

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

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

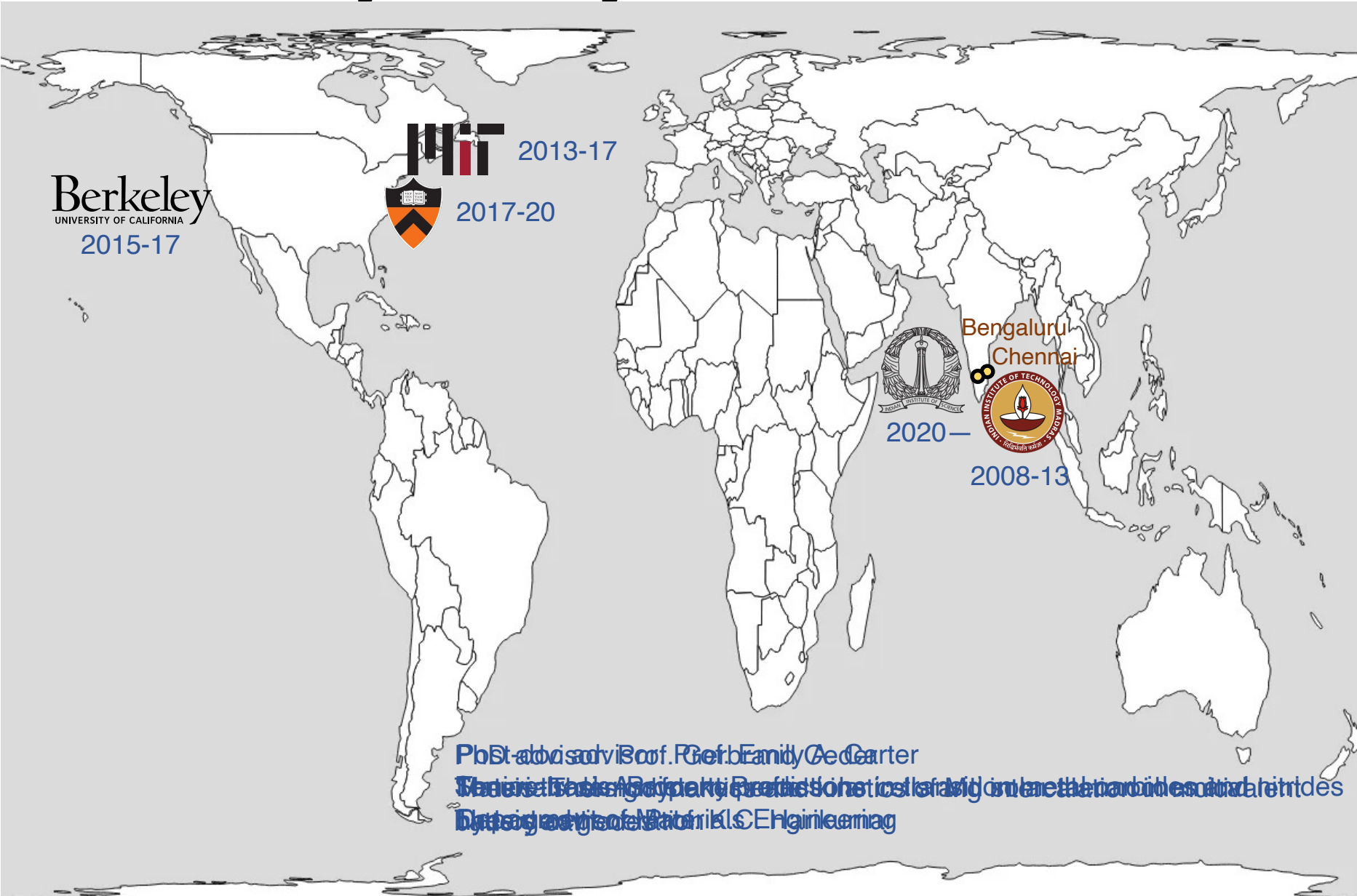
Indian Institute of Science & Princeton University

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Pratidhwani, Indian Institute of Technology Delhi

Nov 12, 2020

Scientific journey so far...



Berkeley
UNIVERSITY OF CALIFORNIA
2015-17

MIT 2013-17
[Shield Logo] 2017-20

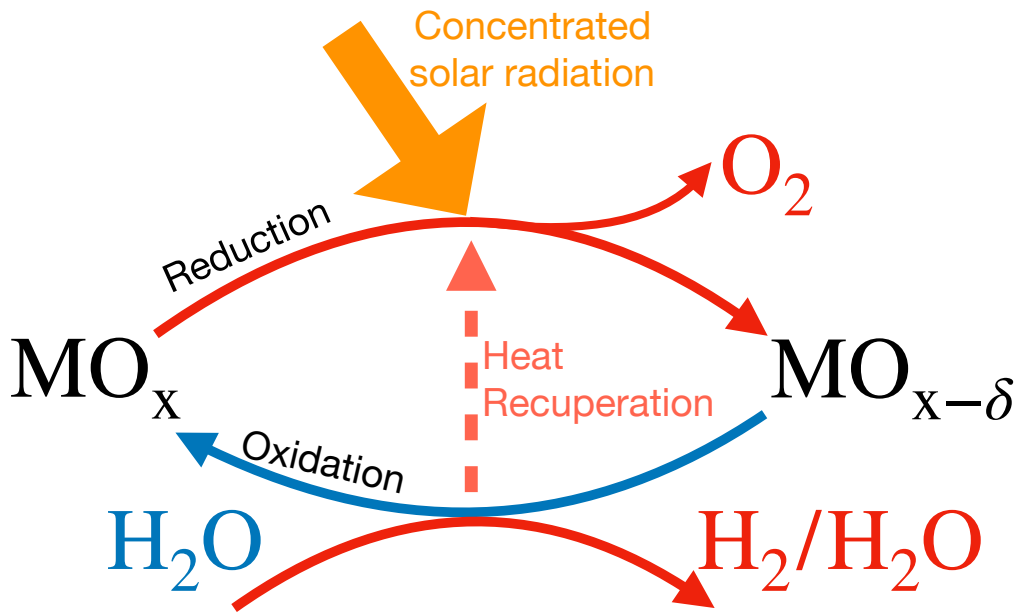
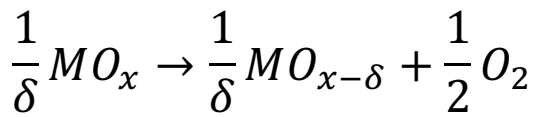
Bengaluru
Chennai
IIT 2020
IIT Madras 2008-13

Post-Doctoral Fellow, Center for Family and Gender Studies, MIT
Senior Fellow, Center for Family and Gender Studies, MIT
Director, Center for Family and Gender Studies, MIT
Professor, Department of Materials Science and Engineering, IIT Madras
Director, Center for Family and Gender Studies, IIT Madras

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

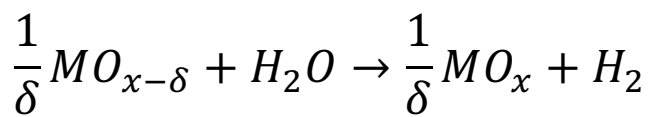
Candidates so far:

- 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?

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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- Fe(Fe,X)₂O₄
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Image: <https://www.solarpaces.org/csp-efficient-solar-split-h2o-hydrogen/>



German research center (DLR), 2017

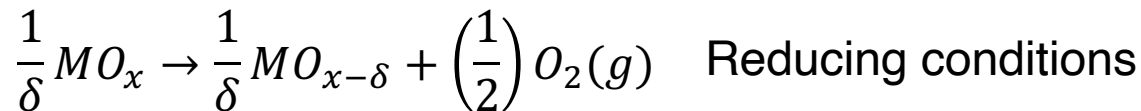
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New candidates?

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

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

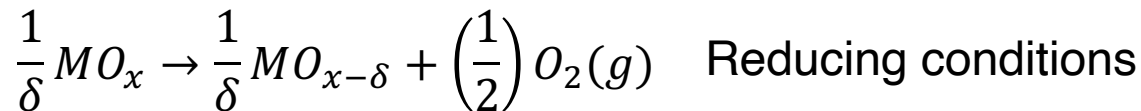
Low $\Delta H_{reduction}$ = large δ

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 $\Delta H_{formation}^{V_{ao}} \sim 3.4\text{-}3.9$ 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)

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Higher entropy of reduction = higher productivity

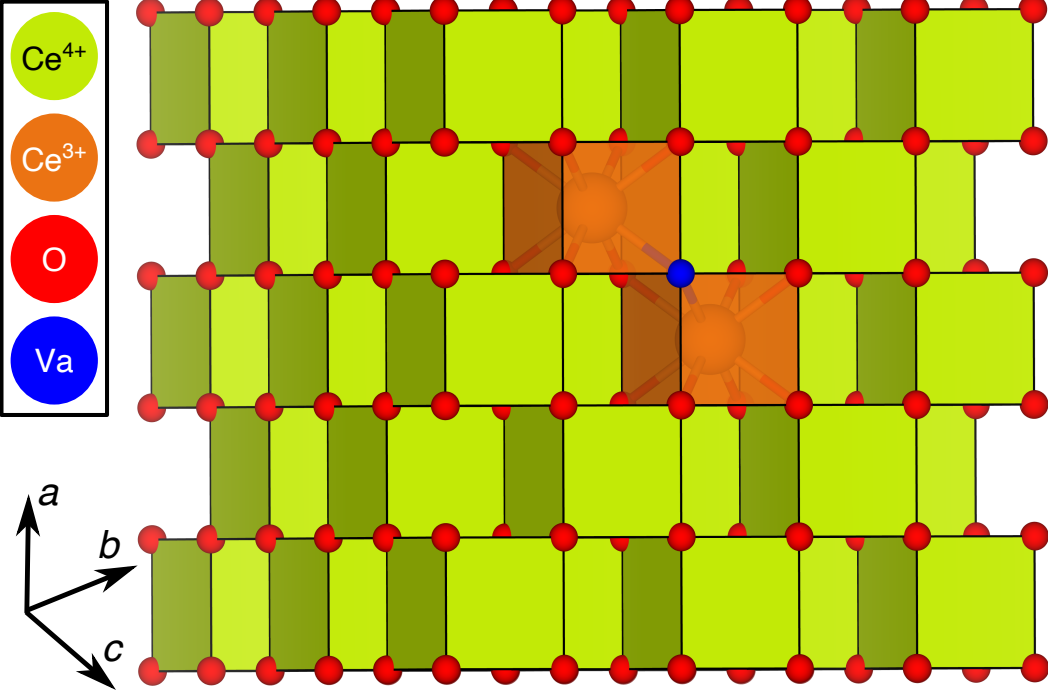
Entropy of reduction for an induced off-stoichiometry, δ , in ABO_3

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

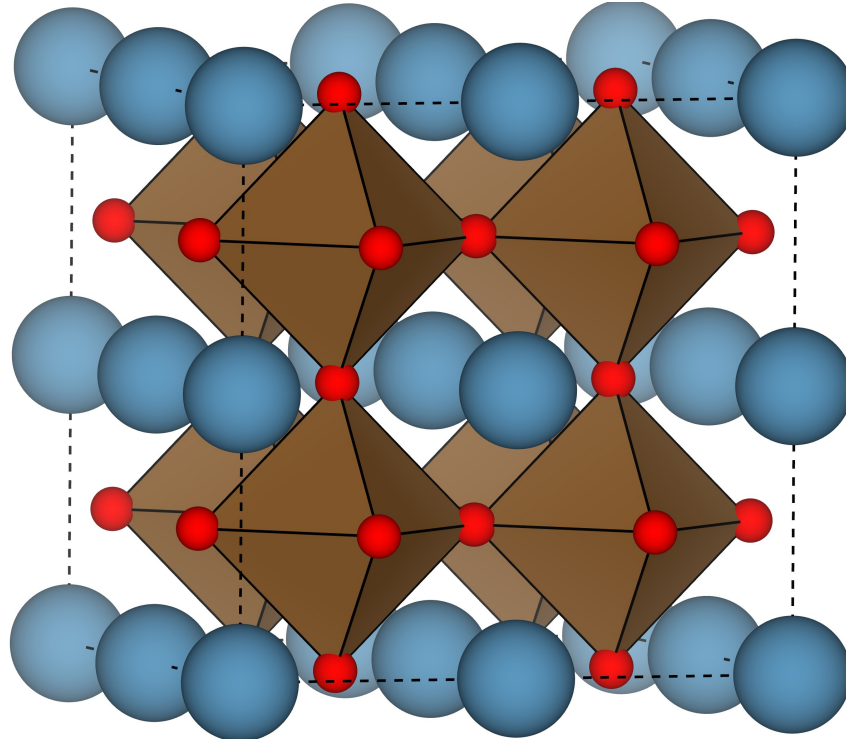
solid
gas

Not easily calculable

Higher $\Delta S_{reduction}$ \rightarrow stabilizes large δ \rightarrow 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

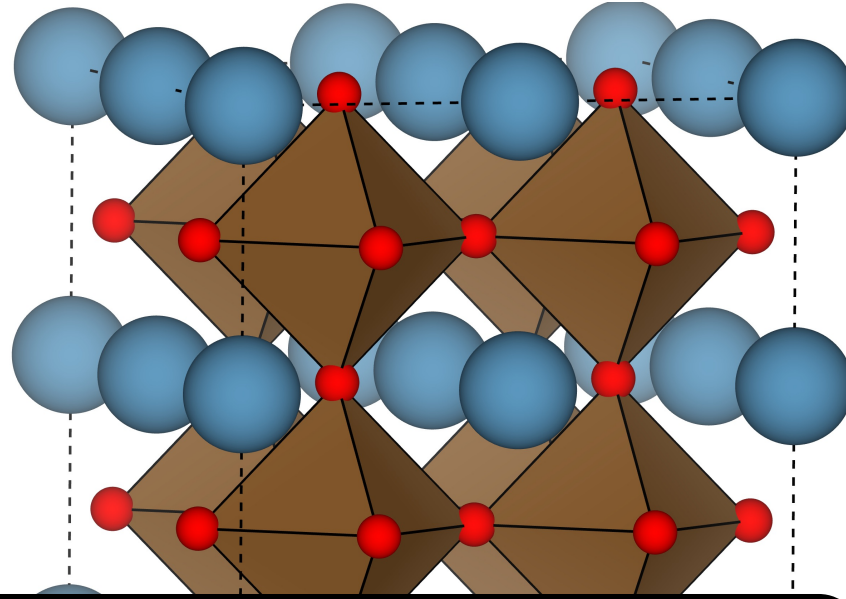
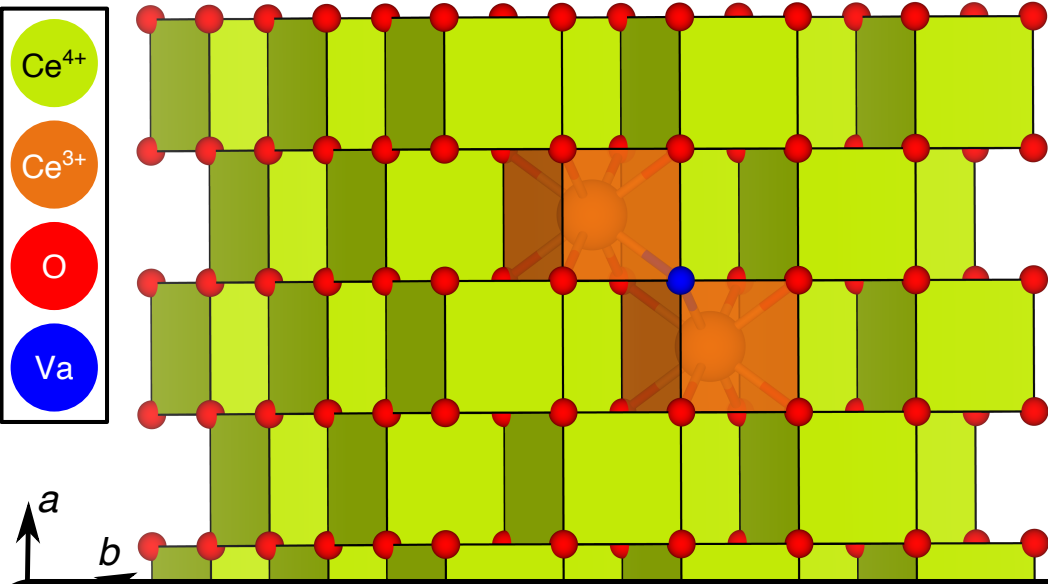
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gas

Not easily calculable

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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?

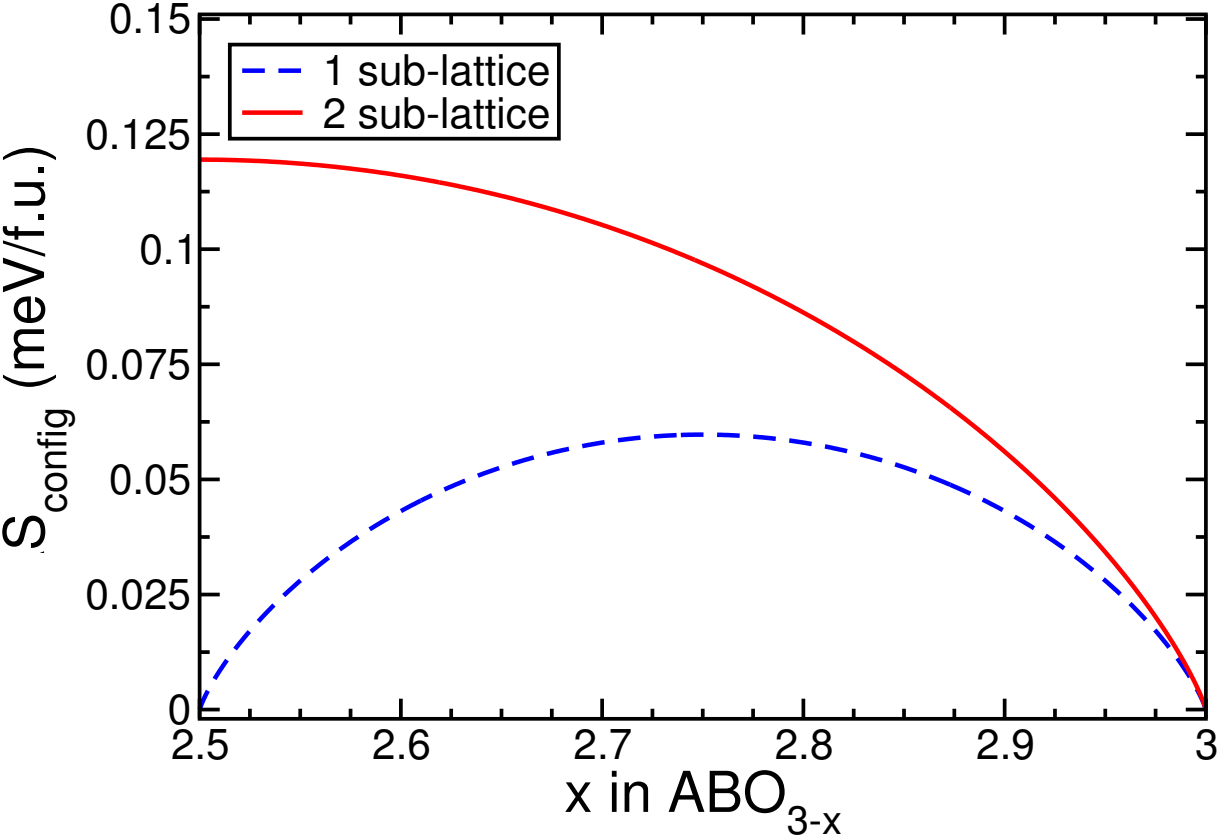
Simultaneous redox-activity = higher productivity

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

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

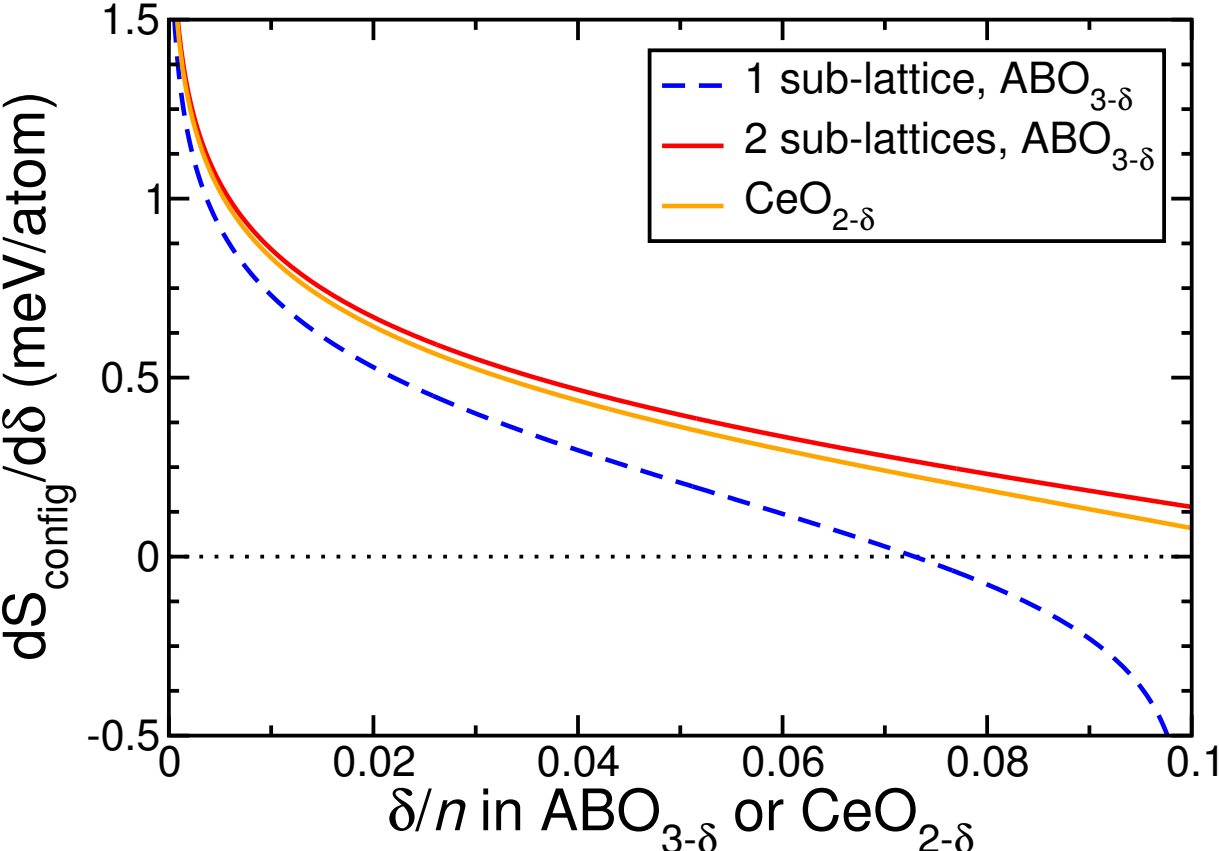
$$S_{config}(2 \text{ sub-lattices}, ABO_x) = -2k_B((3-x)\ln(3-x) + (x-2)\ln(x-2))$$

$f(x*\ln(x))$

Simultaneous redox-activity = higher productivity

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

$$\Delta S_{reduction} = \underbrace{\frac{S_{ABO_{3-\delta}} - S_{ABO_3}}{\delta}}_{\text{solid}} + \underbrace{\left(\frac{1}{2}\right) S_{O_2(g)}}_{\text{gas}} \quad \text{Not easily calculable}$$



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

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

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

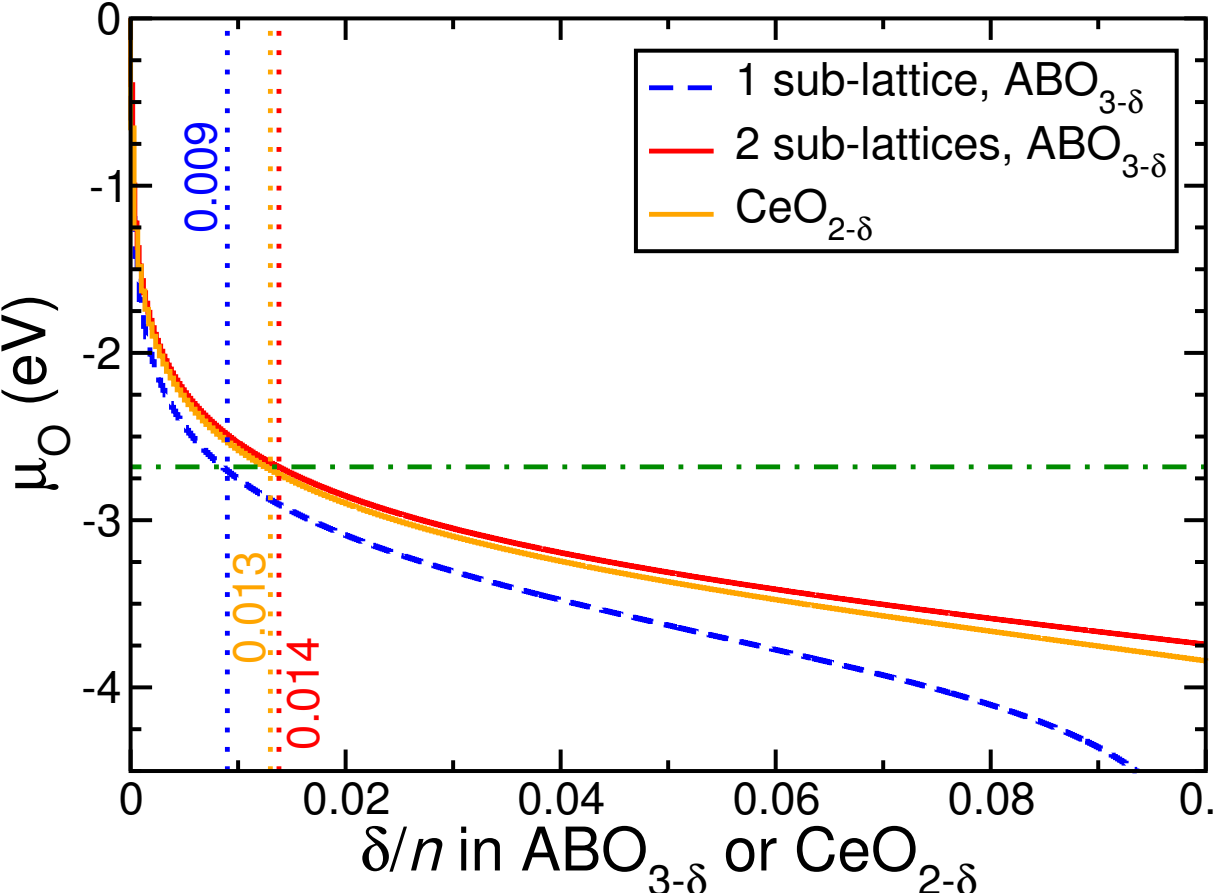
Simultaneous redox-activity = higher productivity

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

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

solid
gas

Not easily calculable



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

Set same $\Delta H_{formation}^{VaO} = CeO_{2-\delta}$

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

Periodic Table of the Elements

1 IA 1A		2 IIA 2A		3-10 IIIB-10B										11-18 IIB-VIIIA 2B-8A					
1 H Hydrogen 1.008	2 He Helium 4.003	3 Li Lithium 6.941	4 Be Beryllium 9.012	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180	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 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948		
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	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 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	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 131.29		
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71 Lanthanide Series	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 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [210]	86 Rn Radon [222]		
87 Fr Francium [223]	88 Ra Radium [226]	89-103 Actinide Series	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 [285]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium [288]	114 Fl Flerovium [289]	115 Uup Ununpentium [288]	116 Lv Livermorium [293]	117 Uus Ununseptium [294]	118 Uuo Ununoctium [294]		

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 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

Callout Box: Atomic Number, Symbol, Name, Atomic Mass, Oxidation States*

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

1	2											13	14	15	16	17	18	
1A	2A											3A	4A	5A	6A	7A	8A	
1	3	4											5	6	7	8	9	10
H	Li	Be											B	C	N	O	F	Ne
Hydrogen	Lithium	Beryllium											Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
1.008	6.941	9.012											10.811	12.011	14.007	15.999	18.998	20.180
11	12											13	14	15	16	17	18	
IA	IIA											IIIA	IVA	VA	VIA	VIIA	VIIIA	
Na	Mg											Al	Si	P	S	Cl	Ar	
Sodium	Magnesium											Aluminum	Silicon	Phosphorus	Sulfur	Chlorine	Argon	
22.990	24.305											26.982	28.086	30.974	32.065	35.453	39.948	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton	
39.098	40.078	44.956	47.88	50.942	51.996	54.938	55.923	58.933	58.933	63.546	65.39	69.723	72.61	74.922	78.972	79.904	84.80	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	Iodine	Xenon	
85.468	87.62	88.906	91.224	92.906	95.95	98.907	101.07	102.906	106.42	107.868	112.411	114.818	118.71	121.760	127.6	126.904	131.29	
55	56	57-71		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba			Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Cesium	Barium			Hafnium	Tantalum	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Polonium	Astatine	Radon
132.905	137.327			178.49	180.948	183.85	186.207	190.23	192.22	195.08	196.967	200.59	204.383	207.2	208.980	209	210	222.018
87	88	89-103		104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra			Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Ff	Uup	Lv	Uus	Uuo
Francium	Radium			Rutherfordium	Dubnium	Seaborgium	Bohrium	Hassium	Mitlerium	Darmstadtium	Roentgenium	Copernicium	Ununtrium	Flerovium	Ununpentium	Livermorium	Ununseptium	Ununoctium
223.020	226.025			[261]	[262]	[266]	[264]	[269]	[268]	[269]	[272]	[277]	unknown	[289]	unknown	[288]	unknown	unknown
Lanthanide Series		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71		
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium		
		138.906	140.115	140.908	144.24	144.913	150.36	151.966	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967		
Actinide Series		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		
		Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium		
		227.028	232.038	231.036	238.029	237.044	244.064	243.061	247.070	247.070	251.080	254.1	257.085	258.1	259.101	262		

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

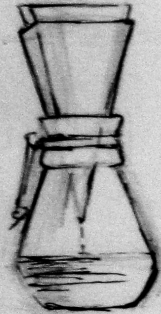
- Ce (+4/+3)

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

Explore Ca-Ce-M-O perovskites (M = 3d 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 $\Delta H!$
- And be thermodynamically stable

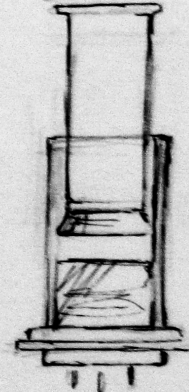
BREW METHODS



CHEMEX



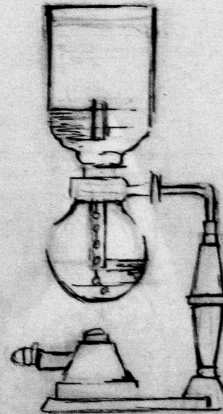
FLAT BOTTOM
POUR OVER FILTER



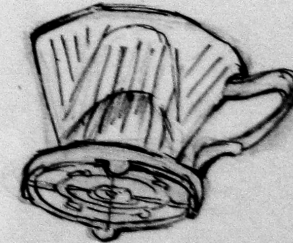
AEROPRESS



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 Total energy at 0 K \approx Gibbs energy \rightarrow Thermodynamics

Density of states + Band structure \rightarrow Band gap

Energy to displace atoms \rightarrow Phonon/vibrational

Barriers for atomic migration \rightarrow Kinetics

Energy of defective structures \rightarrow Defect thermodynamics



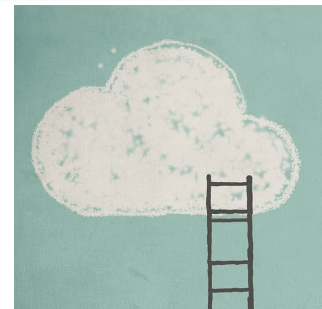
Density functional theory^{1,2}: approximate electronic interactions into a non-interacting mean-field

- 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

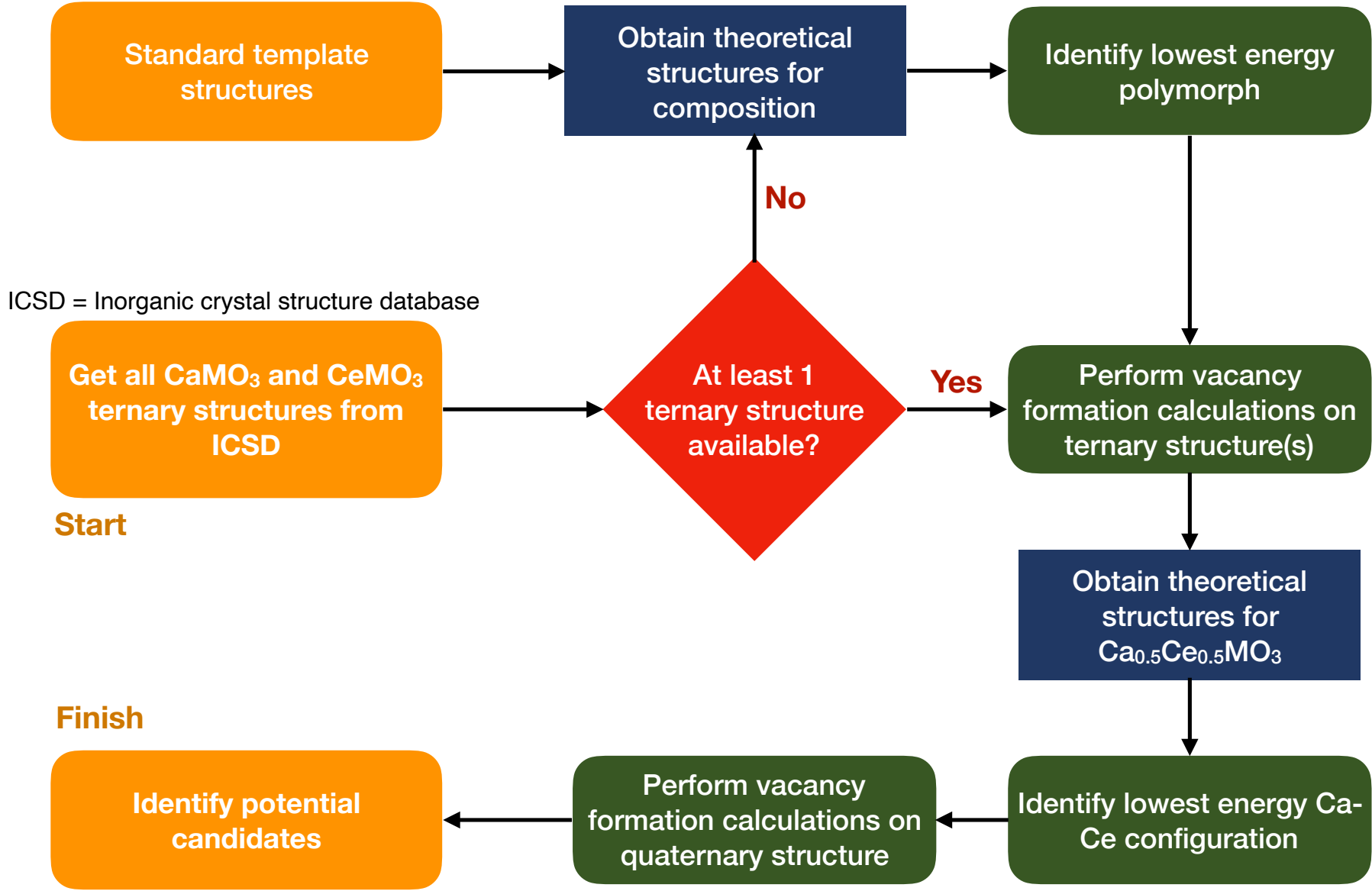


Need structural input!

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

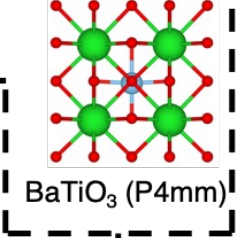
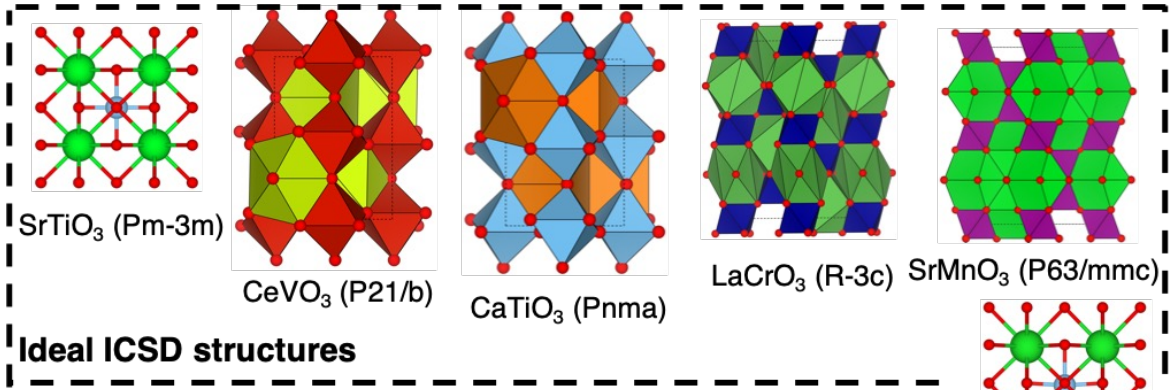
1. Hohenberg and Kohn, *Phys. Rev.* **1964**, *136*, B864
2. Kohn and Sham, *Phys. Rev.* **1965**, *140*, A1133

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

Obtain all ICSD structures with ABO_3 composition



Required perovskite composition (ABO_3) + space group combination

ICSD structure with matching A-site?

ICSD structure with matching B-site?

- Space groups considered
- i) Cubic ($Pm\bar{3}m$)
 - ii) Tetragonal ($P4mm$)
 - iii) Hexagonal ($P6_3/mmc$)
 - iv) Hexagonal ($R\bar{3}c$)
 - v) Orthorhombic ($Pnma$)
 - vi) Monoclinic ($P21/b$)

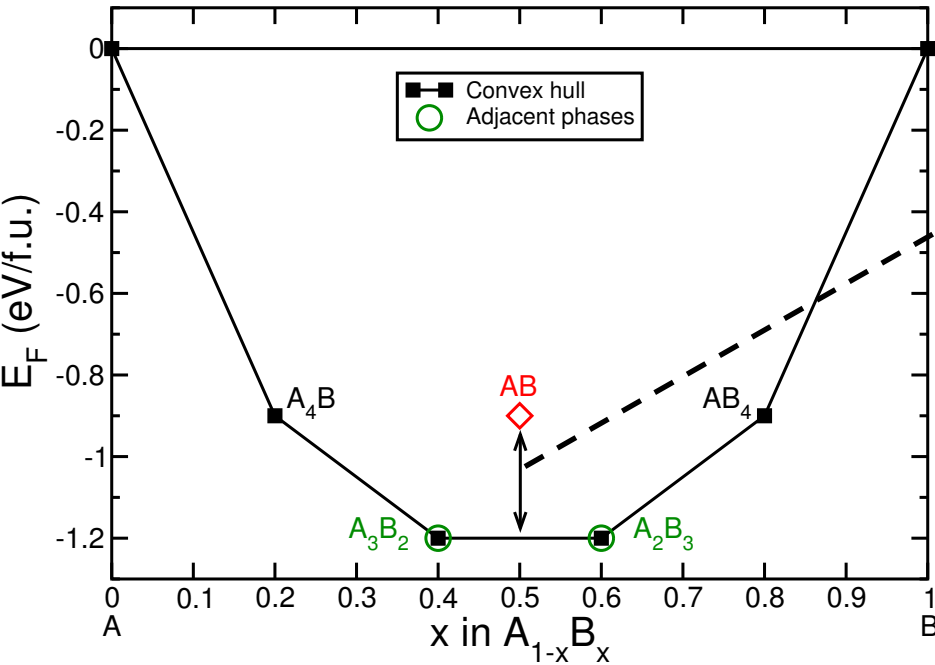
Obtained template structure

Scale structure using atomic radii

DFT calculations

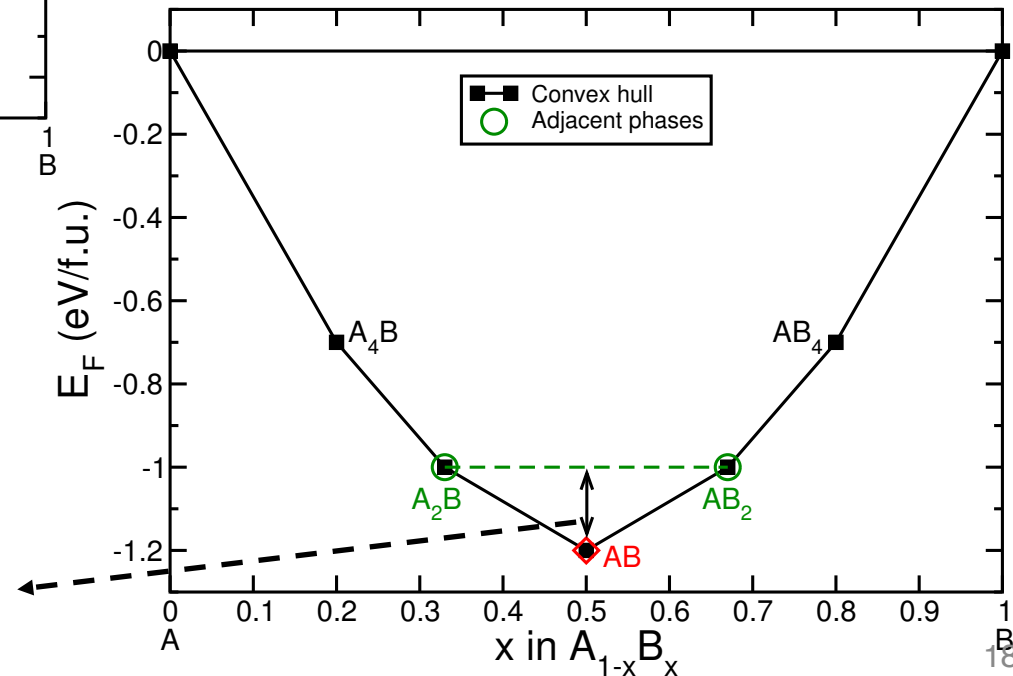
0 K thermodynamics: convex hull

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)

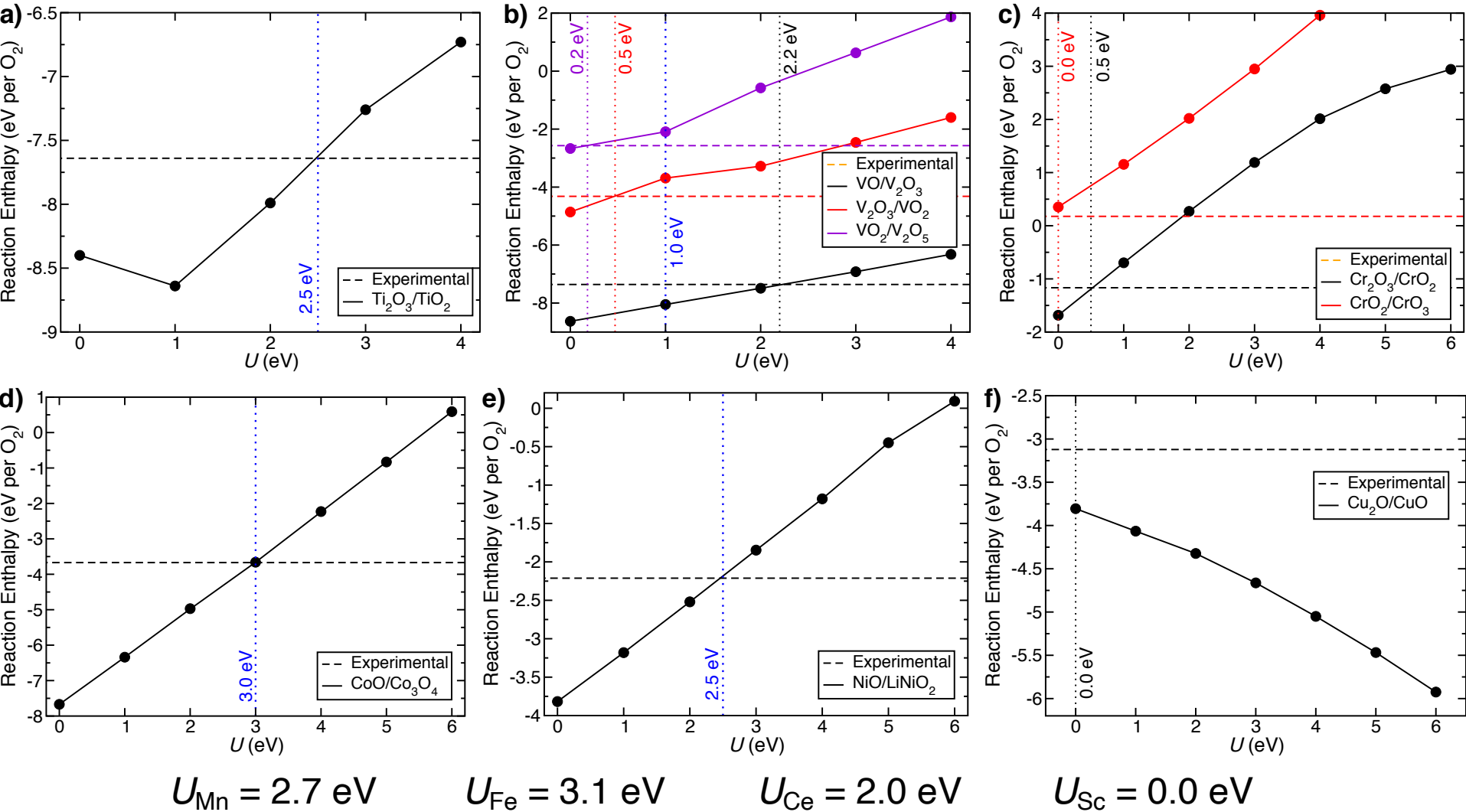
- Largest energy release via decomposition of AB



Negative E^{hull} : stable

- Lowest energy release via formation of AB

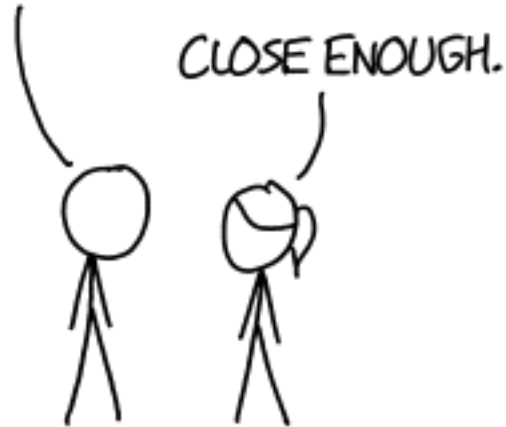
XC functional: a U correction to SCAN



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

$$\Delta H_{reduction} \approx E_F[VaO]$$

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

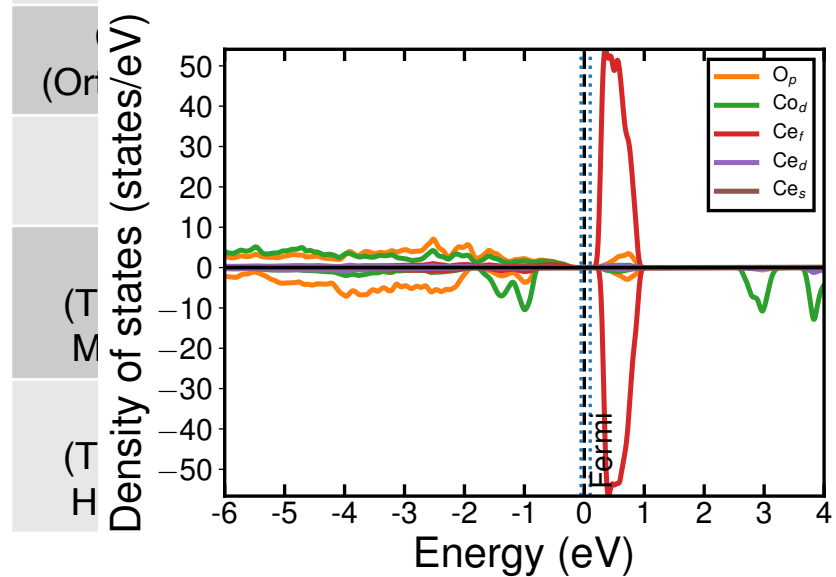
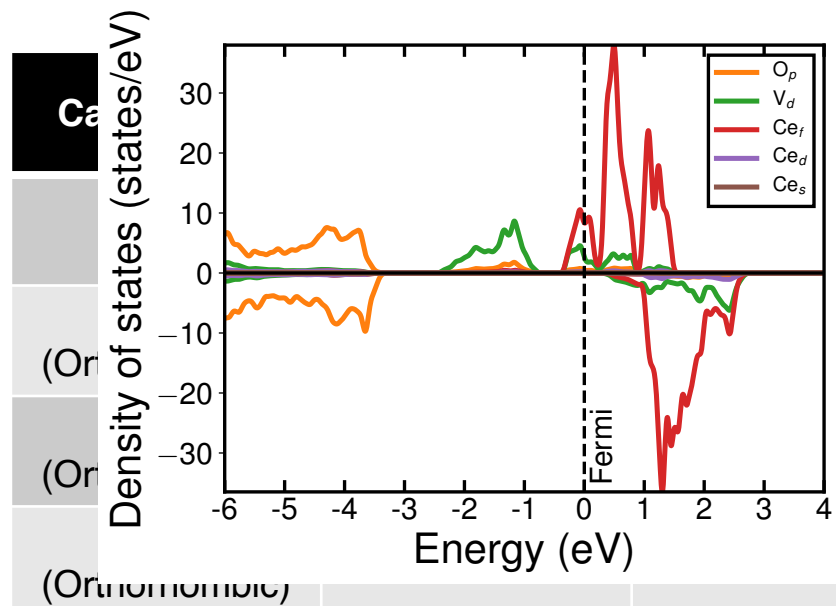
- Vacancy formation
- Stability

Structures and oxidation states: 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

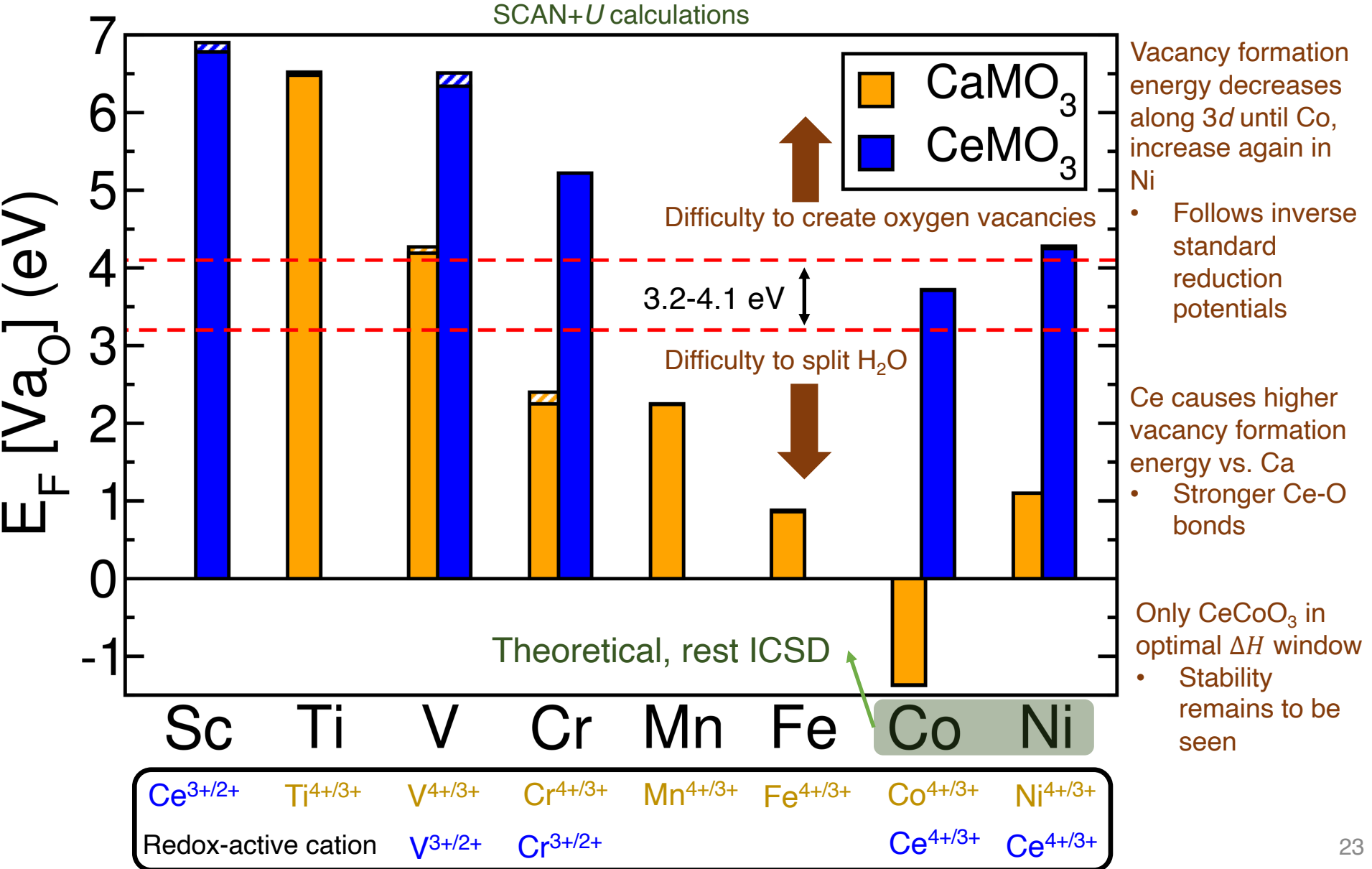
Structures and oxidation states: CaMO_3 and CeMO_3



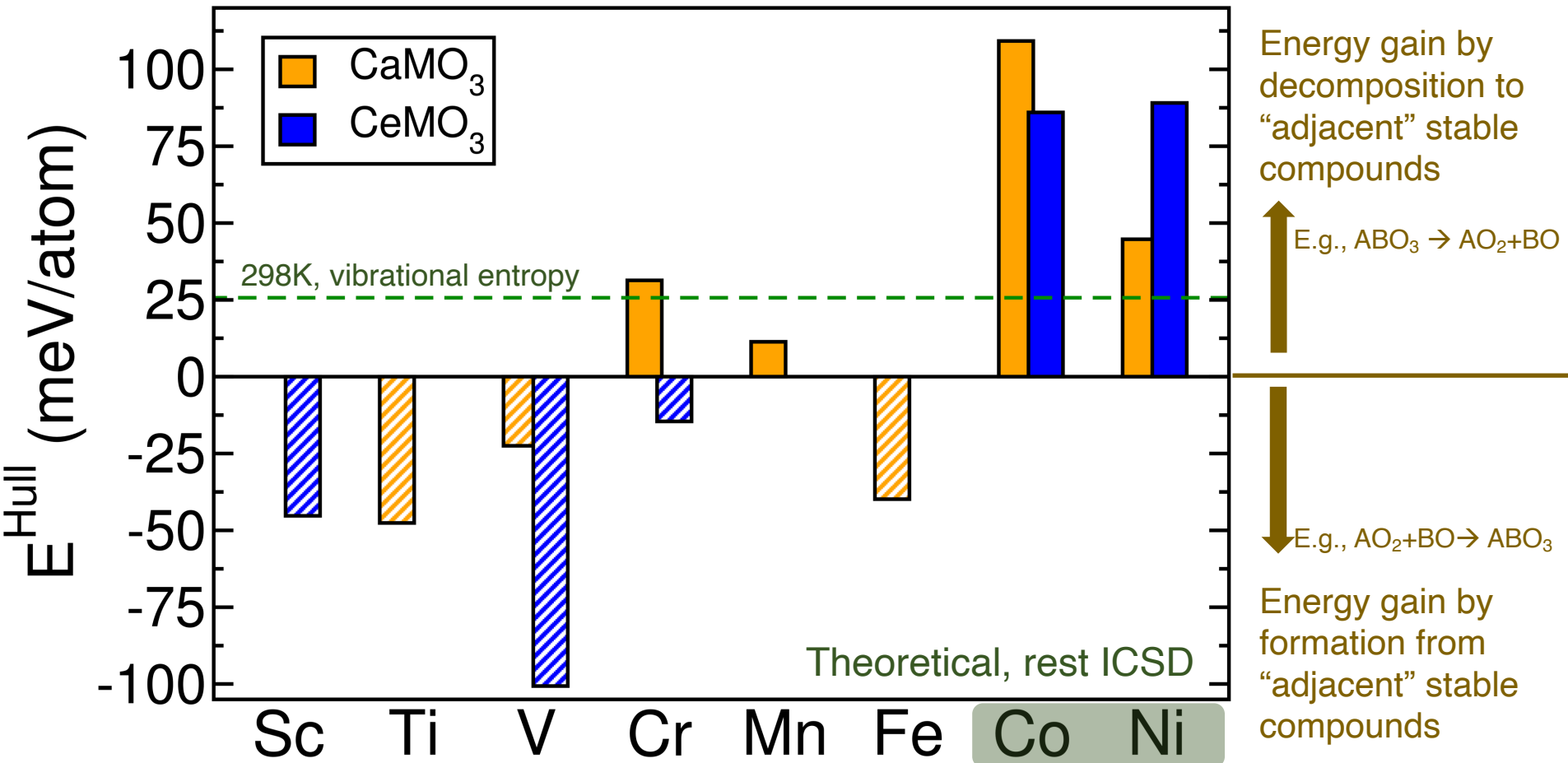
	Ce-ternaries	Ce	M
	CeScO ₃ (Orthorhombic)	+3	+3
(Or)	CeTiO ₃		—
(Or)	CeVO ₃ (Monoclinic)	+3	+3
(Orthorhombic)	CeCrO ₃ (Cubic)		
(Or)	CeMnO ₃		—
(T)	CeFeO ₃		
(T)	CeCoO ₃ (Theoretical, Orthorhombic)	+4	+2
(H)	CeNiO ₃ (Theoretical, Monoclinic)		

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



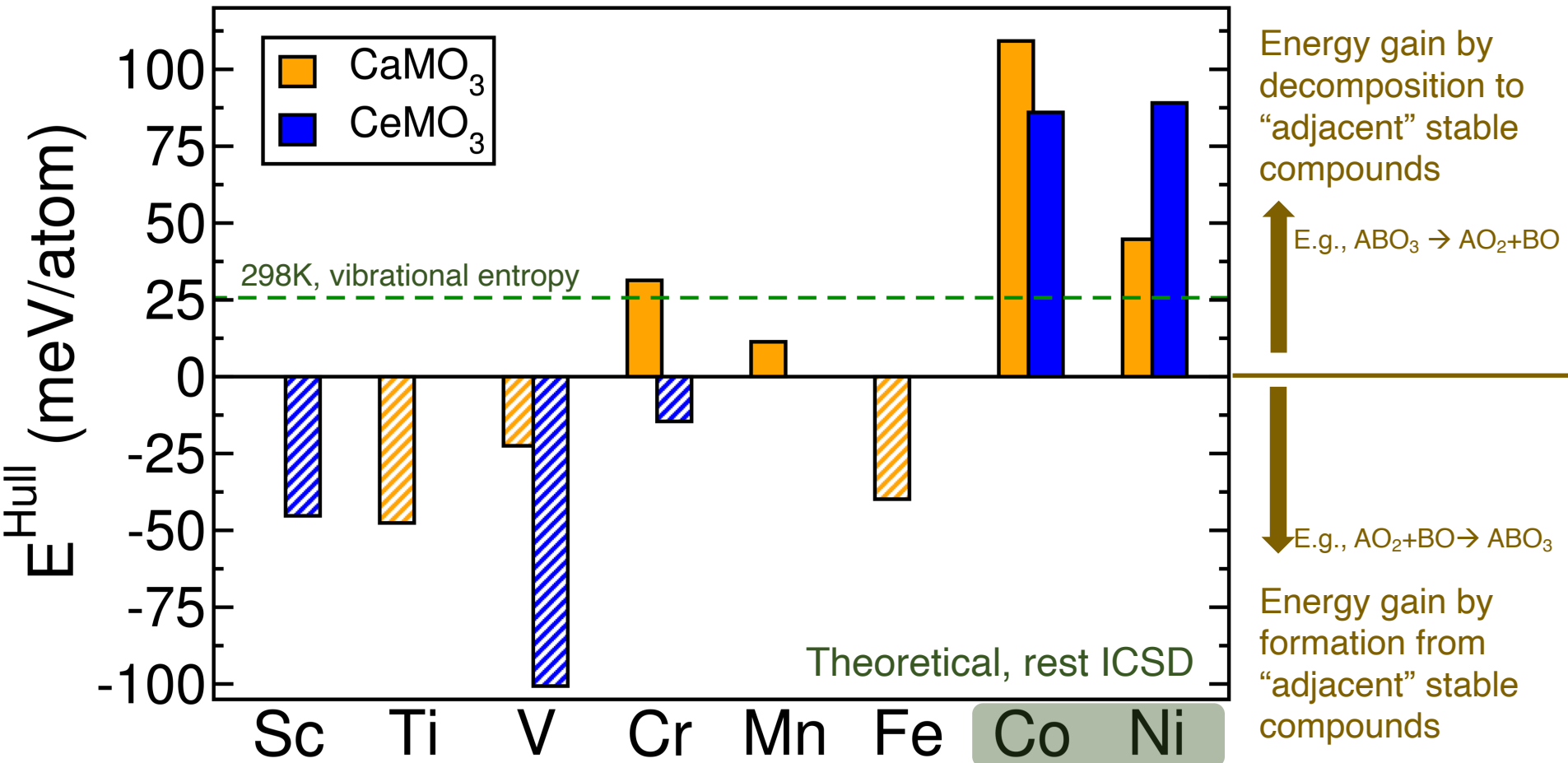
ICSD structures: either negative E^{hull} or small positive E^{hull}

Theoretical structures: large positive E^{hull}

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

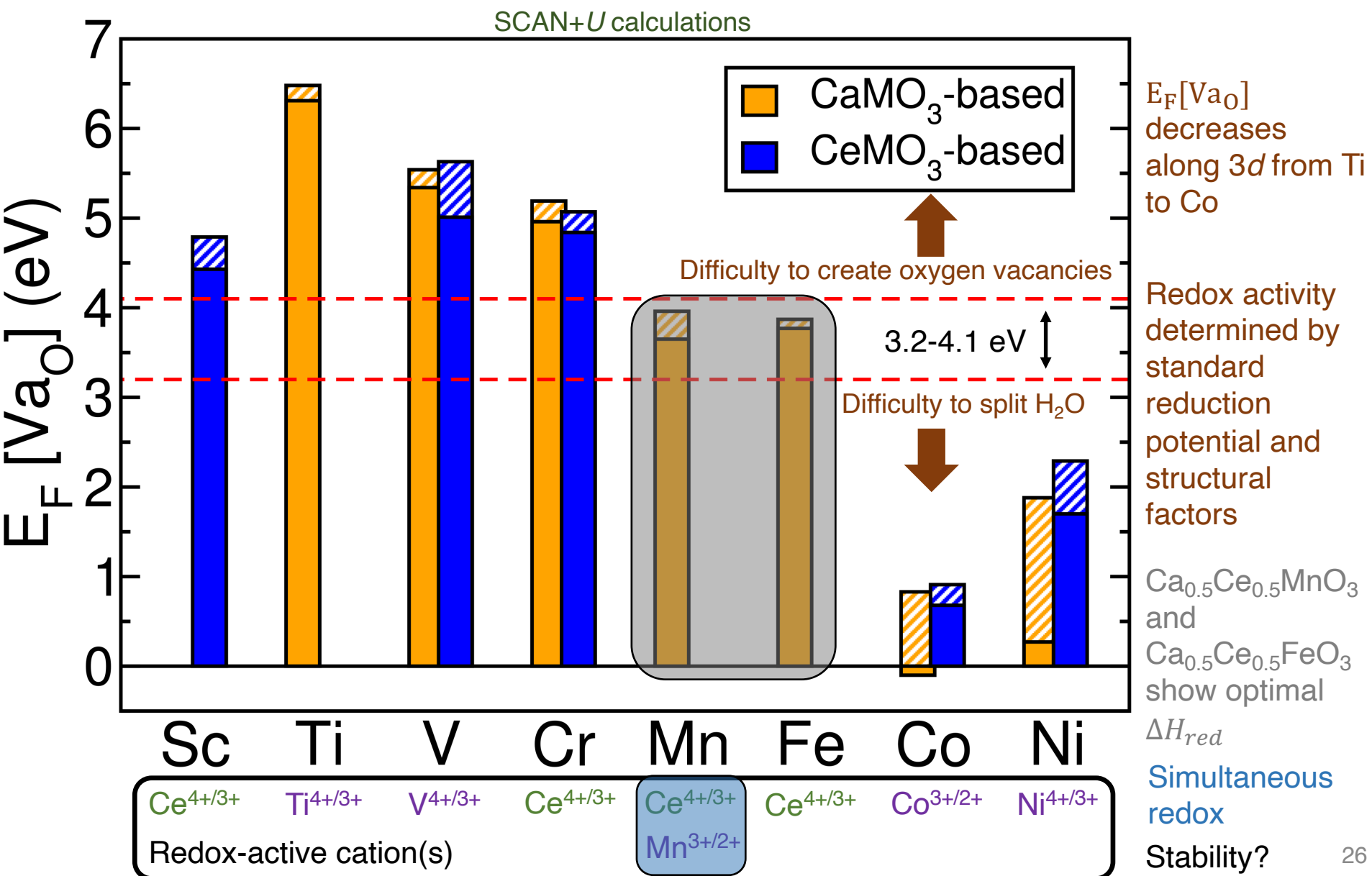
CeCoO_3 is highly unstable!

0 K stability: CaMO_3 and CeMO_3

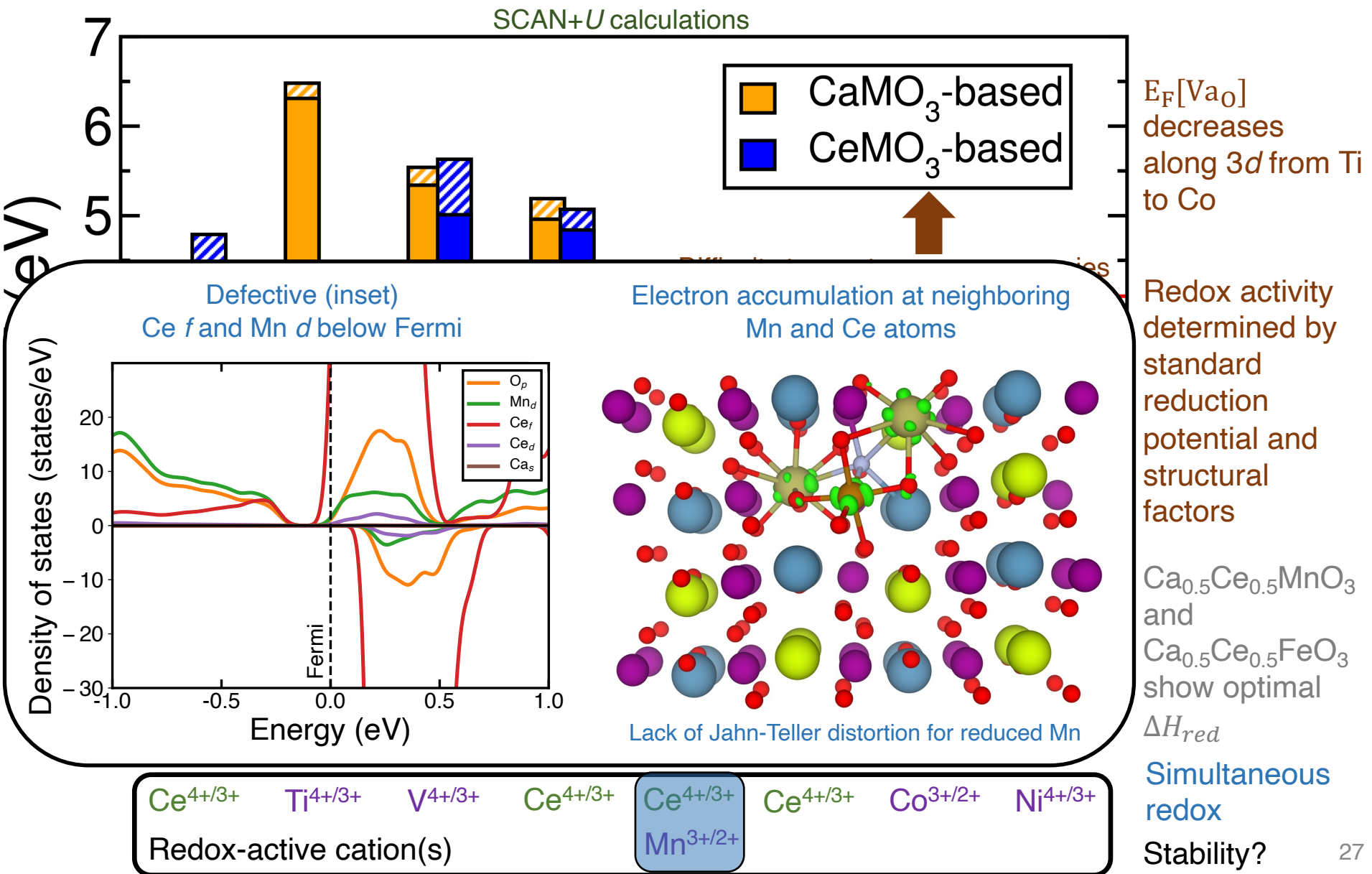


No candidates among ternaries in terms of simultaneous redox and optimal enthalpy of reduction: what about quaternaries?

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

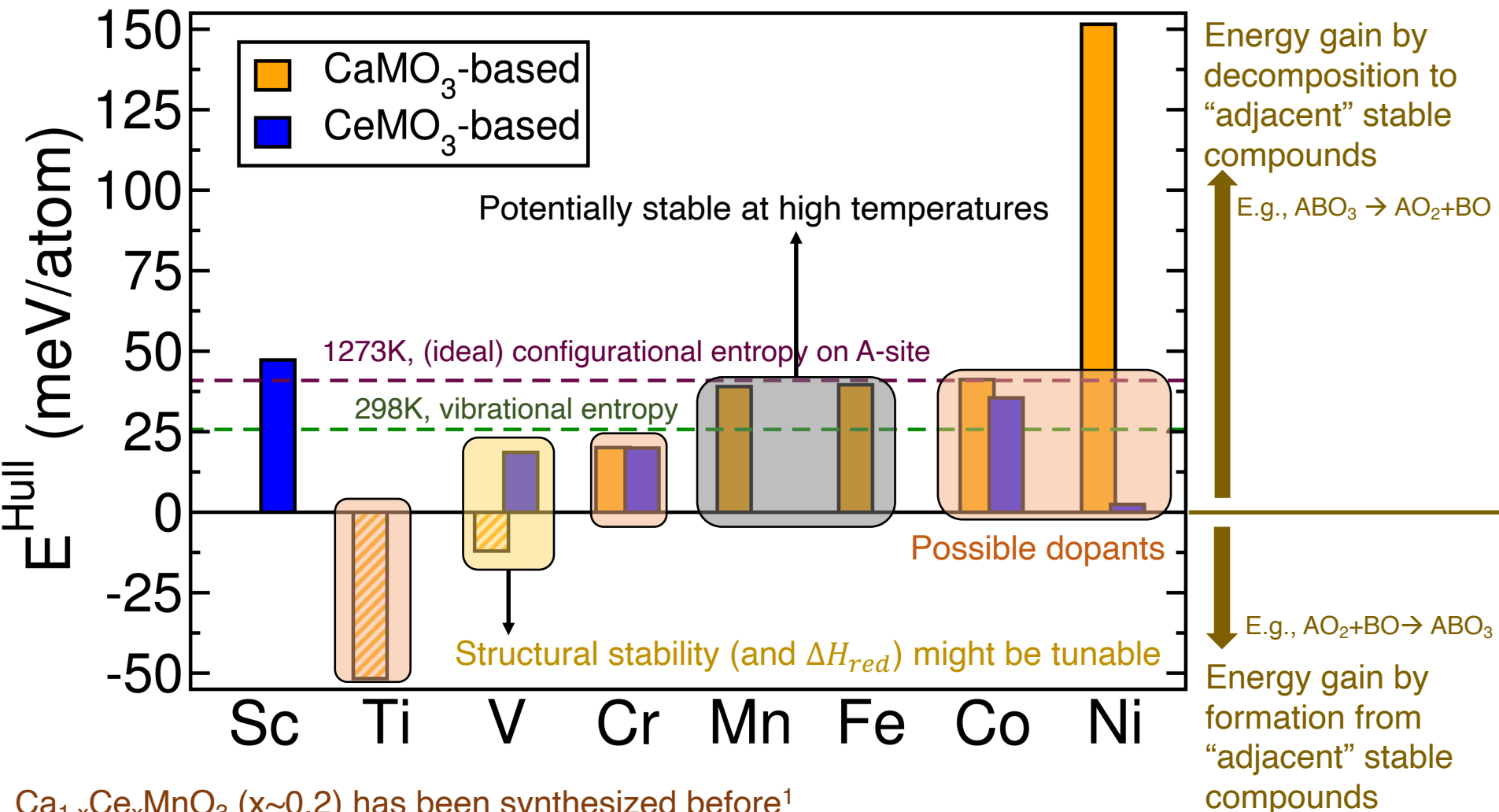


Oxygen vacancy formation energy in $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MO}_3$: $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MnO}_3$ and $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{FeO}_3$ are promising



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

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: $\text{Ca}_{0.5}\text{Ce}_{0.5}\text{MnO}_3$ 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



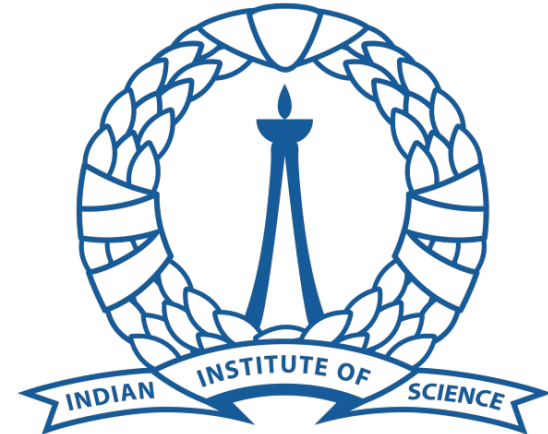
Carter group, Summer 2019



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Organizers of Pratidhwani
IIT-Delhi
The (virtual) audience



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

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