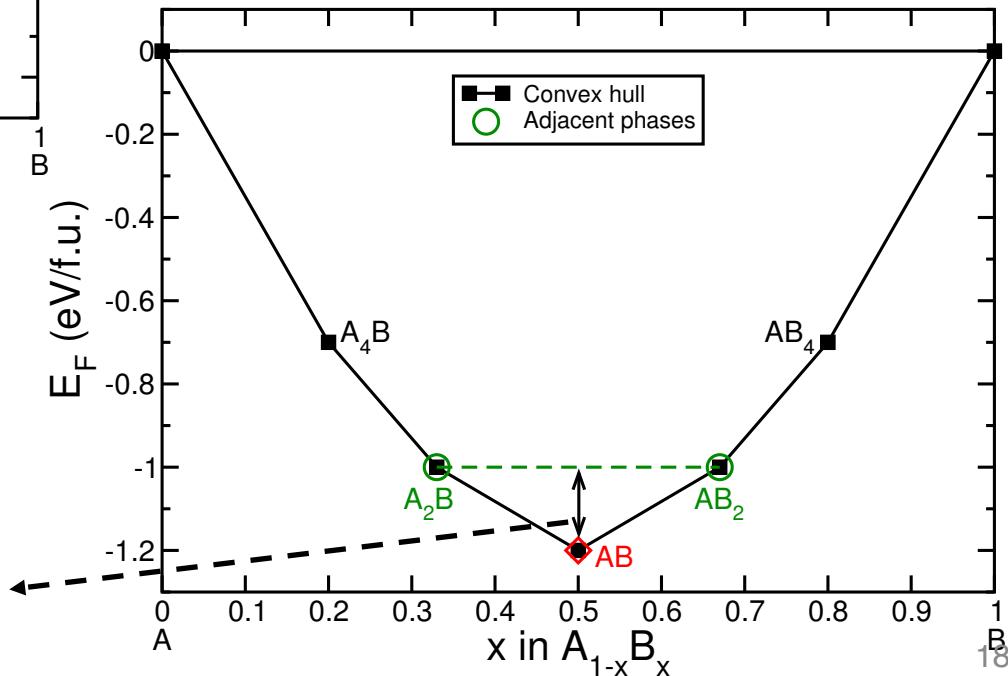
0 K thermodynamics: convex hull

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)

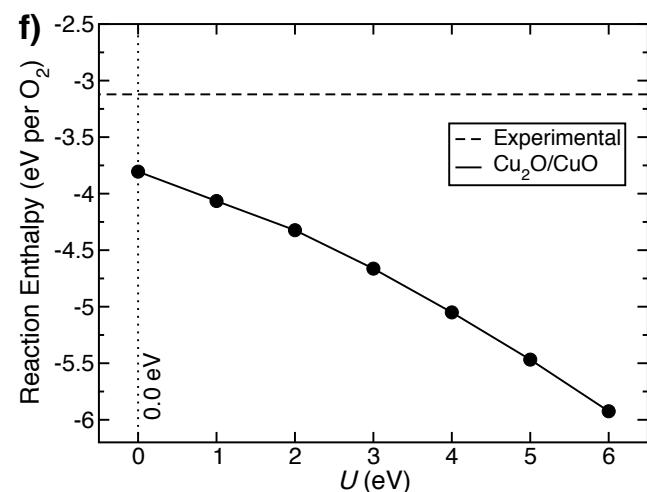
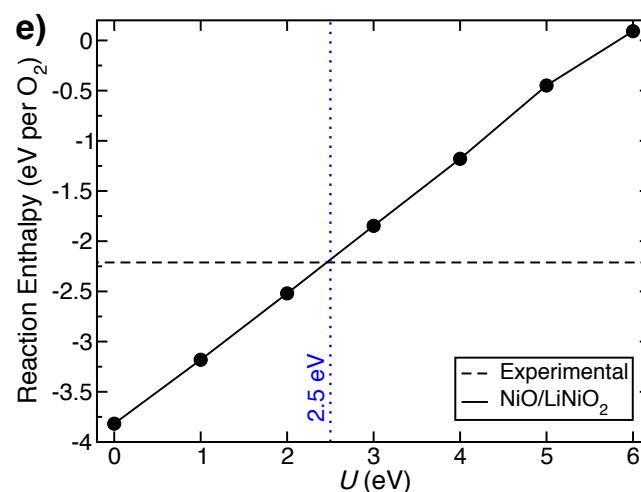
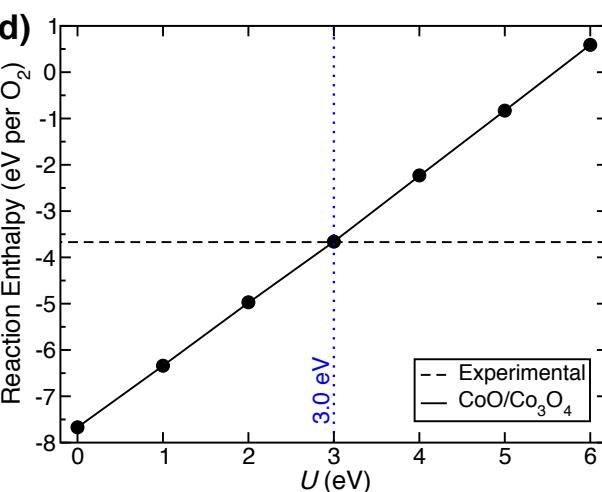
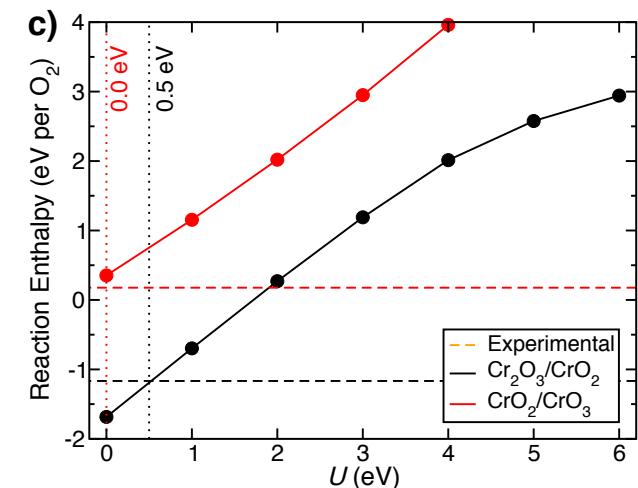
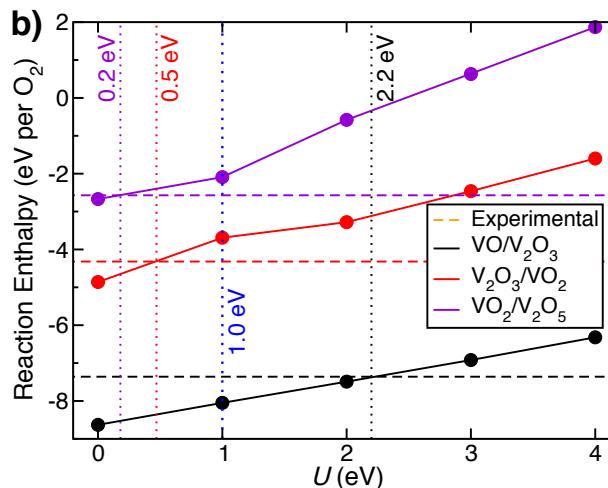
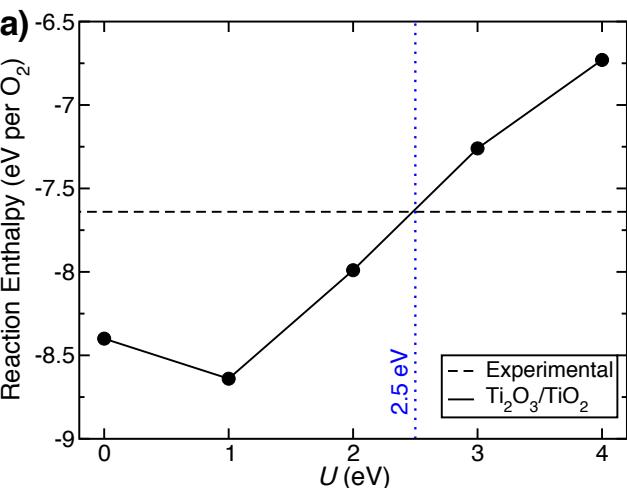
- Largest energy release via decomposition of AB



Negative E^{hull} : stable

- Lowest energy release via formation of AB

XC functional: a U correction to SCAN



$$U_{\text{Mn}} = 2.7 \text{ eV}$$

$$U_{\text{Fe}} = 3.1 \text{ eV}$$

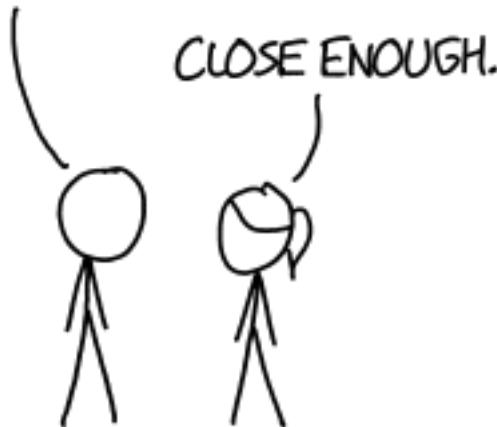
$$U_{\text{Ce}} = 2.0 \text{ eV}$$

$$U_{\text{Sc}} = 0.0 \text{ eV}$$

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

$$\Delta H_{\text{reduction}} \approx E_F[\text{Va}_0]$$

THE SECOND LAW OF THERMODYNAMICS STATES
THAT A ROBOT MUST NOT INCREASE ENTROPY,
UNLESS THIS CONFLICTS WITH THE FIRST LAW.



Results

Ternaries

- Structures
- Vacancy formation
- Stability

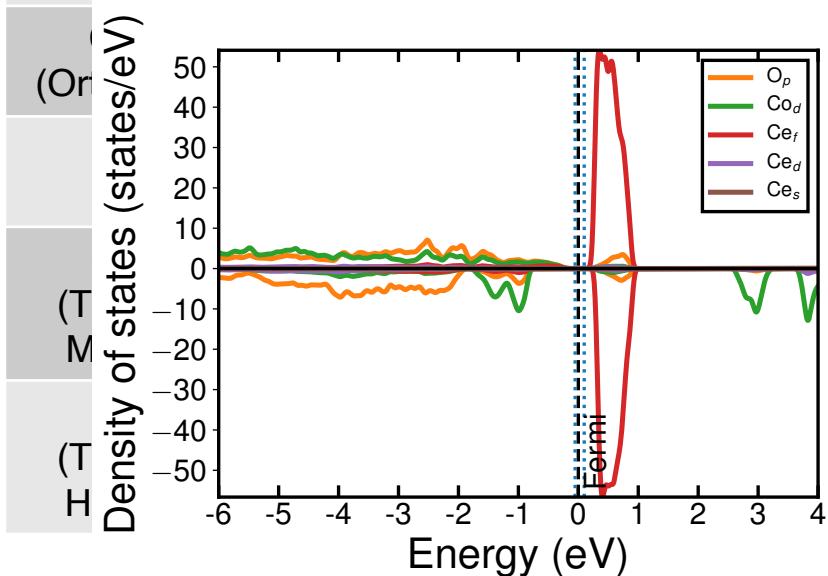
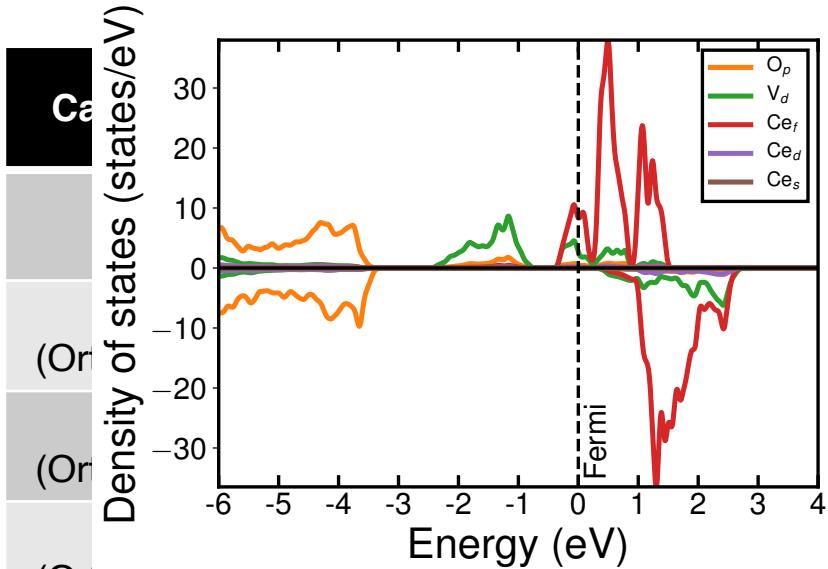
Quaternaries

- Vacancy formation
- Stability

Structures and oxidation states: CaMO₃ and CeMO₃

Ca-ternaries	Ca	M	Ce-ternaries	Ce	M
CaScO ₃	—		CeScO ₃ (Orthorhombic)	+3	+3
CaTiO ₃ (Orthorhombic)			CeTiO ₃	—	
CaVO ₃ (Orthorhombic)			CeVO ₃ (Monoclinic)	+3	+3
CaCrO ₃ (Orthorhombic)			CeCrO ₃ (Cubic)		
CaMnO ₃ (Orthorhombic)	+2	+4	CeMnO ₃	—	
CaFeO ₃			CeFeO ₃		
CaCoO ₃ (Theoretical, Monoclinic)			CeCoO ₃ (Theoretical, Orthorhombic)	+4	+2
CaNiO ₃ (Theoretical, Hexagonal)			CeNiO ₃ (Theoretical, Monoclinic)		

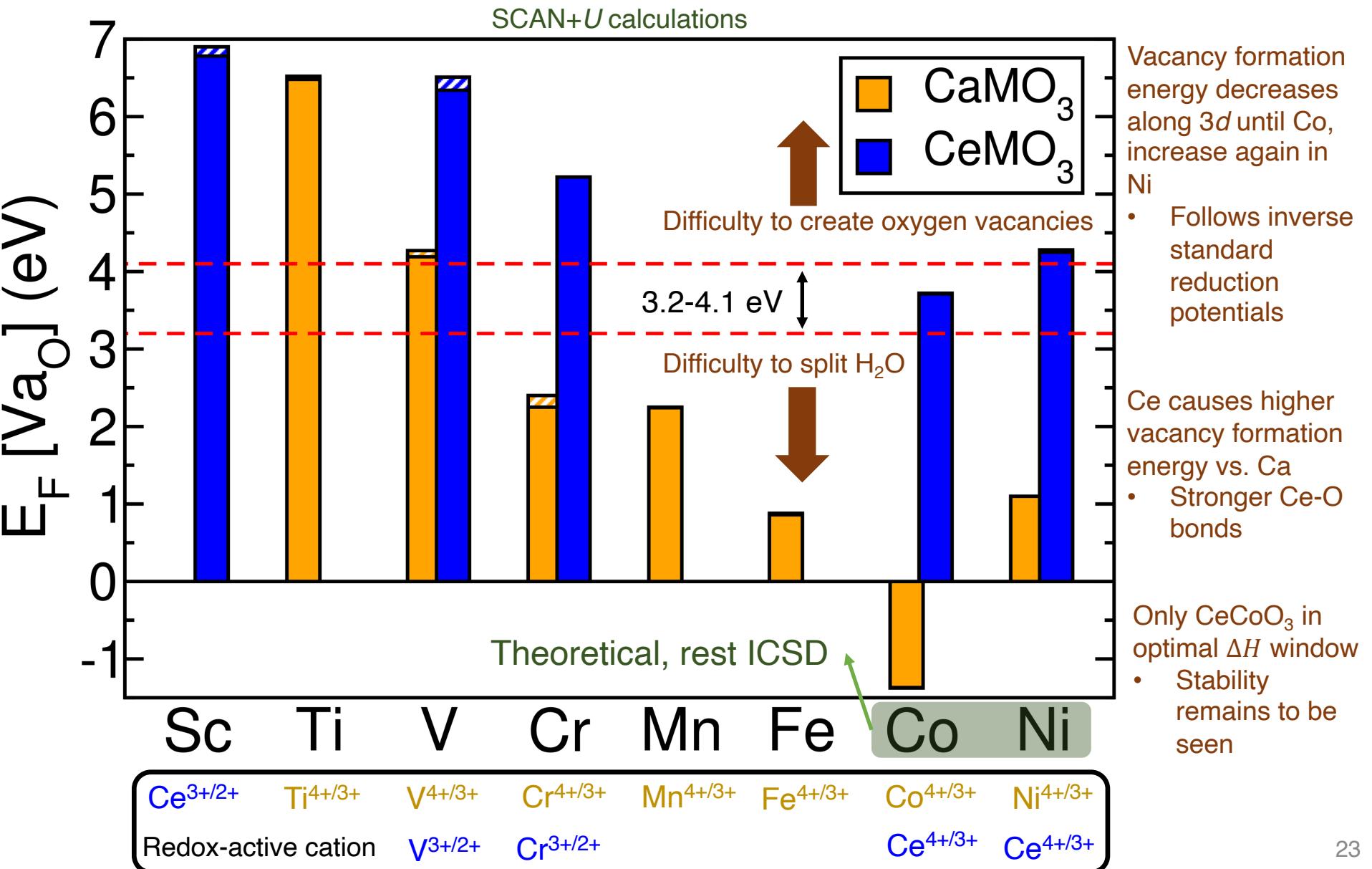
Structures and oxidation states: CaMO_3 and CeMO_3



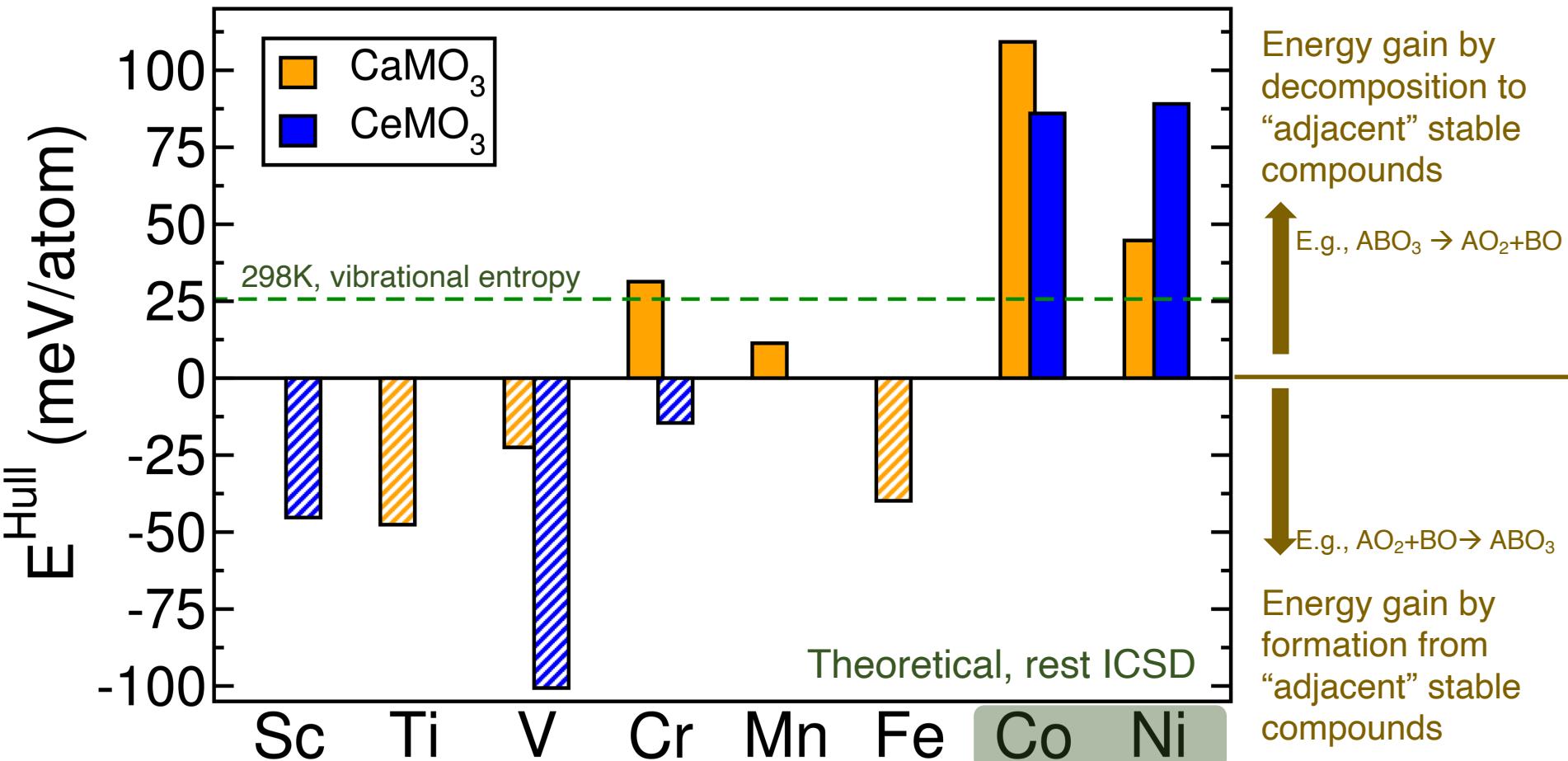
Ca	Ce-ternaries	Ce	M
(Or)	CeScO_3 (Orthorhombic)	+3	+3
(Or)	CeTiO_3	-	
(Orthorhombic)	CeVO_3 (Monoclinic)	+3	+3
(Or)	CeCrO_3 (Cubic)		
(Or)	CeMnO_3		
(T)	CeFeO_3	-	
(T)	CeCoO_3 (Theoretical, Orthorhombic)	+4	+2
H	CeNiO_3 (Theoretical, Monoclinic)		

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

Oxygen vacancy formation in CaMO_3 and CeMO_3 : no obvious candidate



0 K stability: CaMO_3 and CeMO_3



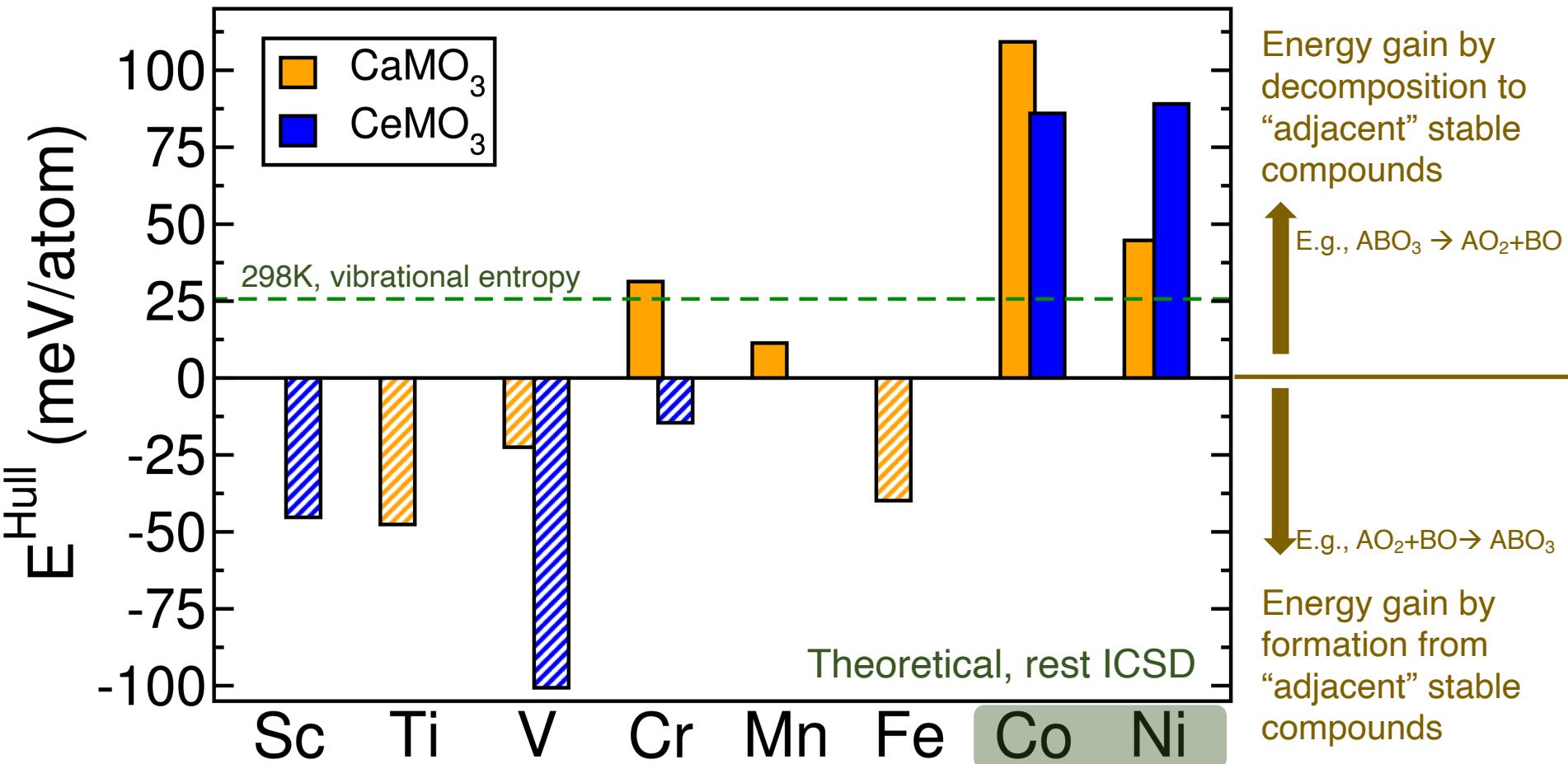
ICSD structures: either negative E^{hull} or small positive E^{hull}

Theoretical structures: large positive E^{hull}

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

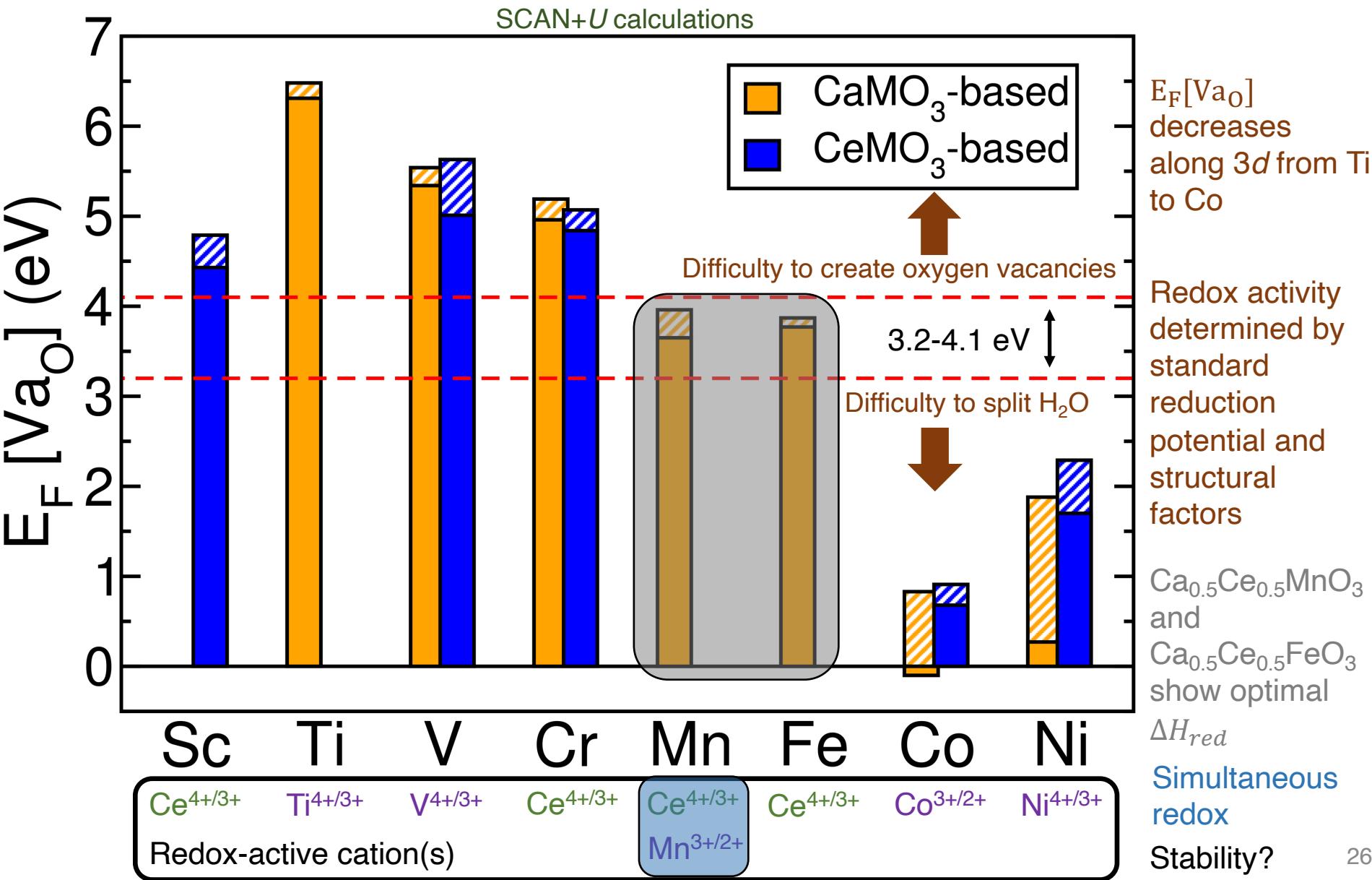
CeCoO₃ is highly unstable!

0 K stability: CaMO₃ and CeMO₃

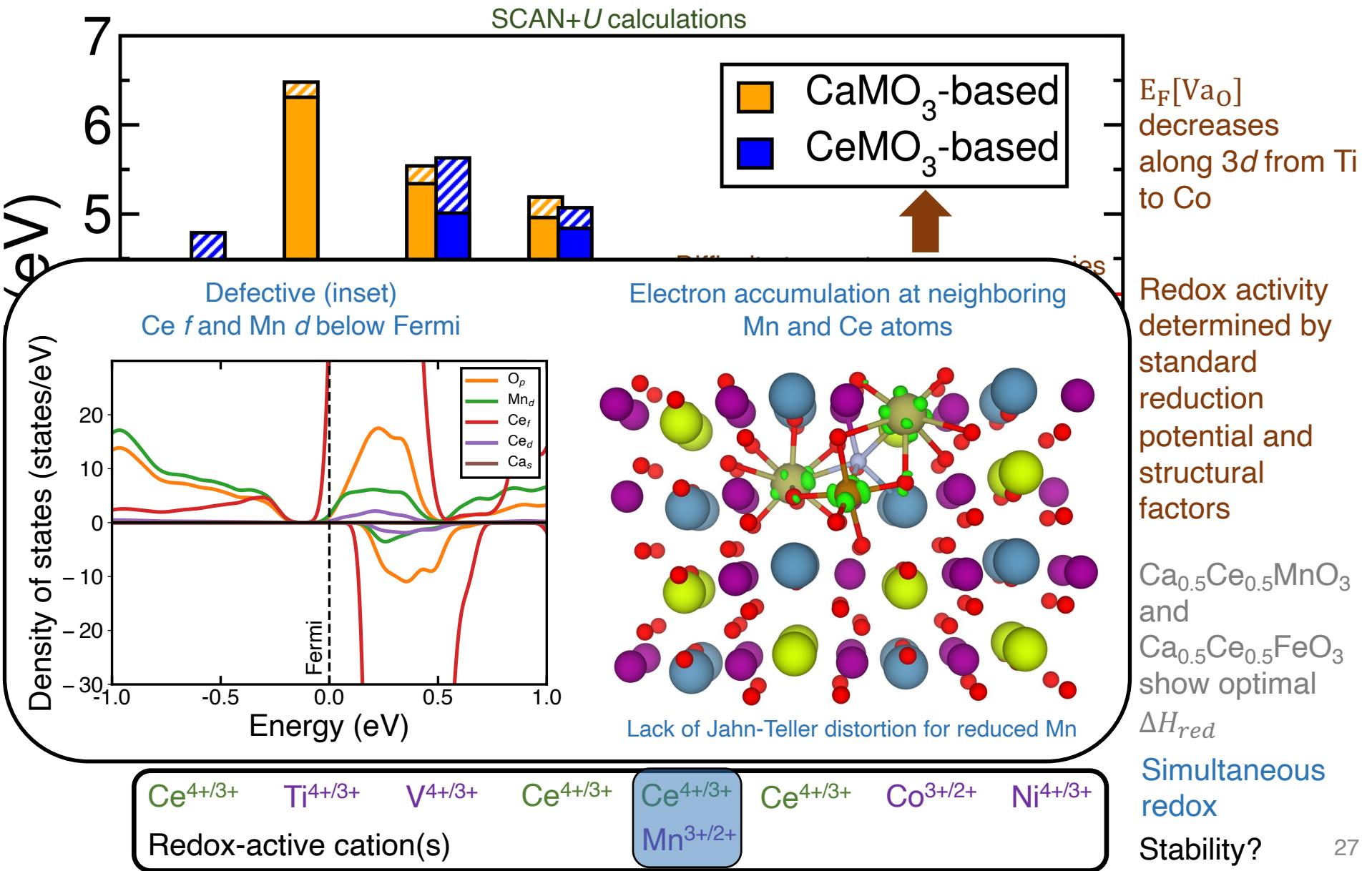


No candidates among ternaries in terms of simultaneous redox and optimal enthalpy of reduction: what about quaternaries?

Oxygen vacancy formation energy in $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MO}_3$: $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MnO}_3$ and $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{FeO}_3$ are promising

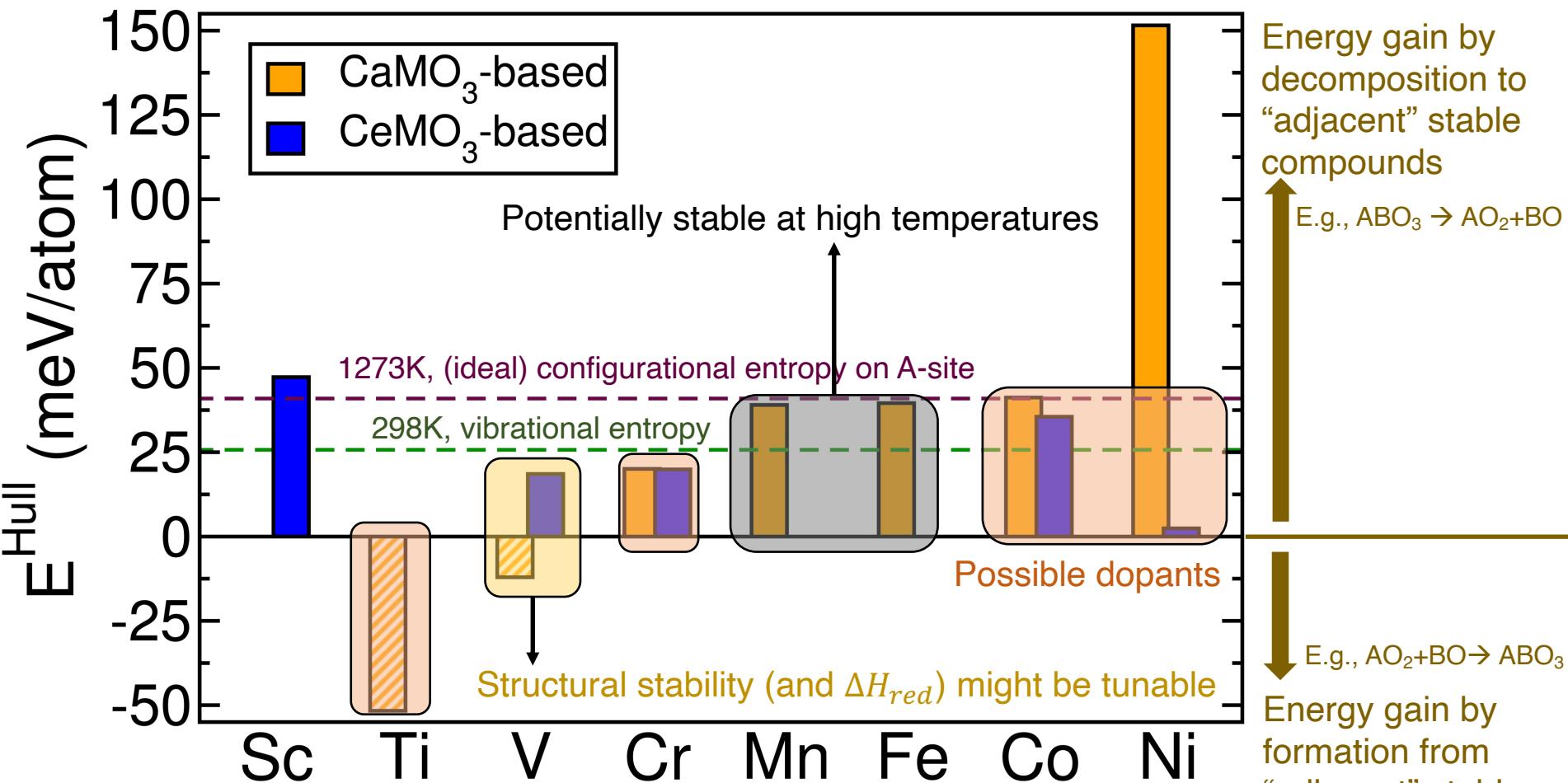


Oxygen vacancy formation energy in $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MO}_3$: $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MnO}_3$ and $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{FeO}_3$ are promising



0 K stability of $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MO}_3$

Impact of configurational entropy (of not reduction)



$\text{Ca}_{1-x}\text{Ce}_x\text{MnO}_3$ ($x \sim 0.2$) has been synthesized before¹

$\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MO}_3$ perovskites: can be stabilized at higher temperatures via A-site configurational entropy

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: $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MnO}_3$ is a promising candidate
 - Candidates based on optimal enthalpy of reduction: $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MnO}_3$, $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{FeO}_3$, $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{VO}_3$ (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 $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MnO}_3$ (theory and experiments)

1. G.S. Gautam, E.B. Stechel, and E.A. Carter, “Exploring Ca-Ce-M-O ($M = 3d$ 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 $3d$ transition-metal oxides within the SCAN+ U framework”, **Phys. Rev. Mater.** **2020**, 4, 045401

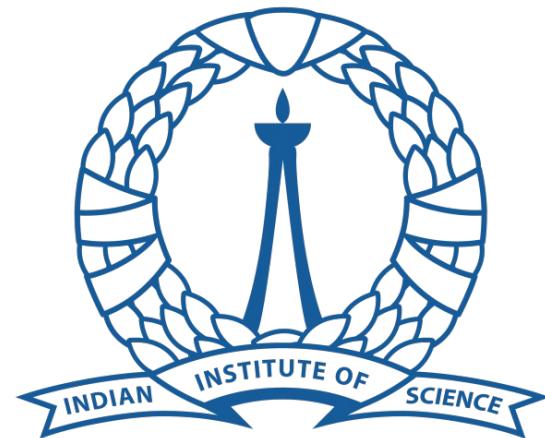
Acknowledgments



Carter group, Summer 2019



Prof. Emily A. Carter
UCLA and Princeton



भारतीय विज्ञान संस्थान

Organizers of Pratidhwani
IIT-Delhi
The (virtual) audience



Dr. Ellen Stechel
(Arizona State)

saiagautamg@iisc.ac.in
 @goths19



Computing resources at NREL (Eagle) and Princeton (Tiger)