Materials discovery for solar thermochemical water splitting applications using computational techniques

Sai Gautam Gopalakrishnan, Robert B. Wexler, Ellen B. Stechel, Emily A. Carter
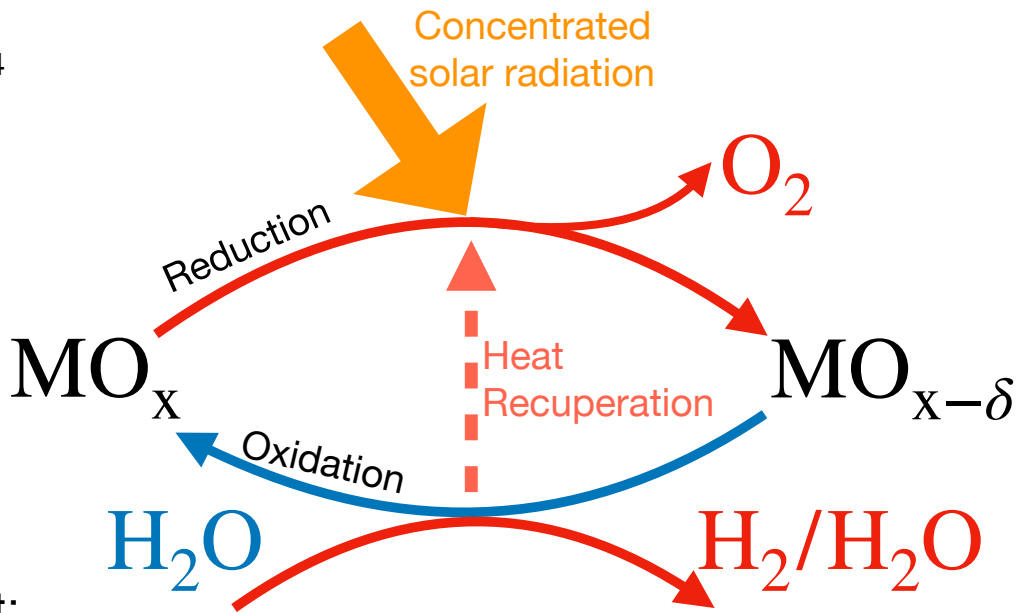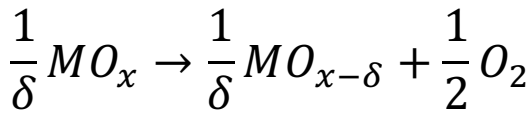
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Solar thermochemical (STC) production of H_2 and/or CO: oxide perovskites are potential candidates

Candidates so far:
- CeO_2
- $Fe(Fe,X)_2O_4$
- $(A,A')BO_3$

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

Concentrated solar radiation

Reduction

O_2

Heat Recuperation

MO_x $MO_{x-\delta}$

Oxidation

H_2O H_2/H_2O
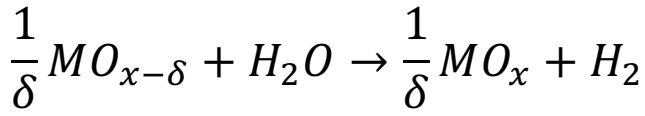
Thermal reduction (TR)
High T (~1673 K)
~vacuum ($p_{O_2} \sim 10$ Pa)

Water splitting (WS)
Low T (~873 K)

High H_2 yield $\left(\frac{p_{H_2O}}{p_{H_2}} = 9 \right)$

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

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

Similar cycle for CO_2 splitting

Needs "good" materials!
- Durability (withstand high TR and low WS temperatures)
- Capacity (tolerate high degrees of oxygen off-stoichiometry)
- Stability (no undesired phase transformations)
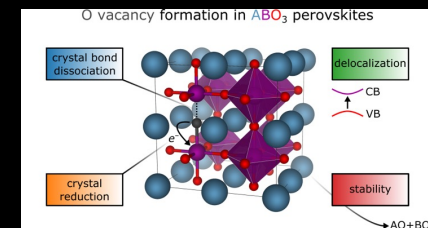
Oxide perovskites: significant current research

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

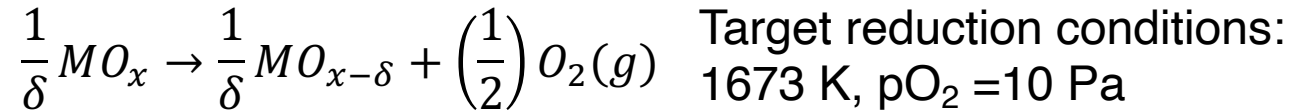# How to use theory to…
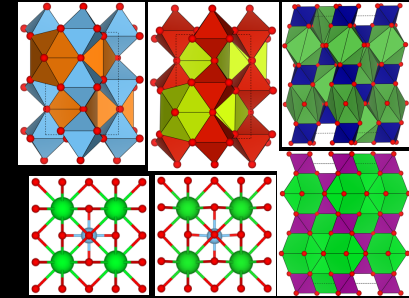
- Screen for H_2O/CO_2 thermochemical splitters with higher entropy of reduction

- Search through a wider chemical space using machine learning (ML) tools?

O vacancy formation in ABO_3 perovskites

Oxygen vacancy formation energy ~enthalpy of reduction

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

Target reduction conditions:
1673 K, pO_2 =10 Pa

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

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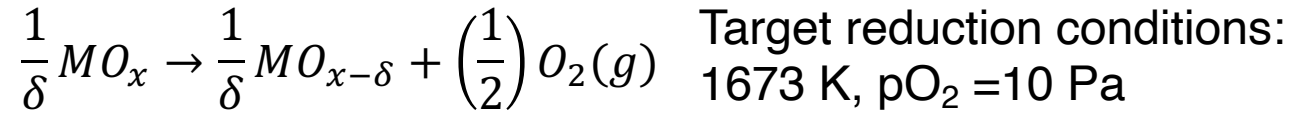
Oxygen vacancy formation energy

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 $\Delta H_{formation}^{Va_O} \sim$ 3.25-3.5 eV (CeO$_2$ is ~4 eV)
For any theoretical screening, 3-3.75 eV range is ok

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
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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,[1,*] Antoine A. Emery,[2] James E. Gubernatis,[1] Turab Lookman,[1,†] Chris Wolverton,[2] and Alex Zunger[3]

1.Stechel, Ermanoski, and Miller, in preparation

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Enthalpy of reduction for the induced off-stoichiometry, δ

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

Several studies have theoretically screened, high-throughput calculations and/or machine learning, for novel ABO$_3$ perovskites, based on the optimal $\Delta H_{formation}^{Va_O}$
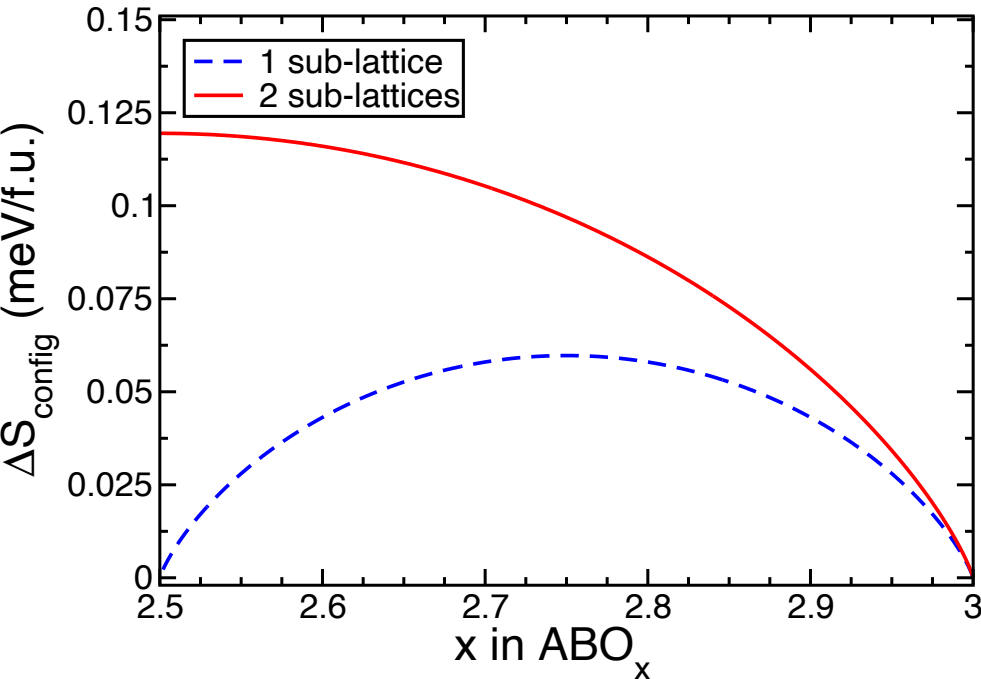- Candidates either exhibit rare elements (e.g., Eu, Ho) or don't exceed CeO$_2$'s performance in experiments (stability or kinetic limitations/theory error)
- Need more viable candidates: can we include other metrics?

Thermodynamic models[1] point to optimal $\Delta H_{reduction}$ or $\Delta H_{formation}^{Va_O}$ ~ 3.25-3.5 eV (CeO$_2$ is ~4 eV)
For any theoretical screening, 3-3.75 eV range is ok

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5

Higher entropy of reduction = higher yield

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

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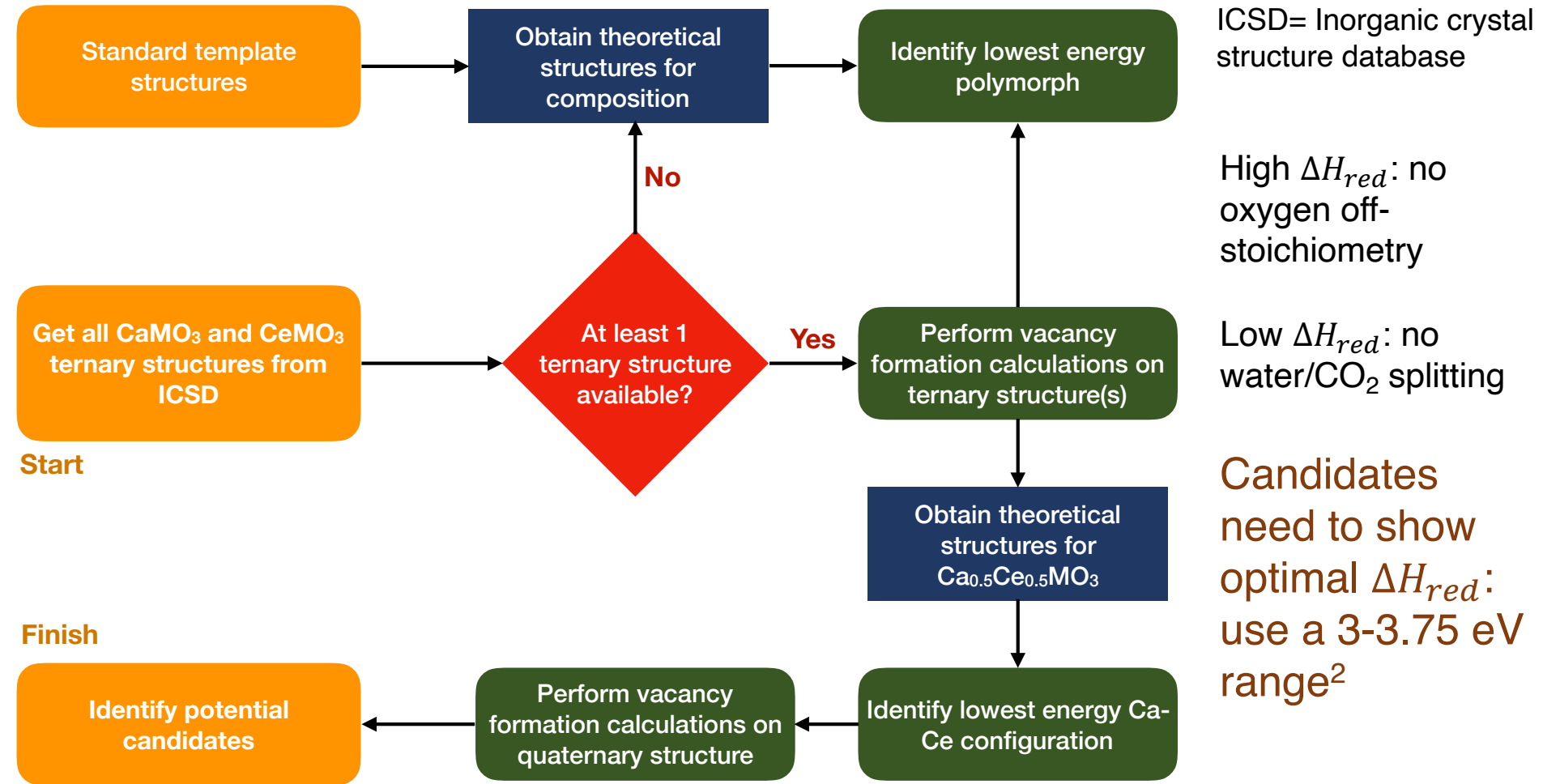
solid   gas

Large contribution to the solid portion of ΔS_{red} comes from configurational entropy

Assuming ideal solution of mixing, large increase in ΔS_{red} with A+B cation reduction in ABO_3

For given (optimal) ΔH_{red}, higher ΔS_{red} = higher capacity

Higher entropy of reduction = higher yield

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

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

solid   gas

Assuming a simple regular solution model, simultaneous A+B reduction can yield ~0.014 (mol of O)/(mol atom ABO_3), higher than B-reduction (~0.009) or CeO_2 (~0.013)

- Oxygen evolution capacity
  - A+B reduction 60% > A or B reduction
  - A+B reduction 9% > CeO_2

- Perovskites with simultaneous cation redox can yield better capacities

Legend:
- 1 sub-lattice, $ABO_{3-\delta}$
- 2 sub-lattices, $ABO_{3-\delta}$
- $CeO_{2-\delta}$

O_2(gas, 1673K, 10Pa)

μ_O (eV)

δ/n in $ABO_{3-\delta}$ or $CeO_{2-\delta}$

Potential simultaneously redox active ABO_3 perovskites?
Required sizes of A and B, charge neutrality, redox-activity constraints = $Ca_{0.5}Ce_{0.5}MO_3$
- M = Sc, Ti, V, Cr, Mn, Fe, Co, and Ni

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

Standard template structures

Obtain theoretical structures for composition

Identify lowest energy polymorph

No

Get all $CaMO_3$ and $CeMO_3$ ternary structures from ICSD

At least 1 ternary structure available?

Yes

Perform vacancy formation calculations on ternary structure(s)

Start

Obtain theoretical structures for $Ca_{0.5}Ce_{0.5}MO_3$

Finish

Identify potential candidates

Perform vacancy formation calculations on quaternary structure

Identify lowest energy Ca-Ce configuration

ICSD= Inorganic crystal structure database

High ΔH_{red}: no oxygen off-stoichiometry

Low ΔH_{red}: no water/CO_2 splitting

Candidates need to show optimal ΔH_{red}: use a 3-3.75 eV range[2]

Density functional theory engine: strongly constrained and appropriately normed (SCAN) functional, corrected with optimal Hubbard U correction[1]

- $\Delta H_{red} \approx E_F[Va_O]$ (oxygen vacancy formation energy)

1. G.S. Gautam and E.A. Carter, **Phys. Rev. Mater. 2018**, *2*, 095401; O.Y. Long *et al.*, **Phys. Rev. Mater. 2020,** *4*, 054101   2. E.B. Stechel *et al.*, **in preparation**

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
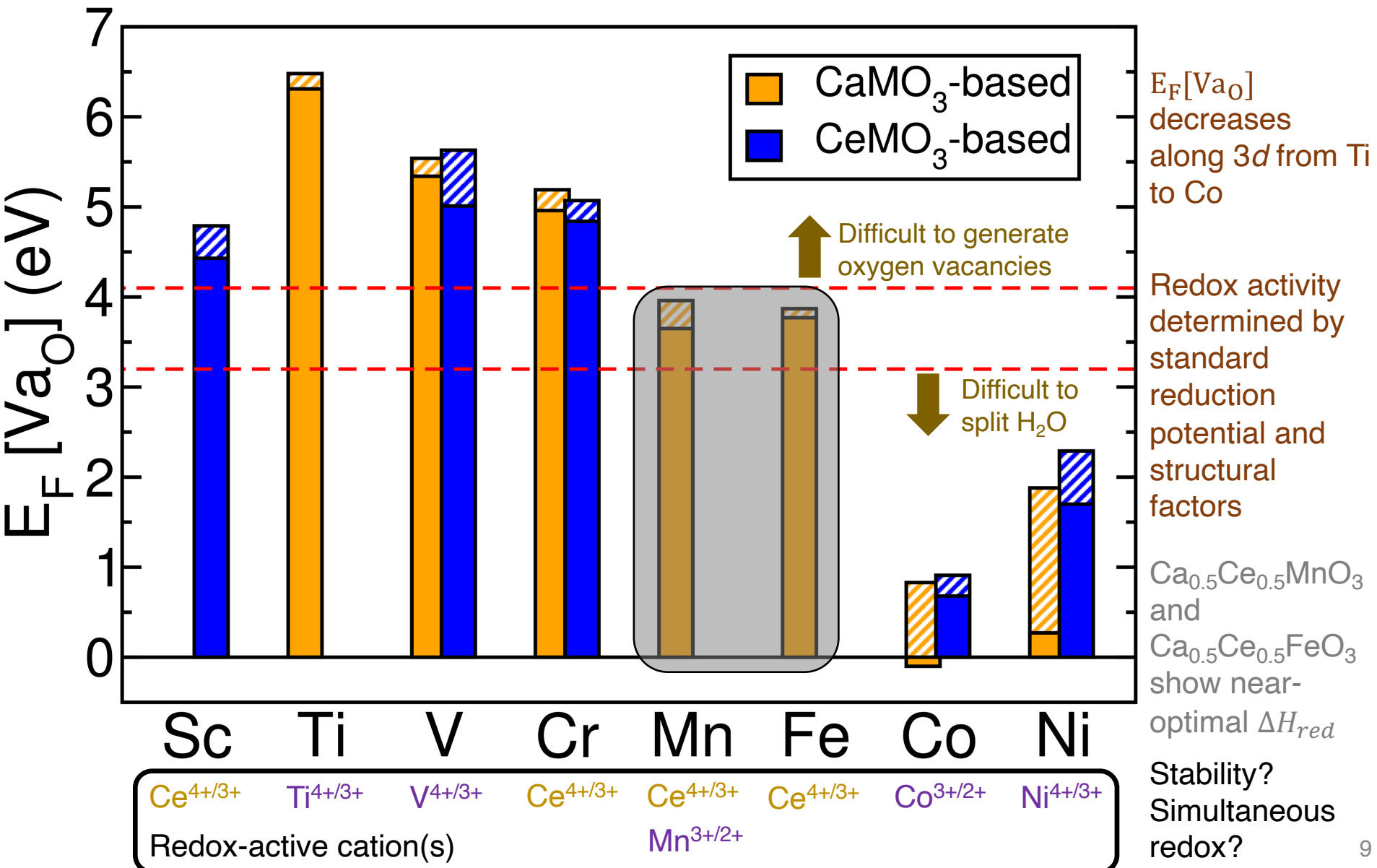
0 K stability of $Ca_{0.5}Ce_{0.5}MO_3$
Impact of configurational entropy (of mixing)
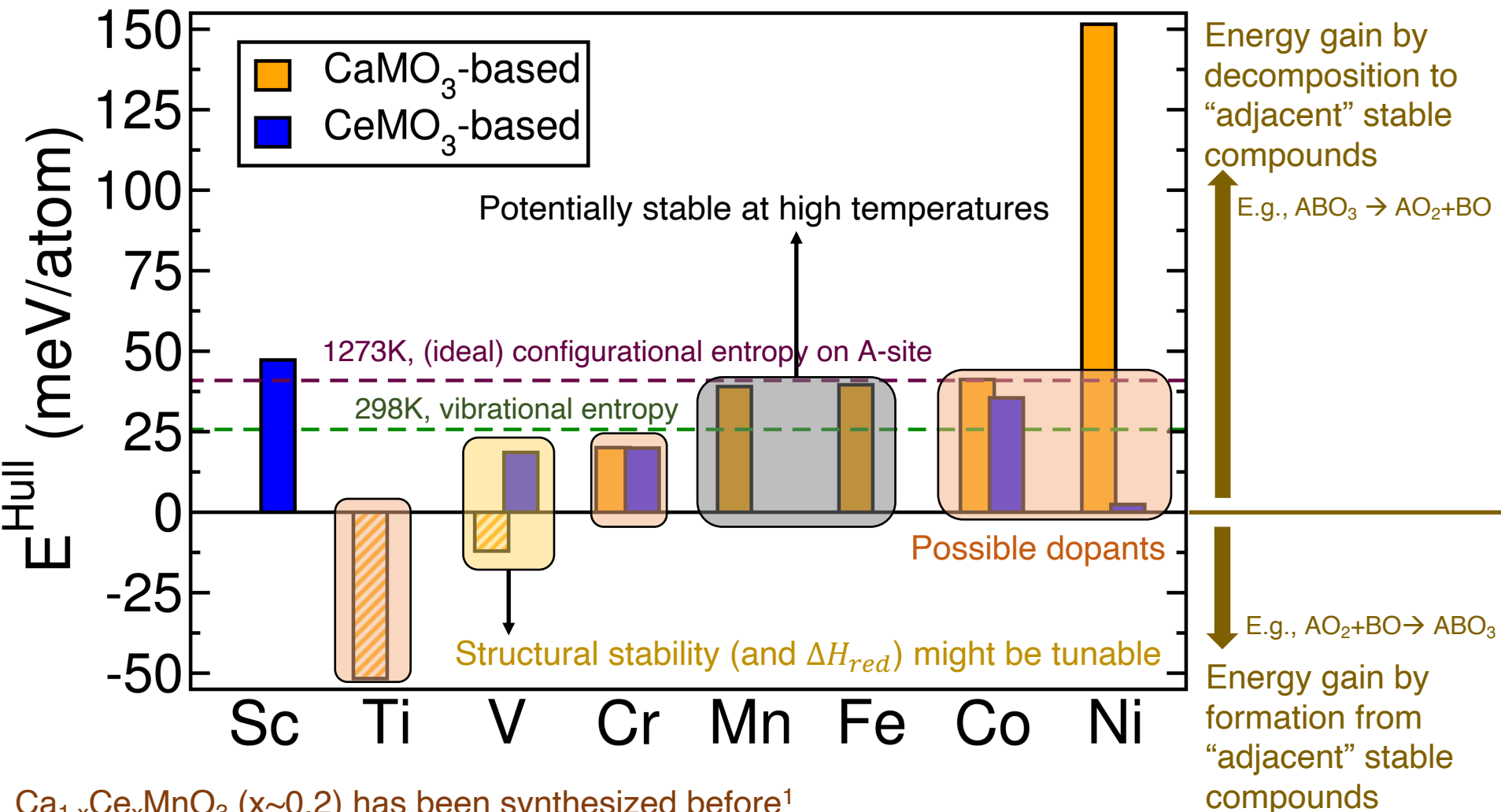
$Ca_{1-x}Ce_xMnO_3$ (x~0.2) has been synthesized before[1]

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

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

Simultaneous Ce+Mn reduction in $Ca_{0.5}Ce_{0.5}MnO_3$

$E_F[Va_O]$ = 3.65-3.96 eV (< CeO_2, 4-4.3 eV[1])

Bulk

Defective (inset)
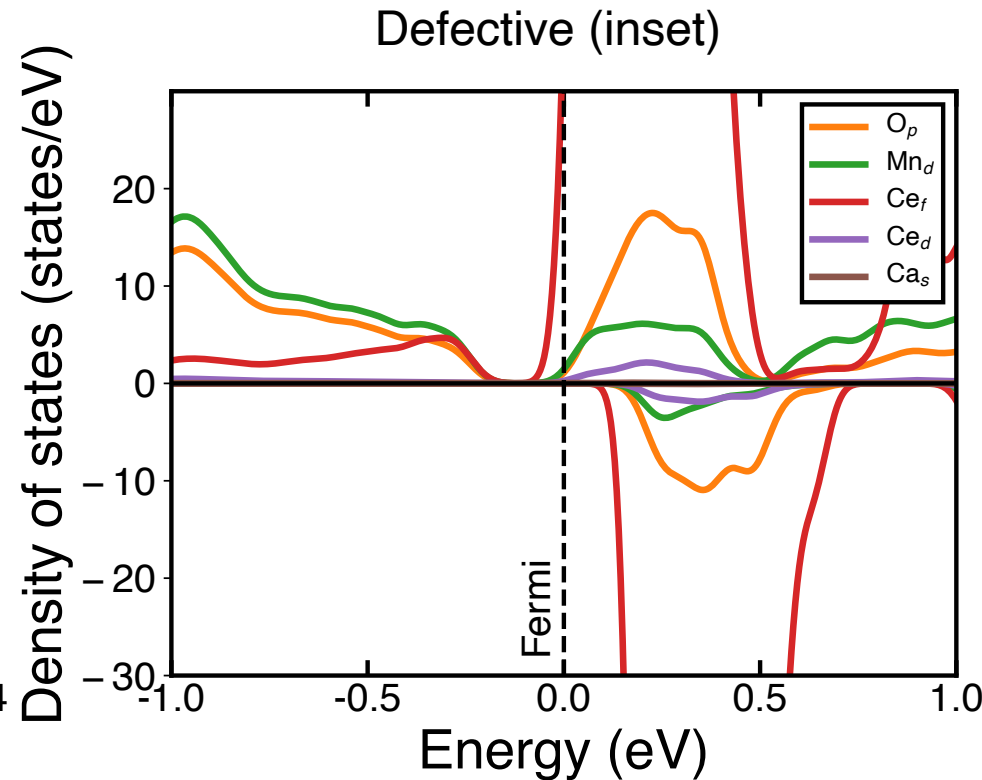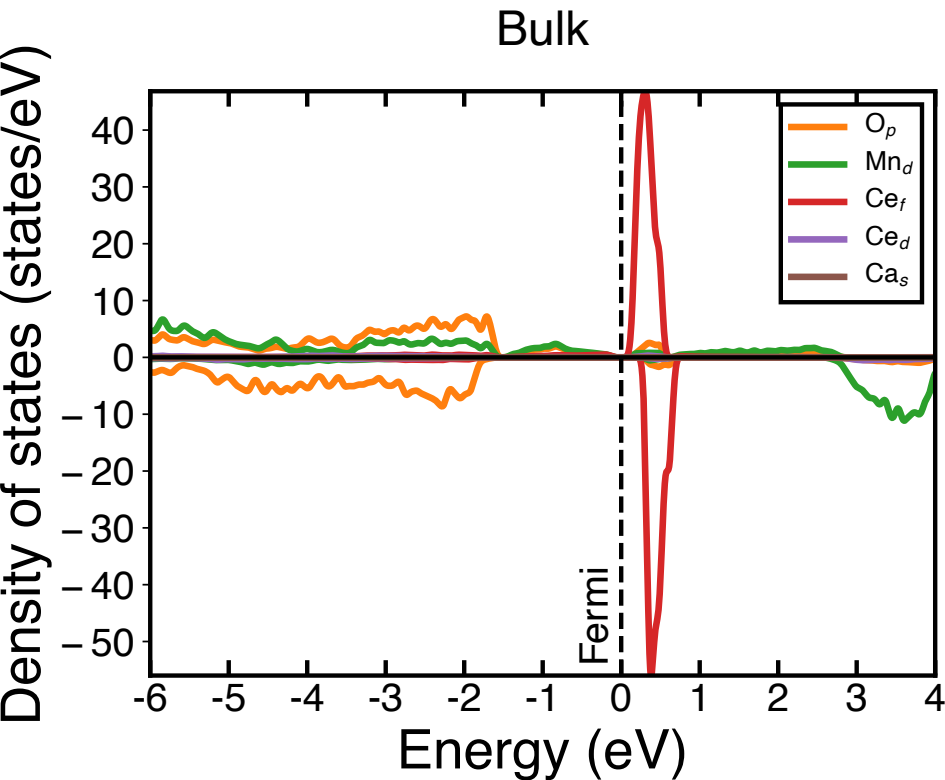
On-site magnetic moments: Ce^{4+}, Mn^{3+} in bulk
Mn^{3+} displays Jahn-Teller distortion
Ce *f* beyond Fermi; small amount of Mn *d* states

On-site magnetic moments: $Ce^{4+/3+}$, $Mn^{3+/2+}$
States: Ce *f* reduction clear, sliver of Mn *d*

1. Zinkevich *et al.*, **Solid State Ionics 2006**, *177*, 989

Simultaneous Ce+Mn reduction in $Ca_{0.5}Ce_{0.5}MnO_3$

$E_F[Va_O] = 3.65\text{-}3.96$ eV ($< CeO_2$, 4-4.3 eV[1])

Oxygen removed

Reduced Ce

Reduced Mn

Electron accumulation

Ca^{2+}

Ce^{4+}

Mn^{3+}

O^{2-}

Reduced Mn doesn't exhibit Jahn-Teller distortion
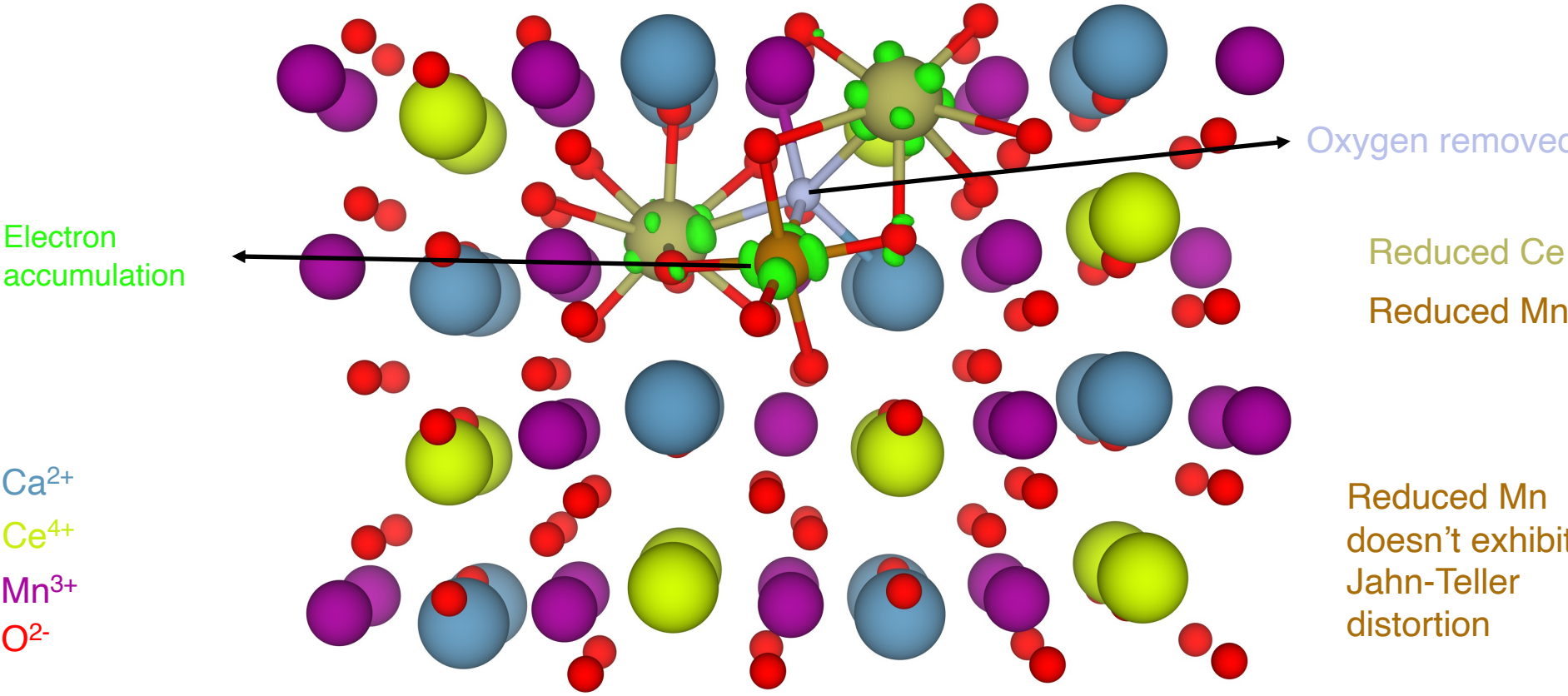
Electron density difference plot: $Ca_{0.5}Ce_{0.5}MnO_3$ with and without oxygen vacancy
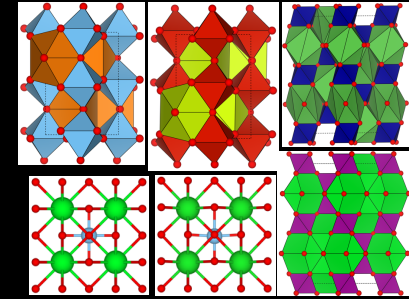
1. Zinkevich *et al.*, **Solid State Ionics 2006**, *177*, 989

Simultaneous reduction = candidate!

How to use theory to…

- Screen for H_2O/CO_2 thermochemical splitters with higher entropy of reduction ✓

- Search through a wider chemical space using machine learning (ML) tools?

O vacancy formation in ABO_3 perovskites
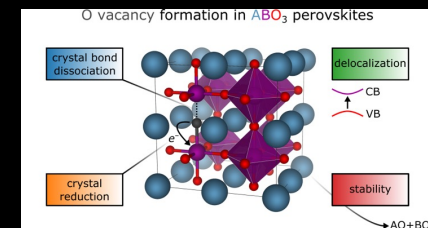
Screening a wider perovskite space for candidates

- Focused computational study on a select class of oxide perovskites: discovery of $(Ca,Ce)MnO_3$ and $(Ca,Ce)FeO_3$

- Possible to identify other candidates?
  - Key property: $E_F[Va_O]$
  - Not possible to look for high entropic candidates in a high-throughput fashion
  - Thermodynamic stability (E^{hull}) also important

- Workflow: construct a theoretical (ML) model that can predict $E_F[Va_O]$
  - Training the model: generate diverse dataset

233 composition-structure combinations, 341 unique $E_F[Va_O]$

Descriptor for ML model: crystal bond dissociation energy (E_b)

Analogous to molecular bond dissociation energy: energy required to break a metal-oxygen bond in a crystal

$$E_b[O^{2-} - M^{n+}] = \frac{E_c[MO_{\frac{n}{2}}]}{N_b[O^{2-} - M^{n+}]}$$

Cohesive energy of $MO_{n/2}$ oxide

Number of M-O bonds per formula unit in $MO_{n/2}$
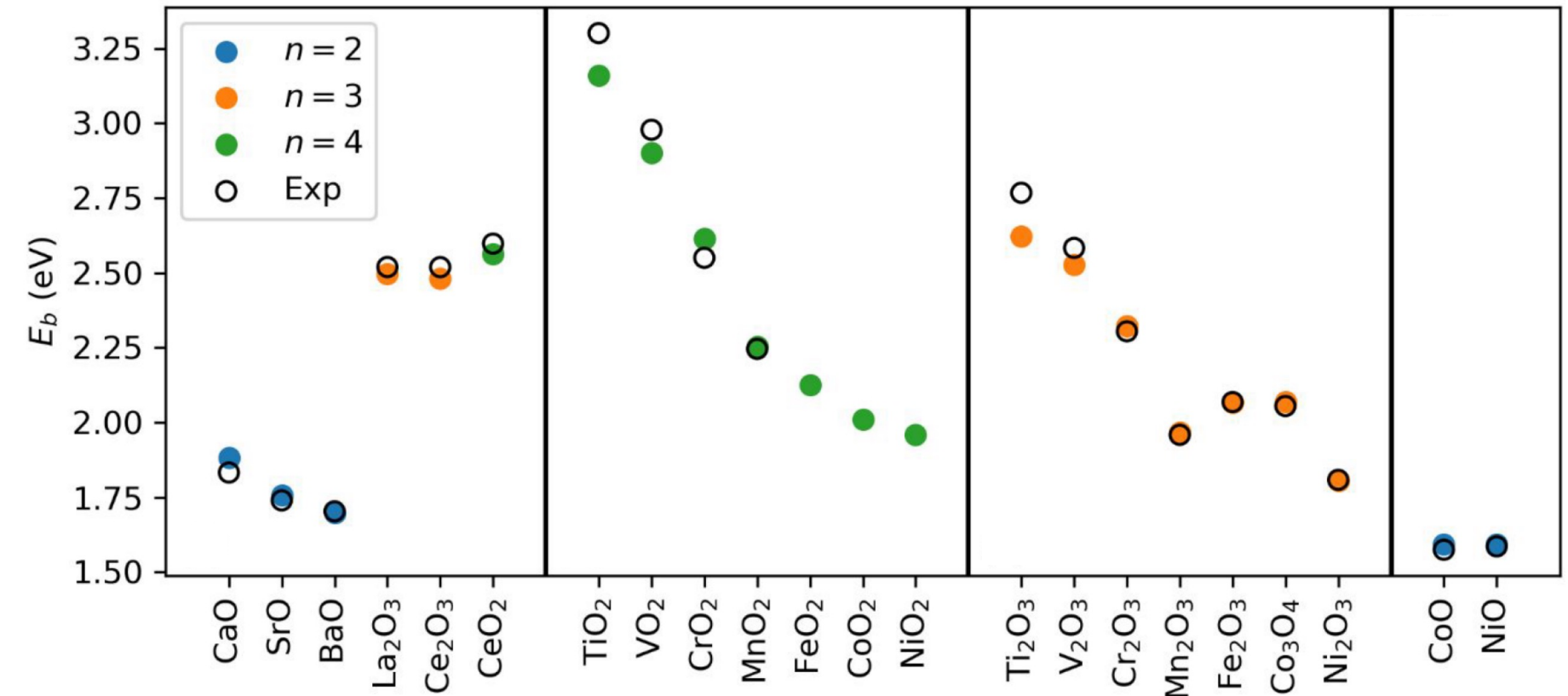
Theoretical E_b in good agreement with experiments

Descriptor for ML model: crystal reduction potential

Oxygen vacancy introduction: reduces (transition-metal) cation, need to account for "ease" of reduction

Standard (aqueous) reduction potentials:

- Are not strictly applicable to solids (no crystal electrostatics included)
- Missing data for few $3d$ transition metal redox couples
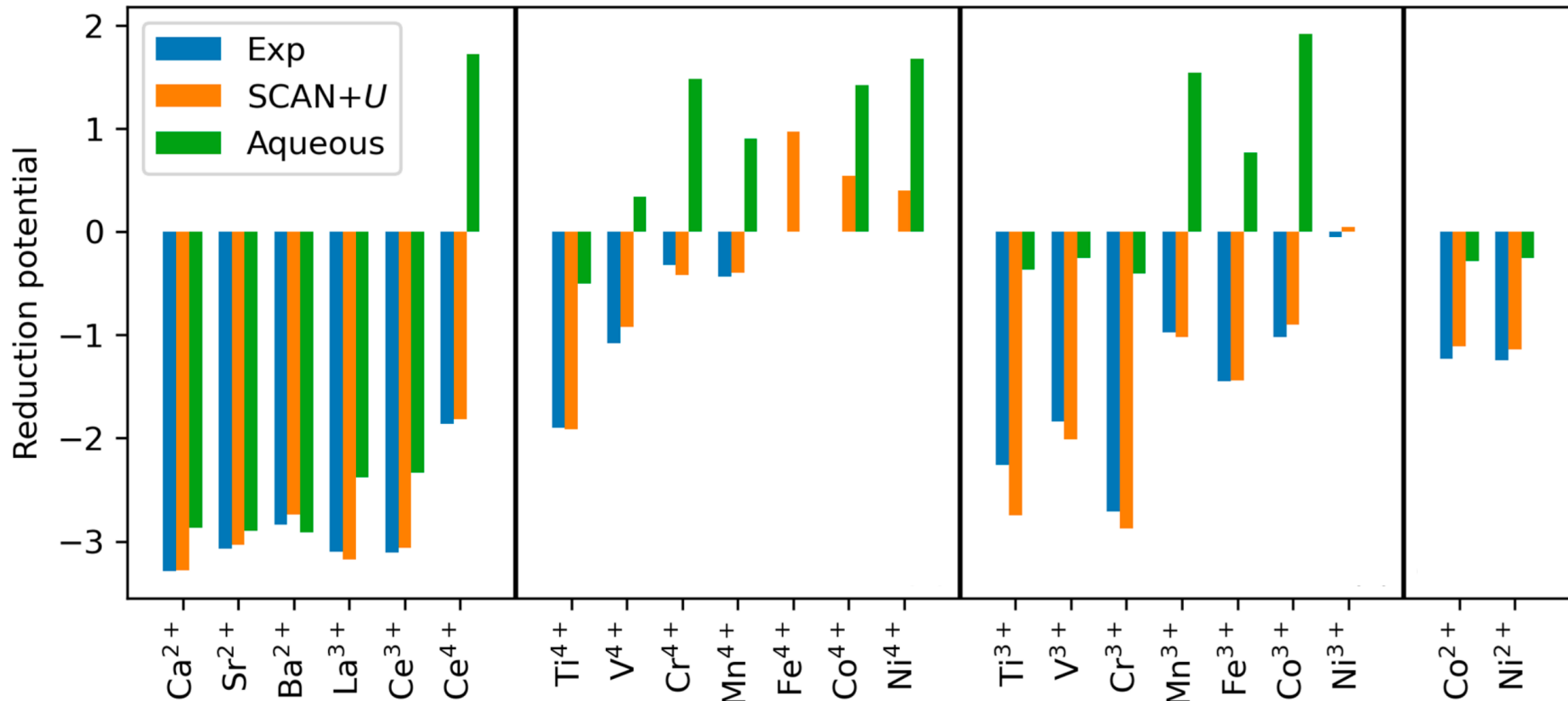
Better systematic trends with crystal reduction than aqueous potential

Descriptor for ML model: thermodynamic stability and band gap

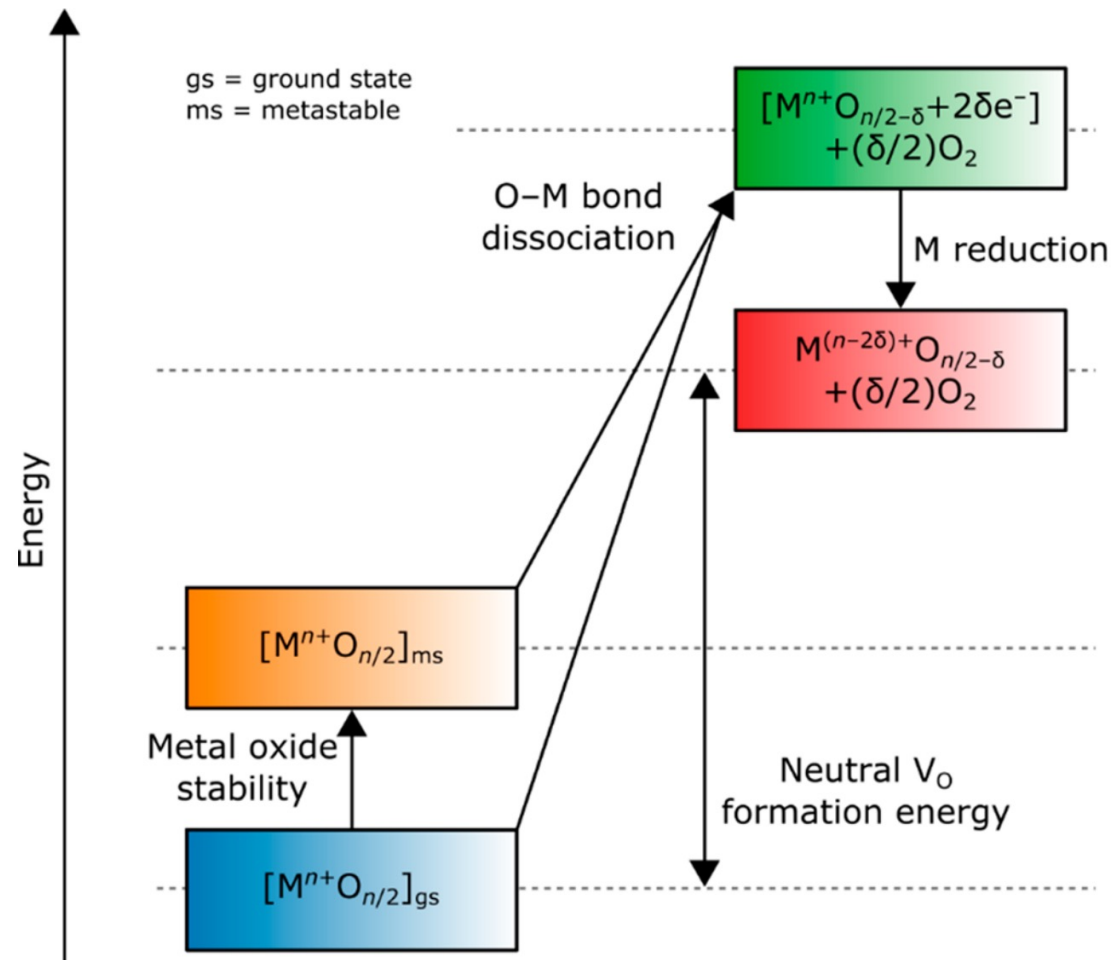Overall thermodynamic stability of perovskite structure can influence $E_F[Va_O]$
- High stability → strong bonding → high $E_F[Va_O]$
- High instability → weak bonding → low $E_F[Va_O]$
- Quantify stability using E^{Hull} at 0 K
- E^{Hull}: includes all possible competing phases

Ease of addition of electrons from oxygen vacancy formation, via delocalization, can alter $E_F[Va_O]$
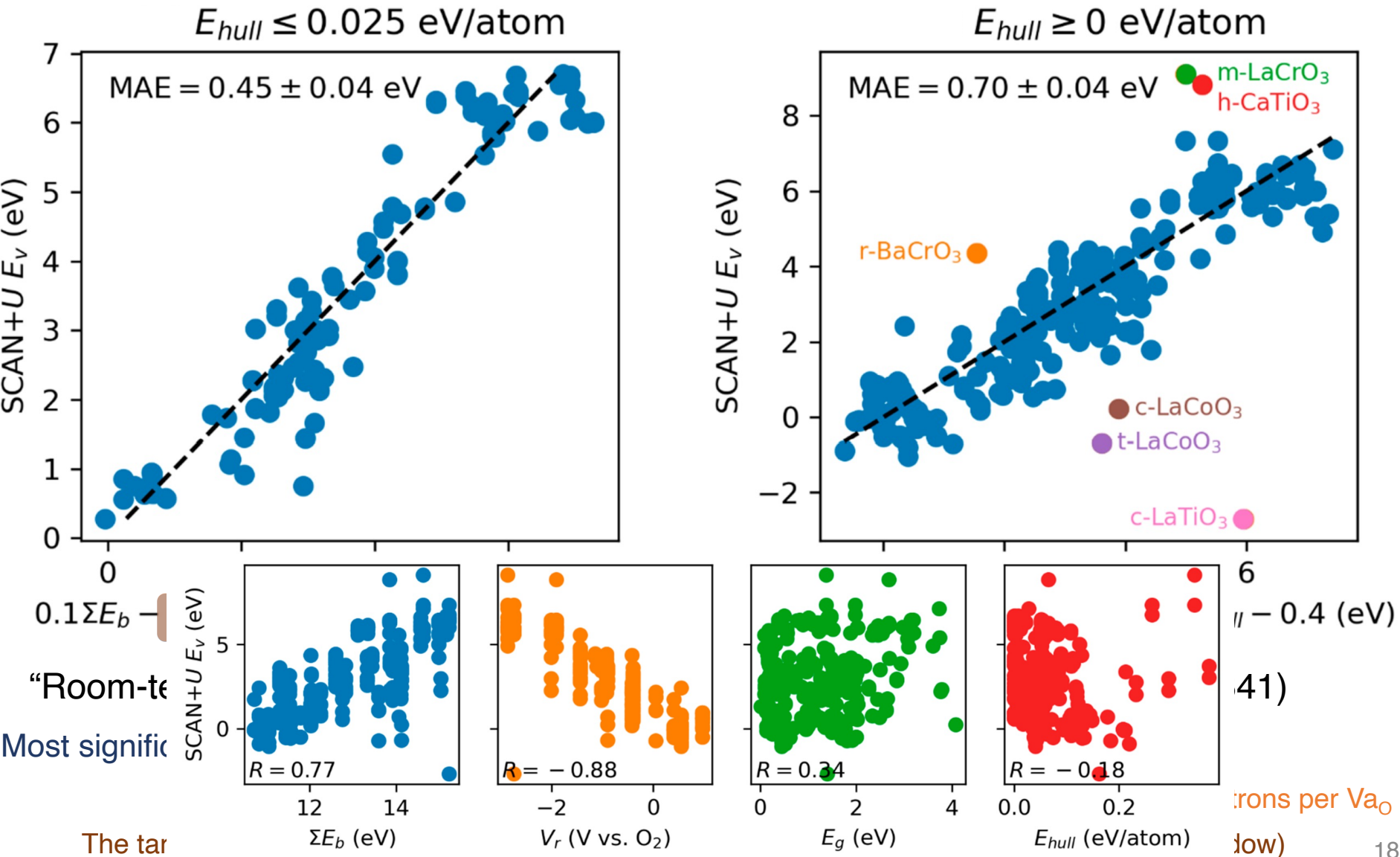- Large band gap→ requires E_g (band gap) energy → difficult to delocalize
- Small band gap → small E_g → facile delocalization
- Quantify with E_g at Γ-point
  - Provides upper bound of E_g
  - Computationally not expensive
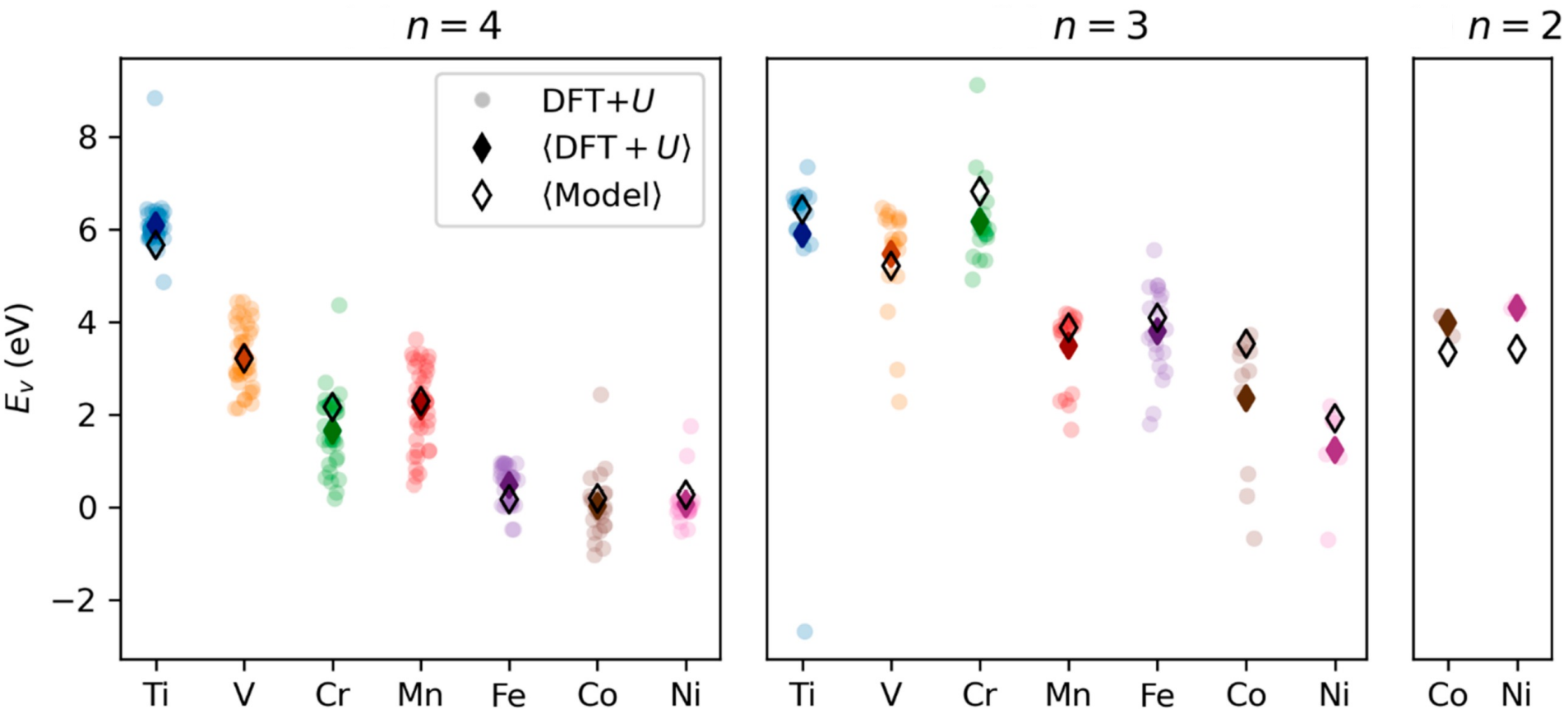
Descriptors: E_b, V_r, E^{Hull}, and $E_g(\Gamma)$

gs = ground state
ms = metastable

$[M^{n+}O_{n/2-\delta}+2\delta e^-] +(\delta/2)O_2$

O–M bond dissociation

M reduction

$M^{(n-2\delta)+}O_{n/2-\delta} +(\delta/2)O_2$

$[M^{n+}O_{n/2}]_{ms}$

Metal oxide stability

Neutral V_O formation energy

$[M^{n+}O_{n/2}]_{gs}$

Energy

Va_O formation can be thought of as a Born-Haber cycle

Model performance: robust especially for perovskites with low (meta)stability

$E_{hull} \leq 0.025$ eV/atom

MAE = 0.45 ± 0.04 eV

SCAN+U E_v (eV)

$0.1\Sigma E_b$

$E_{hull} \geq 0$ eV/atom

MAE = 0.70 ± 0.04 eV

m-LaCrO$_3$
h-CaTiO$_3$

r-BaCrO$_3$

c-LaCoO$_3$
t-LaCoO$_3$

c-LaTiO$_3$

SCAN+U E_v (eV)

$R = 0.77$ ΣE_b (eV)

$R = -0.88$ V_r (V vs. O$_2$)

$R = 0.34$ E_g (eV)

$R = -0.18$ E_{hull} (eV/atom)

$- 0.4$ (eV)

"Room-te   41)

Most signific

trons per Va$_O$

The tar   low)

18

New candidates

Trends for low/intermediate/high E_v: identify candidates

Possible B-site cations for solar thermochemical (3-3.75 eV): V^{4+}, Mn^{3+}, Fe^{3+}, $Co^{3+/2+}$, and Ni^{2+}

Candidates from outside the training set:
- $R\bar{3}c$-BiFeO$_3$ (model E_v = 3.99 eV)
- $P4mm$-BiCoO$_3$ (model E_v = 3.80 eV)

Experimental validation of new candidates in progress

Conclusions and Acknowledgments

O vacancy formation in ABO_3 perovskites

- Need better materials for STC H_2O/CO_2 splitting

  - Oxide perovskites: tunable ΔH_{red}, low ΔS_{red}

  - Identify simultaneously redox-active perovskites with optimal ΔH_{red} (3-3.75 eV) to improve ΔS_{red}

  - Size + charge-neutrality + redox-activity constraints = $Ca_{0.5}Ce_{0.5}MO_3$ (M = Sc, Ti,…,Ni)

- $Ca_{0.5}Ce_{0.5}MnO_3$ and $Ca_{0.5}Ce_{0.5}FeO_3$ exhibit near-optimal $\Delta H_{red}(\approx E_F[Va_O])$

  - Most quaternaries are not stable at 0 K, but A-site configurational entropy can help

  - $Ca_{0.5}Ce_{0.5}MnO_3$: simultaneous redox-active candidate

- Built a machine learned model on a diverse set of perovskite structures to predict Va_O formation energy

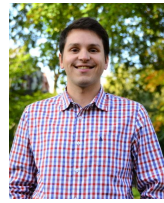 - Two candidates from outside the training set: $BiFeO_3$ and $BiCoO_3$
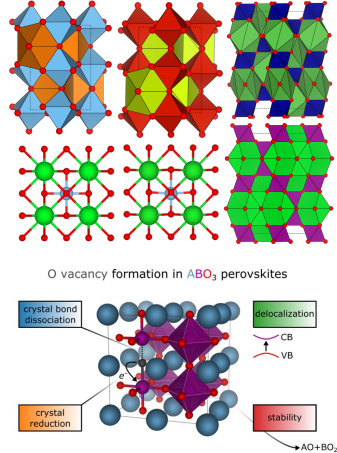
Tiger (Princeton)   NREL (Eagle)

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