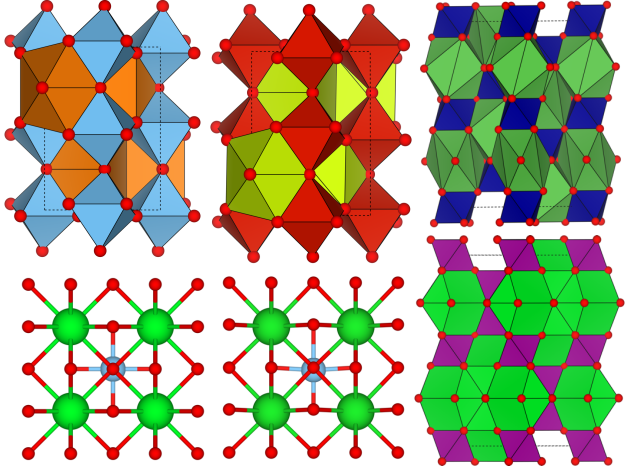

First-principles screening of Ca-Ce-M-O (M = 3*d* transition metal) oxide perovskites for solar thermochemical applications

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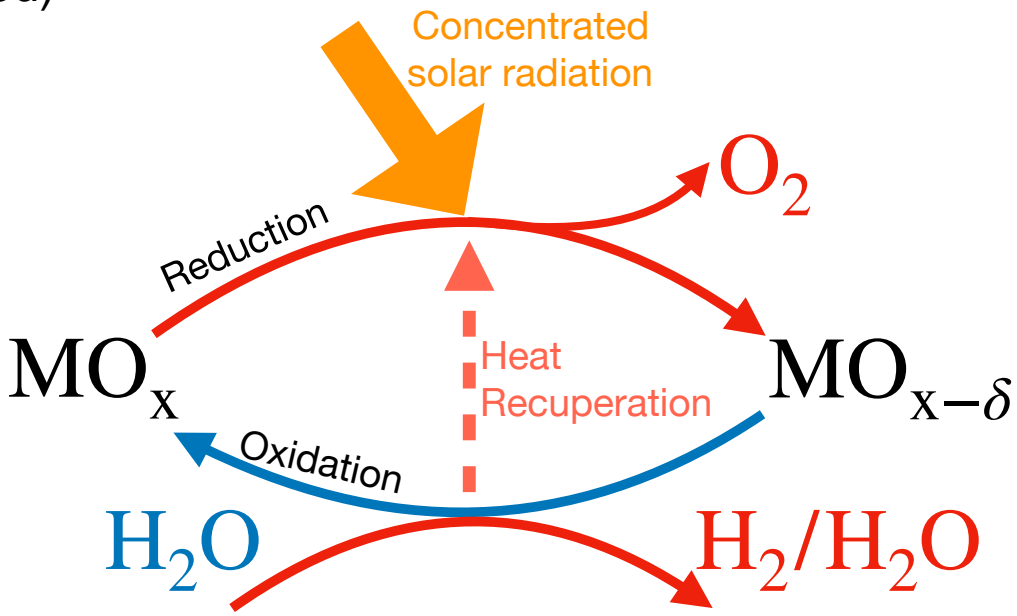
EN05.05: Solar Thermochemical Water Splitting II
Materials Research Society Spring Meeting
Apr 19, 2021

Solar thermochemical (STC) production of H_2 and/or CO: oxide perovskites are potential candidates

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

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



Thermal reduction (TR)
High T (~1673 K)
~vacuum (p_{O_2}~10 Pa)

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

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

Similar cycle for CO_2 splitting

1.Scheffe *et al.*, **Energy Fuels 2013**, *27*, 4250
2. Barcellos *et al.*, **Energy Environ. Sci. 2018**, *11*, 3256
3. Emery and Wolverton, **Scientific Data 2017**, *4*, 170153
4. Deml *et al.*, **Chem. Mater. 2014**, *26*, 6595

Oxide perovskites have been explored as new candidates[1-4]
- Large composition space = tunability of enthalpy of reduction (ΔH_{red}) within "optimal" range
- Non redox-active "A" cation (in ABO_3) = loss in entropy of reduction (ΔS_{red}) = lower capacity

Can we identify perovskites with higher ΔS_{red}?

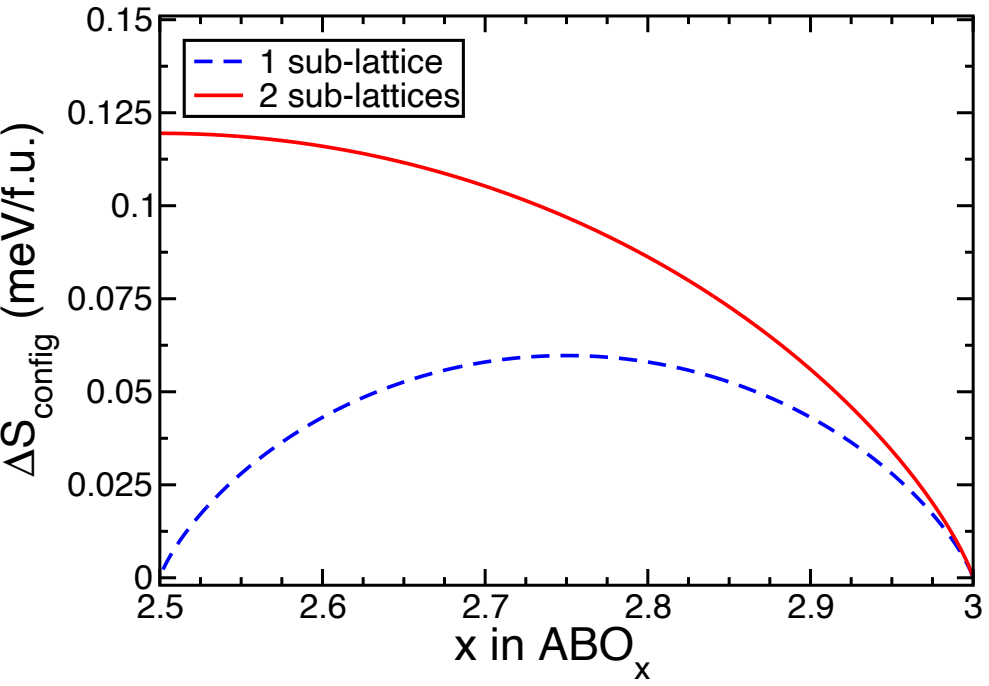
Siegel *et al.*, **Ind. Eng. Chem. Res. 2013**, *52*, 3276
Carillo and Scheffe, **Sol. Energy 2017**, *156*, 3

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

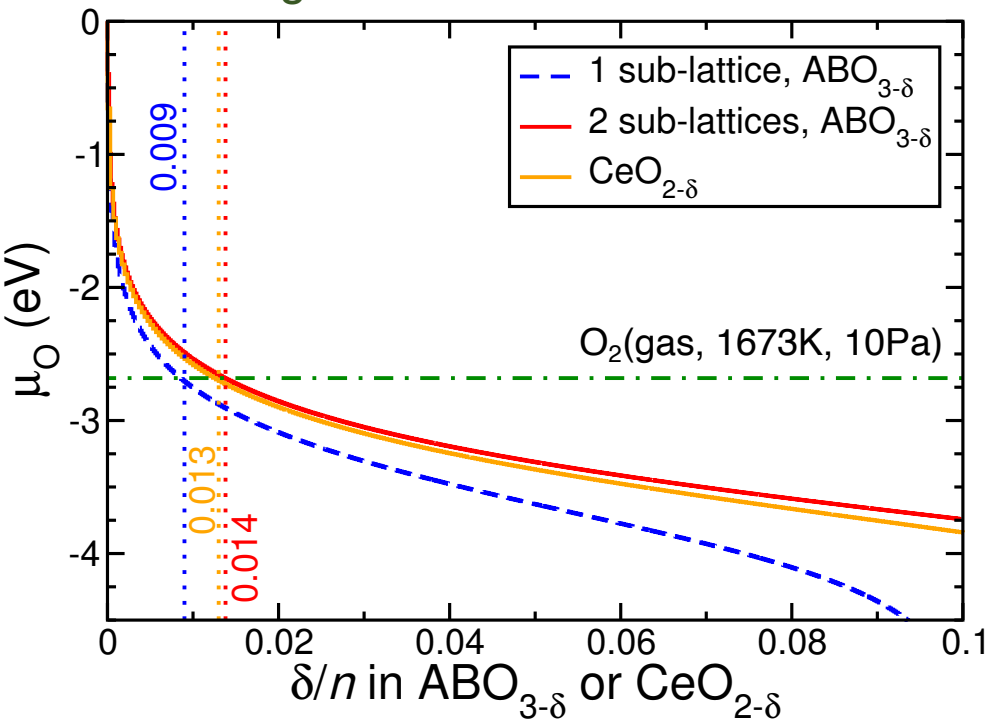
Entropy of reduction for an induced off-stoichiometry, δ, in ABO_3

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

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

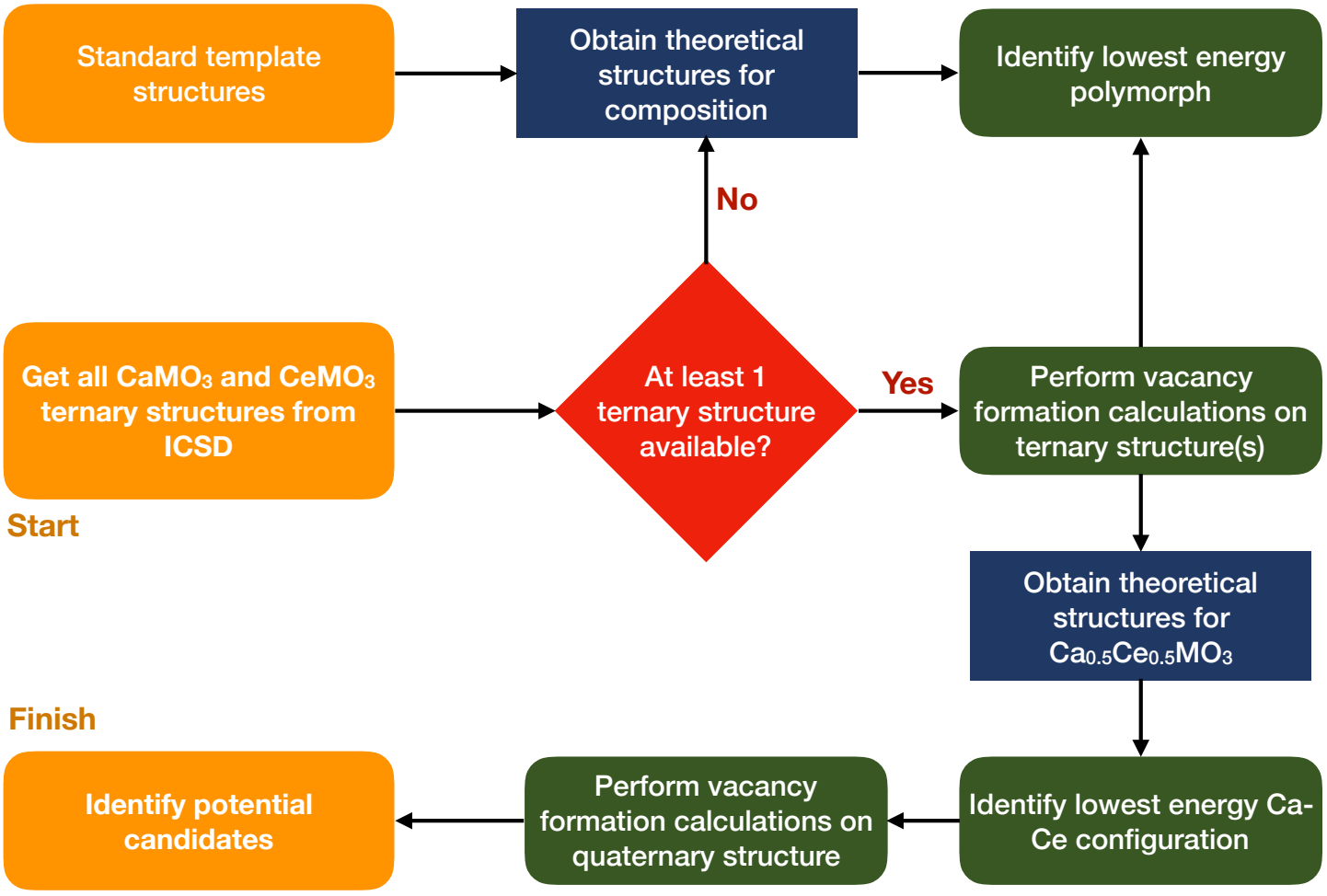


Potential simultaneously redox active ABO_3 perovskites?

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 $CeMO_3$



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]

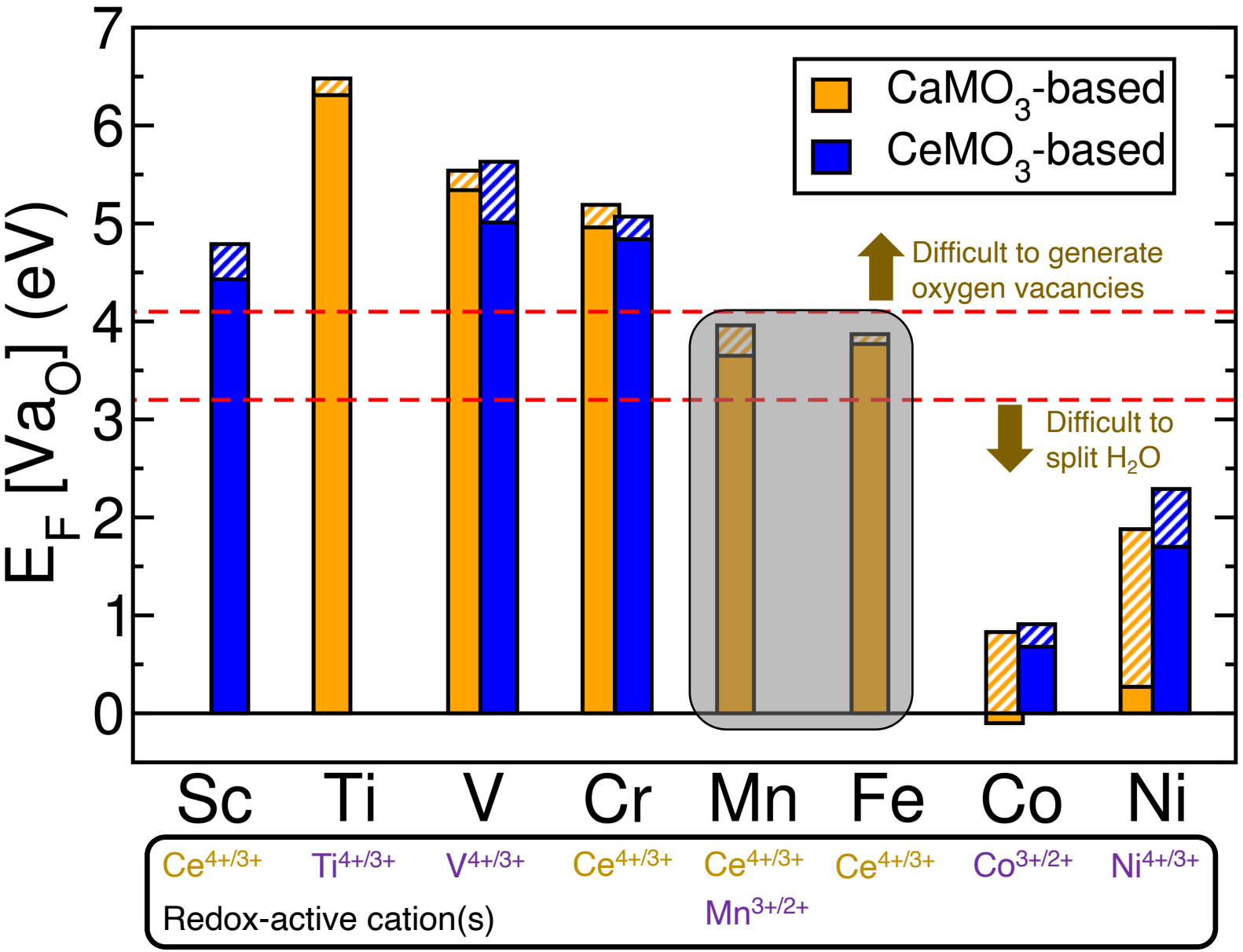
Density functional theory engine: strongly constrained and appropriately normed (SCAN) functional, corrected with optimal Hubbard *U* correction[1]

- $\Delta H_{red} \approx \mathrm{E_F}[\mathrm{Va_O}]$ (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



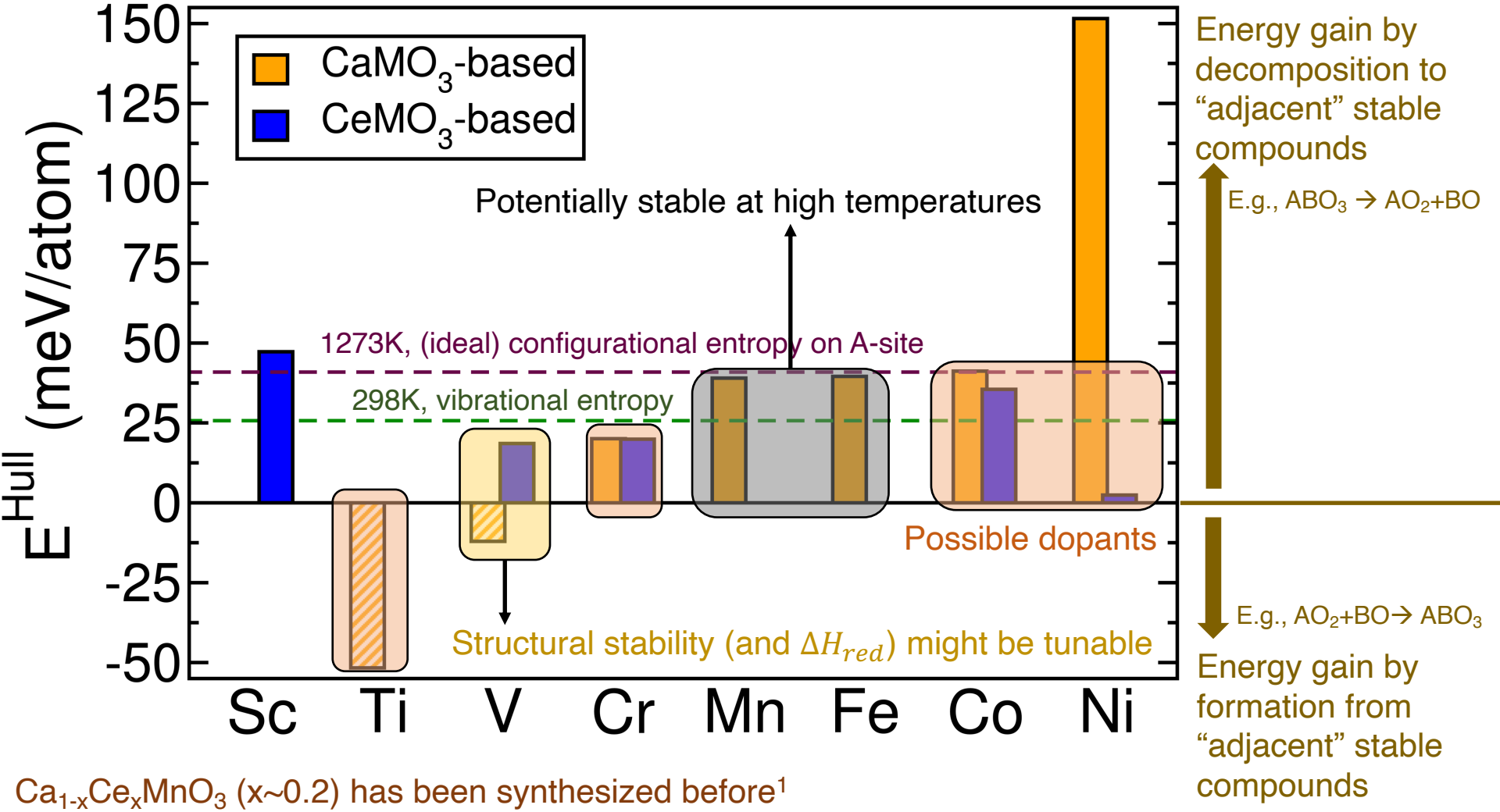
$E_F[Va_O]$ decreases along 3*d* from Ti to Co

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 near-optimal ΔH_{red}

Stability? Simultaneous redox?

0 K stability of $Ca_{0.5}Ce_{0.5}MO_3$
Impact of configurational entropy (of mixing)



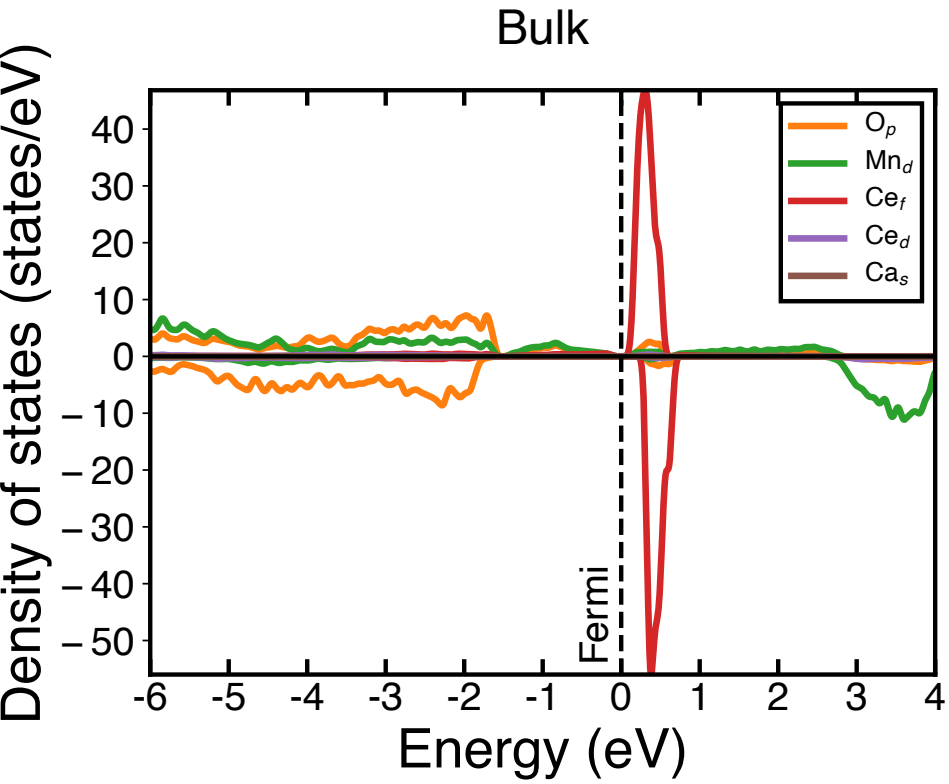
$Ca_{1-x}Ce_xMnO_3$ (x~0.2) has been synthesized before[1]

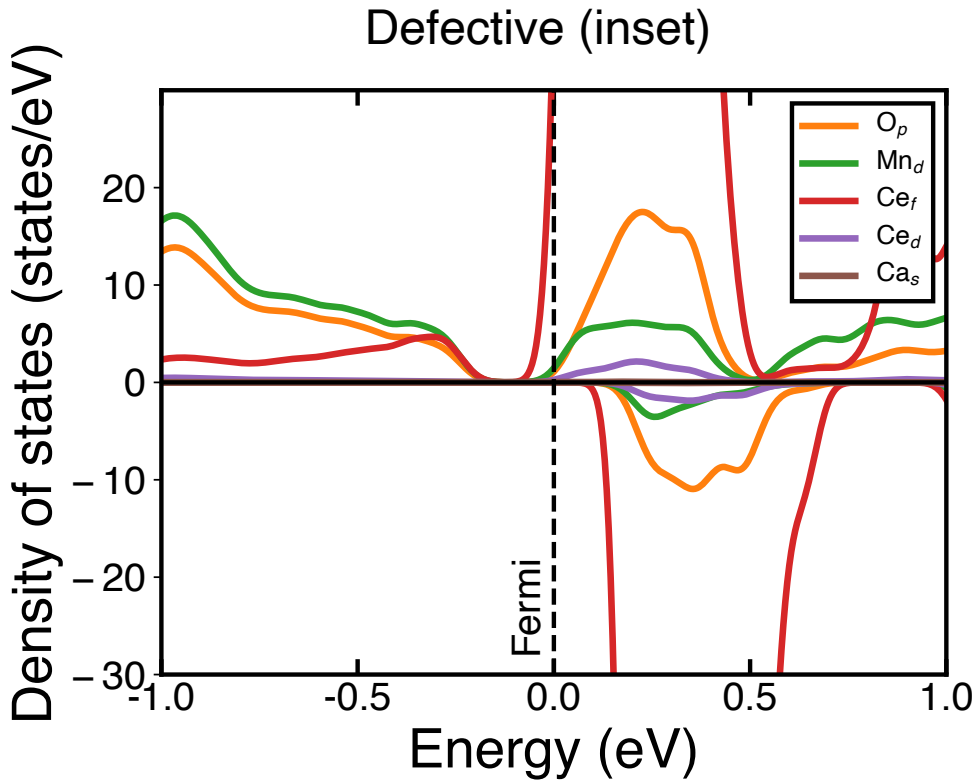
$Ca_{0.5}Ce_{0.5}MO_3$ perovskites: can be stabilized at higher temperatures via A-site configurational entropy

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])





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 $Ca_{0.5}Ce_{0.5}MnO_3$

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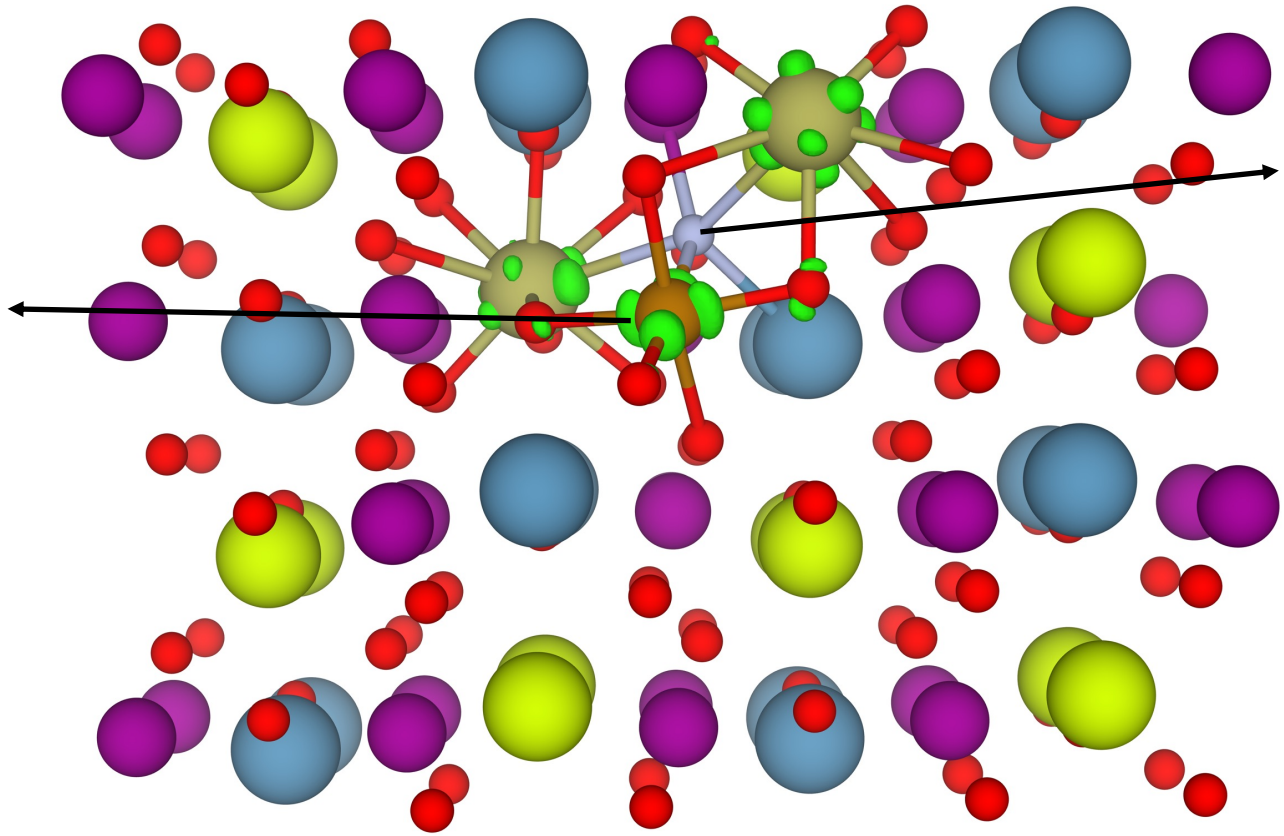
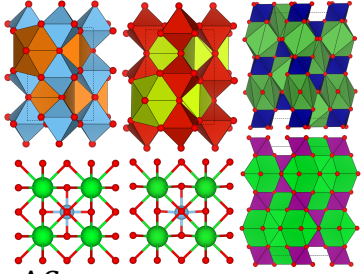


Electron density difference plot: $Ca_{0.5}Ce_{0.5}MnO_3$ with and without oxygen vacancy

Simultaneous reduction = candidate!

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

Conclusions and Acknowledgments



- 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 $\Delta H_{red} (\approx \mathrm{E_F}[\mathrm{Va_O}])$
  - Most quaternaries are not stable at 0 K, but A-site configurational entropy can help

- Density of states calculations + On-site magnetic moments + (Lack of) Jahn-Teller distortion + Electron density different plots = Evidence for simultaneous Ce and Mn reduction in $Ca_{0.5}Ce_{0.5}MnO_3$

"Exploring Ca-Ce-M-O (M=3*d* transition metal) oxide perovskites for solar thermochemical applications", G.S. Gautam, E.B. Stechel and E.A. Carter, **Chem. Mater. 2020**, *32,* 9964-9982

"Evaluating optimal *U* for 3*d* transition-metal oxides within the SCAN+*U* framework", O.Y. Long, G.S. Gautam, and E.A. Carter, **Phys. Rev. Mater. 2020**, *4,* 054101

"A first-principles-based sub-lattice formalism for predicting off-stoichiometry in materials for solar thermochemical applications: the example of ceria", G.S. Gautam, E.B. Stechel, and E.A. Carter, **Adv. Theory Simul. 2020**, *3*, 2000112

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