



Transformative Materials for High-Efficiency Thermochemical Production of Solar Fuels

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Project ID 167
DE-EE0008089

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Project Overview

Project Partners

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Project Vision

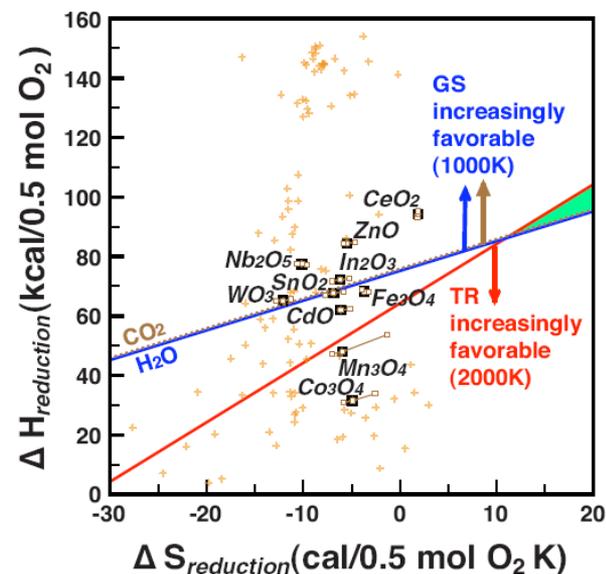
Combine high-throughput computation and experiment to discovery and design novel, improved STCH materials.

Project Impact

Will explore enormous combinatorial space of materials, to “tune in” desired STCH enthalpy and entropy of reduction. We will design materials with reduced temperatures of reduction but sufficient gas-splitting rates.

Award #	EE0008089
Start/End Date	04/01/2019 – 03/31/2020
Year 1 Funding*	\$250K
Year 2 Funding*	\$375K

** this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*





Approach- Summary

Project Motivation

Project builds on background of PIs in STCH materials, attempt to combine high-throughput computational and experimental exploration of oxygen off-stoichiometric oxides and phase change materials for enhancing the efficiency of STC production of solar fuels.

Barriers

Risk mitigated by exploring large space of novel STCH materials, and the combined use of high-throughput calculations and experimental efforts to explore this space. Focus to date is on perovskite and double-perovskite oxide materials.

Key Impact

Identify compounds which show: a) synthesizability, b) thermodynamics favorable for $<1400^{\circ}\text{C}$ reduction and c) thermodynamics favorable for facile water splitting. State-of-the-art currently CeO_2 and SLMA perovskite.

Partnerships

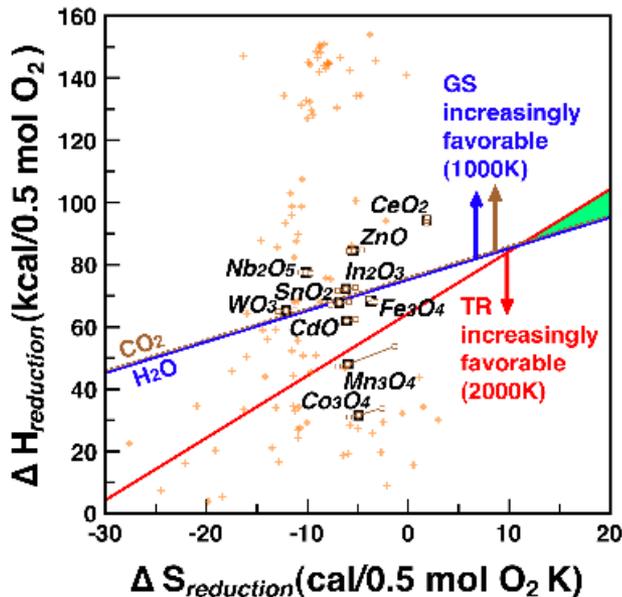
Productive collaborations with three HydroGEN nodes and other seedling projects: Ginley (NREL) – in-situ XRD and synthesis, Zakutayev (NREL) – thin-film composition gradient synthesis, McDaniel/Coker (SNL) high-T XRD, O'Hayre (CSM) – $(\text{Sr,Ce})_2\text{MnO}_4$ layered perovskite



Approach- Innovation

A Design Map for Materials:

Thermodynamics very challenging for stoichiometric reactions (at moderate pressure)



need moderate enthalpy and high entropy

B. Meredig and C. Wolverton, *Phys. Rev. B.* 80, 245119 (2009) (Data from SSUB database)

Perovskites (ABO_3 or $AA'BB'O_6$)

- ✓ Until recently : ceria (CeO_2) [1]
- ✓ More recently: perovskites [2]
- ✓ Perovskites have several good qualities for TWS
 - Tolerate large oxygen off-stoichiometry
 - High Stability
 - Studied for other applications (e.g. SOFC)



- ✓ Enormous compositional space
- ✓ **High-Throughput Density Functional Theory,** The Open Quantum Materials Database (OQMD)
- ✓ High-Throughput screening of ~11,000 ABO_3 perovskites based on **stability and reduction enthalpy**

[1] W.C. Chueh, et. al, *Science* 330 (2010)

[2] A.H. McDaniel, et.al, *Energy & Environmental Science* 6, 2424 (2013)

[3] S. Kirklin, et. al, *npj Computational Materials* 1, 15010 (2015)



Summary of Year-1 Scope of Work

- (a) Experimentally measure the reduction enthalpy and entropy of twelve predicted simple perovskites
- (b) Validate high-throughput methodology for measuring thermodynamic property using thin film through electrochemical impedance
- (c) Initiate high-throughput computational search for promising double-perovskite compounds

This project relies heavily on the computational predictions, the correct ranking of computed vacancy formation energy relative to experimental reduction enthalpy of the nine perovskites will be validated. The obtained reduction entropy will be used to establish models to predict compounds based on reduction entropy.



Relevance & Impact

- This project aims to identify promising compounds which show:
 - a) ground state stability/synthesizeability of compound,
 - b) thermodynamics favorable for <1400C reduction and
 - c) thermodynamics favorable for facile water splitting.

State-of-the-art currently CeO_2 and SLMA perovskite.

- Discovery of new, higher-efficiency materials is critical towards the practical use of STCH for H_2 production (and solar fuels, more generally). ***Our combined high-throughput computation + experimental approach is greatly accelerating this materials discovery effort.***
- ***Collaborations with HydroGEN nodes (NREL, SNL) and other Seedling projects (CSM) will greatly facilitate research progress***



Accomplishments – Synthesis and Reduction of Oxide Materials

Objective

Experimental measurements of redox thermodynamics of computationally predicted perovskites by TGA

Aims:

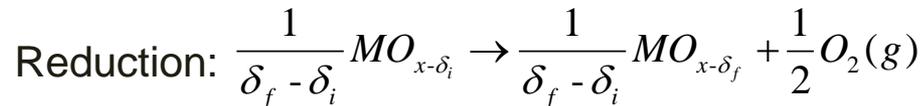
- (i) Validate the enthalpy calculation
- (ii) Obtain high-quality entropy data to guide/validate future entropy calculations

Material	Structure Type	Crystal System	Space Group
LuFeO₃	Perovskite	Orthorhombic	Pbnm
HoFeO₃	Perovskite	Orthorhombic	Pbnm
YFeO₃	Perovskite	Orthorhombic	Pnma
LuCrO₃	Perovskite	Orthorhombic	Pbnm
ErCrO₃	Perovskite	Orthorhombic	Pbnm
HoCrO₃	Perovskite	Orthorhombic	Pbnm
PrCoO₃	Perovskite	Orthorhombic	Pbnm
SmCoO₃	Perovskite	Orthorhombic	Pbnm
LaCoO₃	Perovskite	Rhombohedral	R-3c
LaNiO₃	Perovskite	Rhombohedral	R-3c
YMnO₃	“LuMnO₃”	Hexagonal	P6 ₃ mc
LuMnO₃	“LuMnO₃”	Hexagonal	P6 ₃ mc
HoMnO₃	“LuMnO₃”	Hexagonal	P6 ₃ mc
SrMnO₃	“BaMnO₃”	Hexagonal	P6 ₃ /mmc
BaMnO₃	”BaNiO₃”	Hexagonal	P6 ₃ /mmc
CaMnO₃	Perovskite	Cubic/Ortho	Pm3m/Pnma
LaMnO₃	Perovskite	Orthorhombic	Pnma



Accomplishments – Thermodynamic Measurements

- 17 ABO_3 compounds were synthesized via sol-gel method and the temperature stability range of each material was tested
- Thermogravimetry (TG) was employed to measure oxygen nonstoichiometry at different oxygen partial pressures and temperatures (remain single phase), and the reduction enthalpy and entropy were extracted



When at Equilibrium: $\Delta G = \Delta G^0 + RT \ln(K^{eq}) = 0$

$$K^{eq} = pO_2^{1/2} = \exp\left(-\frac{\Delta G^0}{RT}\right) = \exp\left(-\frac{\Delta H^0 - T\Delta S^0}{RT}\right)$$

$$\frac{R}{2} \ln(pO_2) = -\frac{\Delta H^0}{T} + \Delta S^0$$

For a given δ , linear relation of $\frac{R}{2} \ln(pO_2)$ vs. $\frac{1}{T}$ gives slope = $-\Delta H^0$, intercept = ΔS^0

ΔH and ΔS control T, P for water splitting

Also, provides key data to validate computational methods



Accomplishments – Measurement Procedure

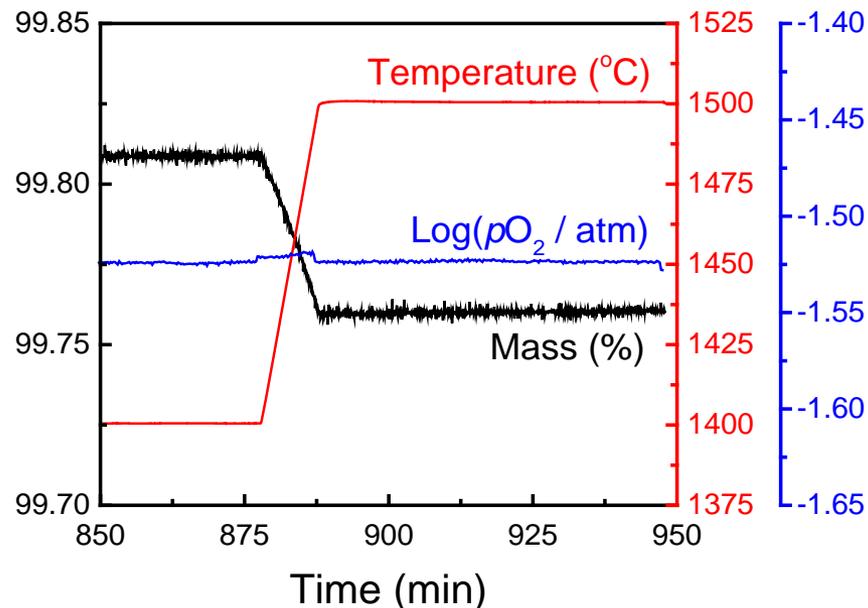
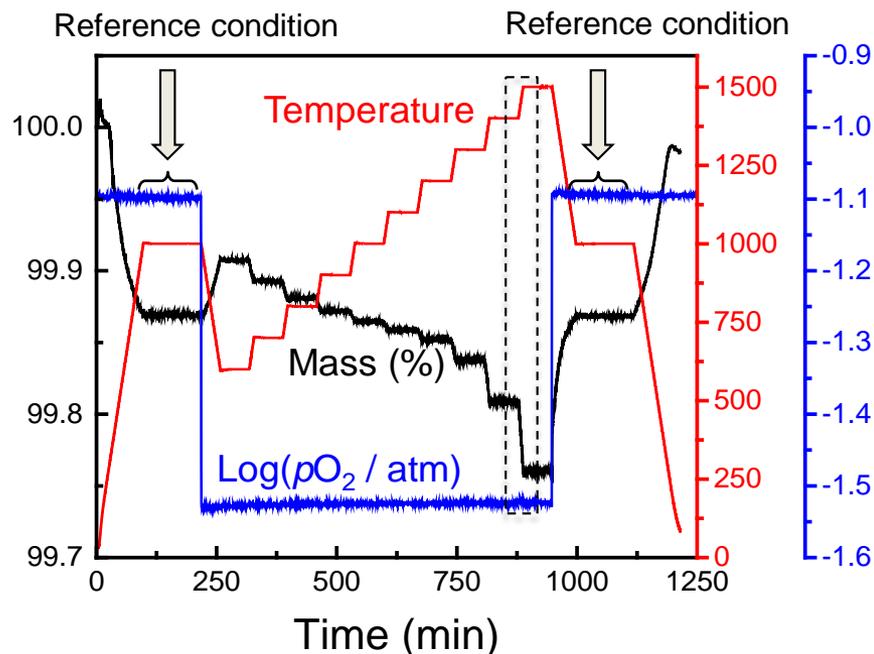
Stepwise heating profile

10 °C/min ramp + 1 h hold

Example:
YMnO₃

Mass change on heating

10 °C/min: 1400 → 1500 °C



Measure under 5 different pO_2 conditions (0.030 atm shown)

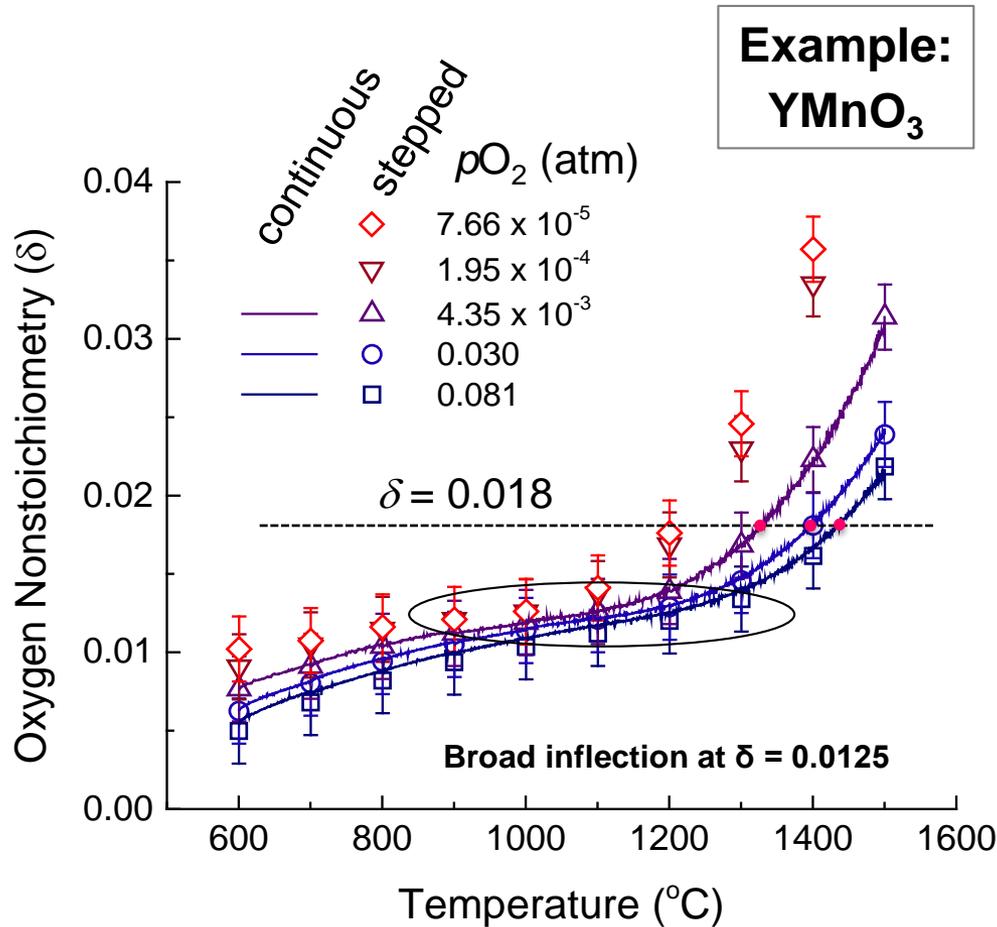
Return to reference mass at end of cycle

At end of ramp step, no mass change during isothermal hold

Sample was equilibrated throughout heating



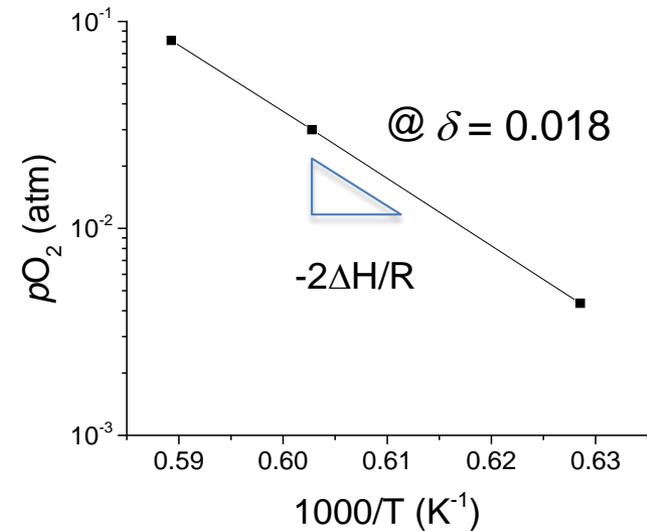
Accomplishments – Measurement Procedure



At a given δ

$$\frac{R}{2} \ln(p\text{O}_2) = -\frac{\Delta H^{\ominus}}{T} + \Delta S^{\ominus}$$

Intercept = $2\Delta S/R$



Analysis inherently smoother using data from continuous profile

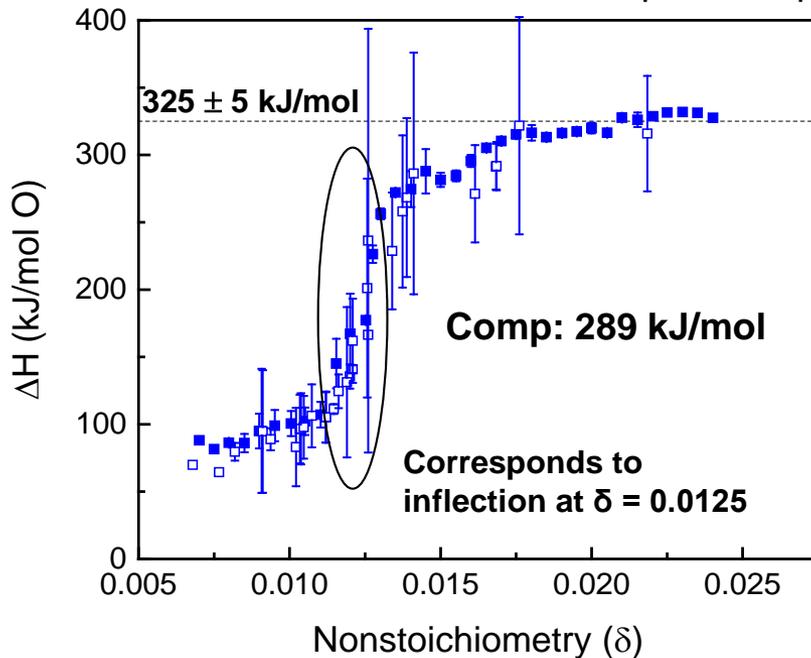


Accomplishments – Measurements of Two Key Thermodynamic Quantities, ΔH and ΔS of Reduction

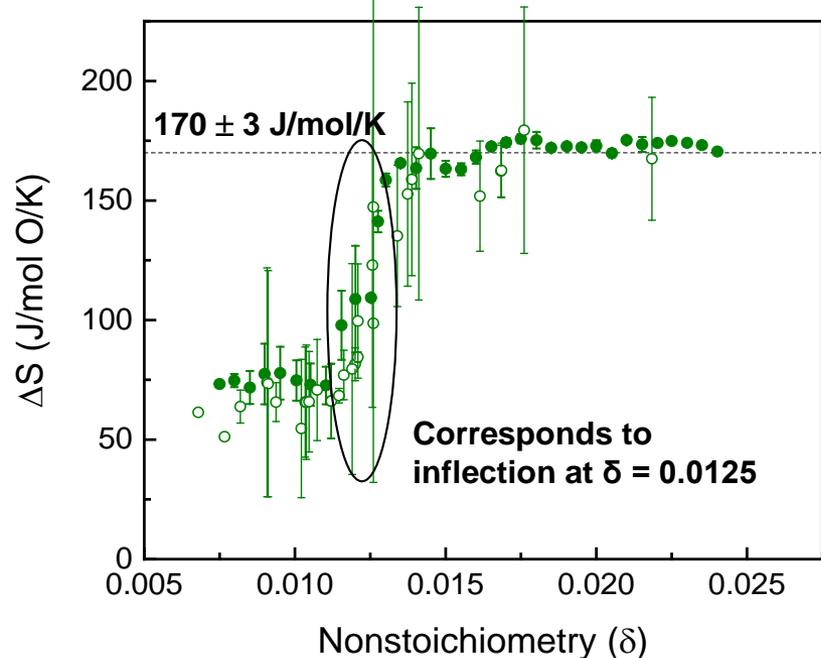
Example:
 YMnO_3

Enthalpy

Open = stepwise; Closed = continuous



Entropy



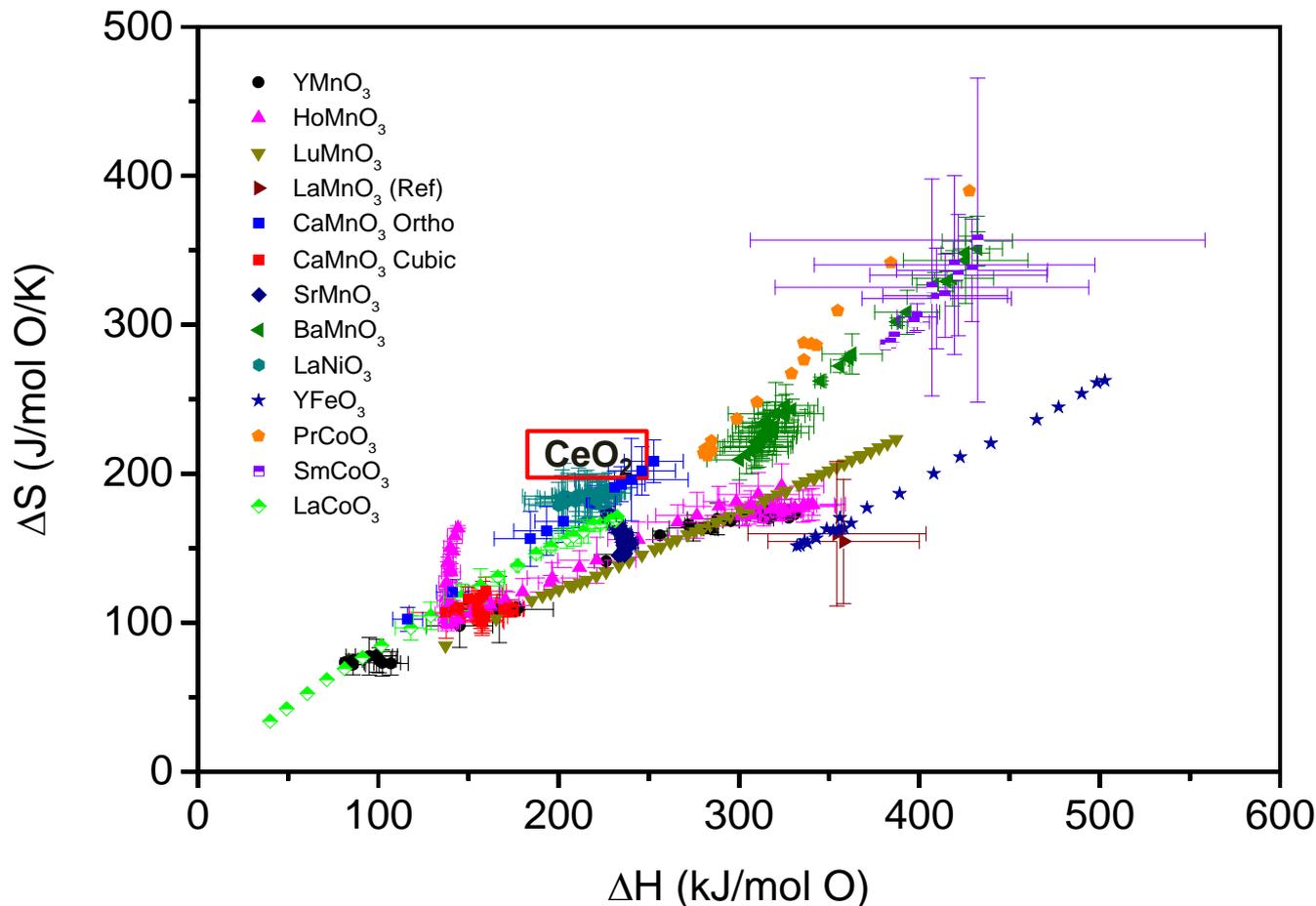
- Data collected in *the same* experiment
- Continuous heating/cooling preferred, so long as equilibration is ensured
- Below inflection δ , access oxygen interstitial sites (?), mechanistic transition (?)



Accomplishments – Are ΔH and ΔS Correlated?

Enthalpy vs. Entropy

Compare the enthalpy vs. entropy of reduction of twelve perovskites evaluated in Year-I



Generally, the higher enthalpy, the higher entropy

Compared with CeO_2 , CaMnO_3 (orthorhombic), LaNiO_3 and SrMnO_3 may be promising perovskites.



Accomplishments: Data-Driven Approach

The Open Quantum Materials Database (OQMD) oqmd.org
Large-scale materials database of ~600,000 compounds

OQMD:

The Open Quantum Materials Database

[Home](#) [Materials](#) [Analysis](#) [Documentation](#) [Download](#)

Newsflash: OQMD v1.1 is out! (Download it [here](#).)

Welcome to the Open Quantum Materials Database

The OQMD is a database of DFT-calculated thermodynamic and structural properties. This online interface is for convenient, small-scale access; for a more powerful utilization of the data, we recommend downloading the entire database and the API for interfacing with it, from the link below.

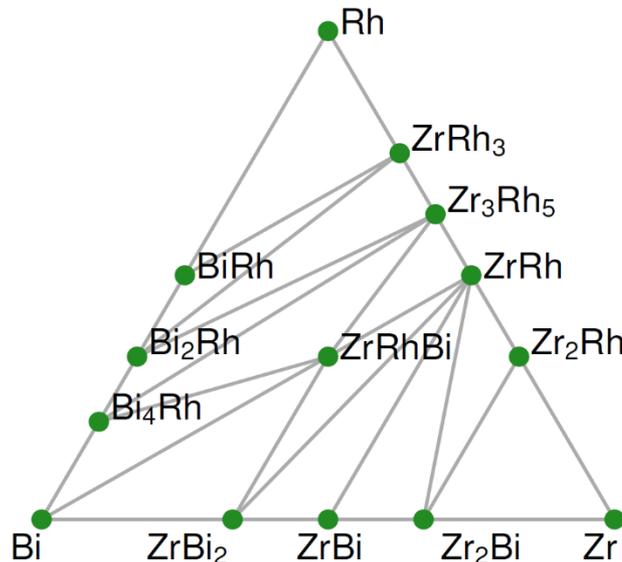
You can...

- [Search](#) for materials by composition,
- [Create](#) phase diagrams using the thermochemical data in OQMD,
- [Determine](#) ground state compounds at any composition,
- [Visualize](#) crystal structures, or
- [Download](#) the entire database (and the API) for your own use!

S. Kirklin, J.E. Saal, B. Meredig, A. Thompson, J.W. Doak, M. Aykol, S. Ruehl and C. Wolverton, *npj Computational Materials* (2015) 1, 15010

Current status

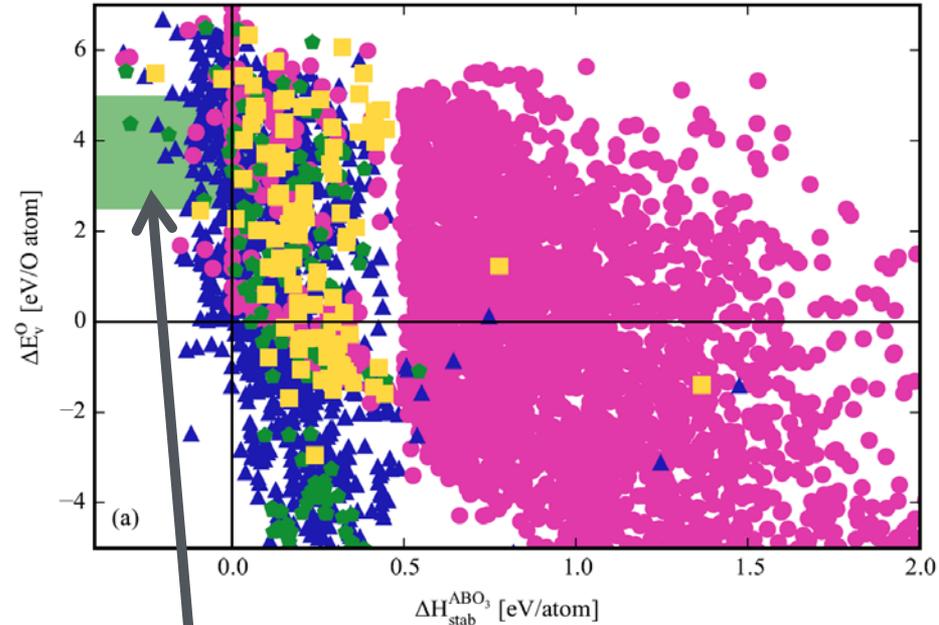
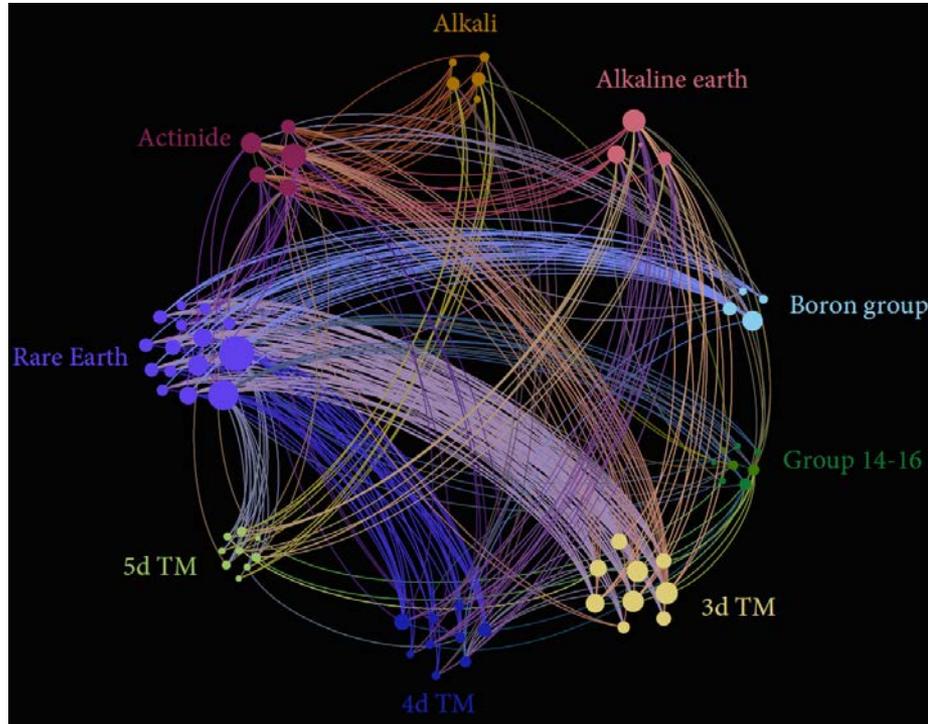
OQMD v1.1 has been released! Download it [here](#).
The database now contains **471857** entries. In addition, calculations of new structures are constantly ongoing!
Recently added compounds include: [EuPaBe](#) [PrPaFe](#) [PaReHg](#) [AcLaPa](#) [KPaMo](#)





Accomplishments: High-throughput DFT Screening of STCH Materials

High-Throughput of ~11,000 ABO_3 Perovskites Screened for Stability and Reduction Enthalpy



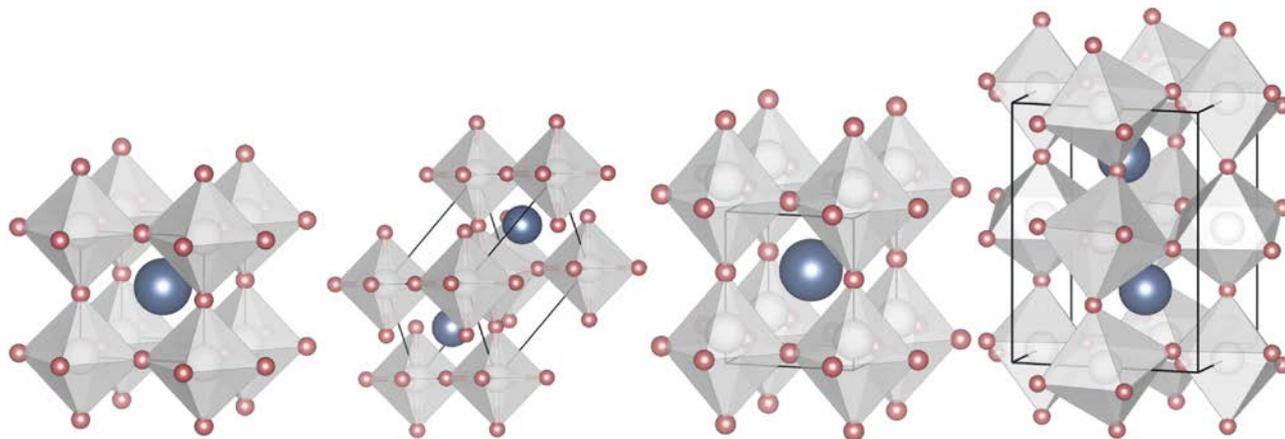
Targeted space: Stable ($x < 0$) and Reduction Suitable for Water Splitting (y between 2.5 to 5 eV)

Provides initial targeted compounds for experimental exploration

A.A. Emery, J.E. Saal, S. Kirklin, V.I. Hegde and C. Wolverton, Chem. Mater. (2016)



Accomplishments: Accurate DFT Vacancy Formation Energies Require Correct Crystal Structure



ABO₃ compounds can exist in many structure types:

- Perovskites, with various types of distortions
- Non-perovskites

Example: YFeO₃

Observed ground state structure is distorted perovskite

Vacancy Formation Energy in **distorted vs. cubic** perovskite = **4.22eV vs.**

3.20 eV

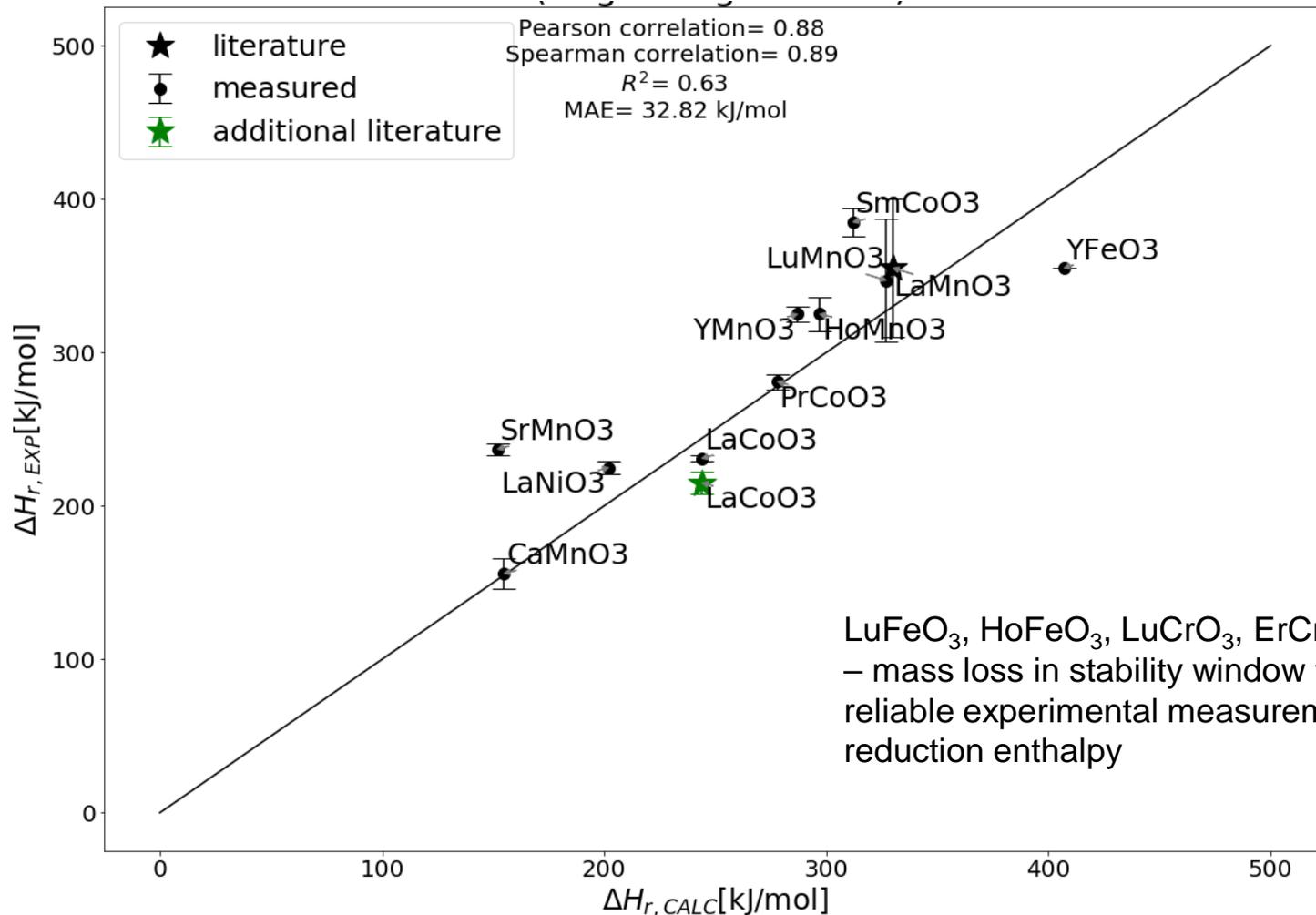
Previous High-Throughput Study (Emery et al., 2016), calculated vacancy formation energies in cubic structures only. Assumption of high-T cubic phases.

We can now compare with experimental results and find this previously-used approximation to be poor! So, we had to re-evaluate many of the vacancy formation energies with the correct ground state structures!



Accomplishments: Quantitative Validation of Approach

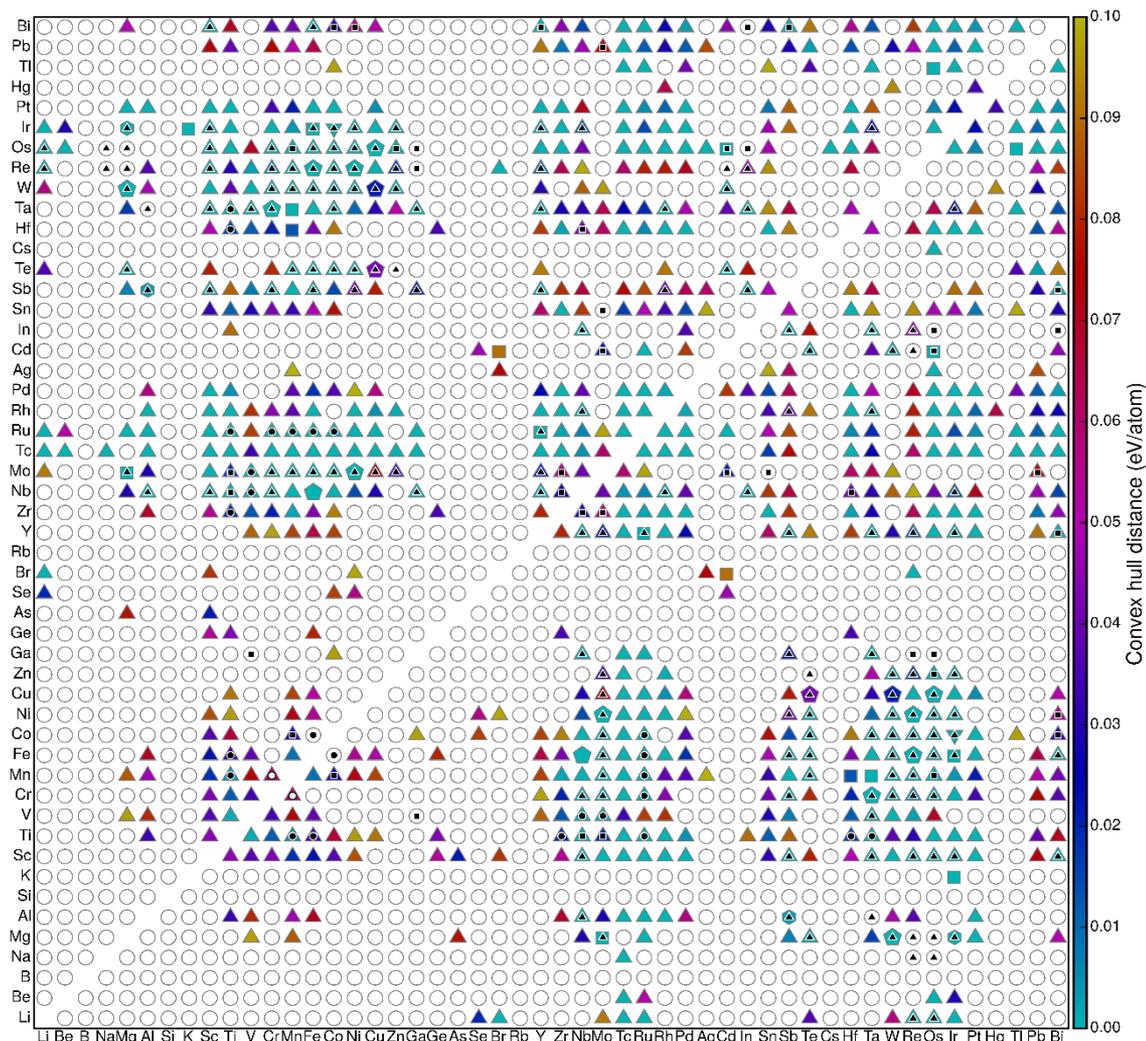
Comparison of Experimental and DFT Calculated Reduction Enthalpies (Key factor for both reduction and water splitting reactions)





Accomplishments: New double perovskites discovery by using high throughput (HT) screening

B-site ordered $Ba_2BB'O_6$

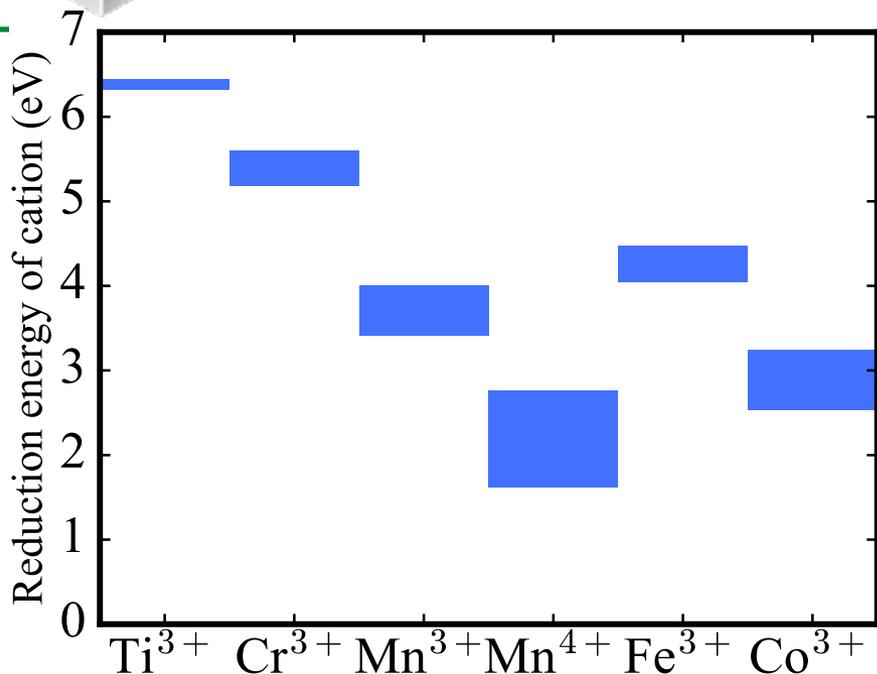


- HT calculations on $\sim 10^4$ double perovskite compounds.
- Our high throughput DFT screening reproduces most already known compounds and predicts ~ 400 new, stable double perovskite compounds.
- Several hundred new $Sr_2BB'O_6$ and $Ca_2BB'O_6$ compounds have been discovered (not shown here)

These predicted double-perovskites will serve as initial points of exploration for Year 2 experiments



Accomplishments: Computational Prediction of Double Perovskites for STCH



Compounds	Structure	E_v^0 (eV/vacancy)
Sr ₂ TiMnO ₆	P21/c	2.190
La ₂ CuMnO ₆	P21/c	2.892
La ₂ ZnMnO ₆	P21/c	3.031
Sr ₂ CuWO ₆	Fm-3m	3.071
Sr ₂ CuWO ₆	I4/m	3.111
Sr ₂ ZrMnO ₆	Fm-3m	3.270
La ₂ NiMnO ₆	P21/c	3.438

- **Key finding: B-site Mn⁴⁺ is much easier to reduce than other cations. Provides a chemical target for our search - double-perovskites with B-site Mn⁴⁺.** (The spread of the value is mainly from the effects of octahedral distortion.)
- Therefore, we performed DFT calculations on known Mn⁴⁺ containing double perovskites, and found the oxygen vacancy formation energy varies from 2.2 to 3.4 eV/vacancy.

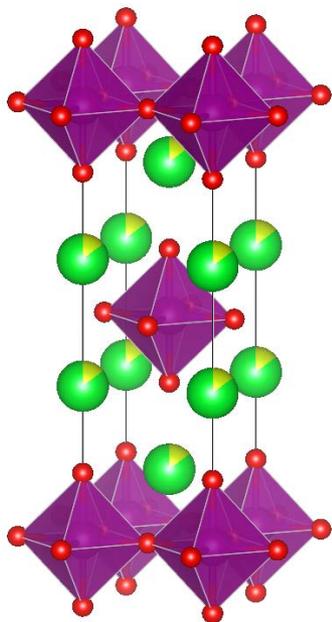
7 New Predictions for Stable Double-Perovskites with Favorable Water Splitting Thermodynamics



Collaboration: Discovery of Layered Perovskite STCH Compound

Collaboration with HydroGEN node (SNL) and other project (CSM)

Layered perovskite
 $Ce_xSr_{2-x}MnO_4$



Formula	Stability [eV/atom]	Decomposition reactions	Oxygen vacancy formation energy [eV/O atom]
$Ce_{0.1}Sr_{1.9}MnO_4$	0	Stable	1.763
$Ce_{0.2}Sr_{1.8}MnO_4$	0	Stable	2.243
$Ce_{0.3}Sr_{1.7}MnO_4$	0	Stable	2.661
$CeSrMnO_4$	0.061	0.500 Ce_2O_3 + 0.500 $Sr_2Mn_2O_5$	-

DFT calculations suggest:

- Stability of layered perovskite for $x \sim 0.1-0.3$.
- Vacancy formation energy suitable for STCH

Experimental results corroborate stability and water-splitting ability of this compound!!

Barcellos, Coury, Emery, Sanders, Tong, McDaniel, Wolverton, Kaufman, O'Hayre, "Phase identification of the layered perovskite $Ce_xSr_{2-x}MnO_4$ and application for solar thermochemical water splitting" submitted, 2018.



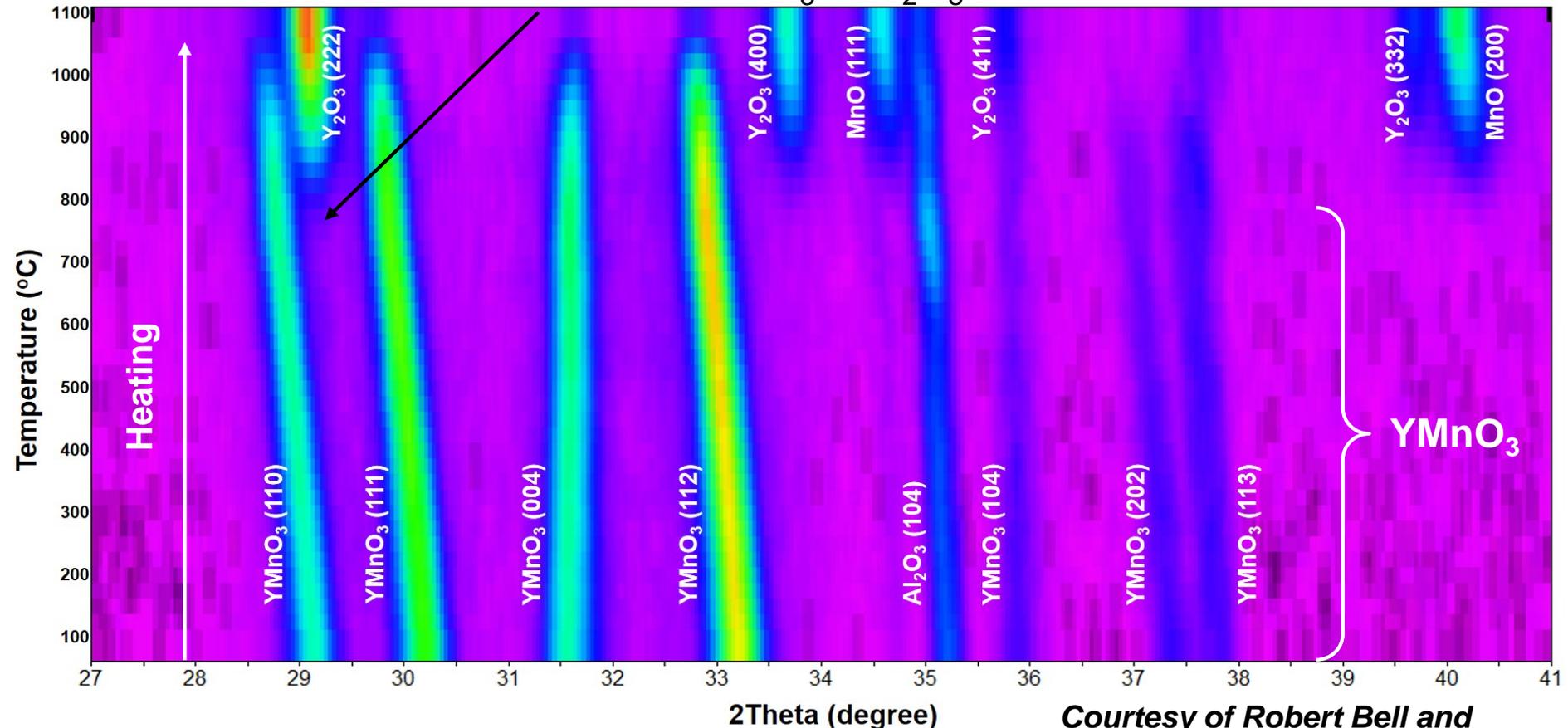
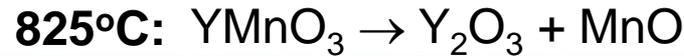
Collaboration: HydroGEN Node In-Situ XRD

Collaboration with HydroGEN, data collected at SNL

Major conclusion: Stability highly dependent on pO_2

need small amount of O_2
in sweep gas for STC use

Waterfall plot shows phase separation behavior



Courtesy of Robert Bell and
David Ginley, NREL



Publications/Presentations

Publications (several in preparation)

D. R. Barcellos, F. G. Coury, A. Emery, M. Sanders, J. Tong, A. McDaniel, C. Wolverton, M. Kaufman, and R. O'Hayre, "Phase identification of the layered perovskite $Ce_xSr_{2-x}MnO_4$ and application for solar thermochemical water splitting" submitted, 2019.

Invited Presentations (partial list)

- 2019 American Chemical Society
- 2019 Materials Research Society
- 2019 Telluride Science Research Center Workshop
- 2018 TMS



Proposed Future Work

Experimental:

- The experimental work will test site-substituted versions of the most promising materials found in Year 1
- Synthesis and testing of double perovskite compounds predicted by computation in Year 1.
- Synthesizing combinatorial samples for electrochemical testing
- Continued testing of electrochemical method and comparison to TGA (e.g., thicker samples).

Computational:

- Significantly expand range of chemistries consider for potential double-perovskites; use experimental data from Year 1 to validate more refined thermodynamic models.
- Entropy calculations of reduction entropy – to compare with TGA experiments
- High throughput DFT screening of oxygen vacancy formation energy of double perovskites
- Tailoring oxygen vacancy formation energy by A- and B-site doping: alloying B-site metals with different reduction energies, e.g., $\text{BaMn}_x\text{Ce}_{1-x}\text{O}_3$; alloying A-site metals to control octahedral rotation, which also has large influence on oxygen vacancy formation energy



Project Summary

- Experimentally measured the enthalpy and entropy of predicted twelve perovskites and validated the high-throughput DFT calculation approach.
- Validated the high-throughput electrochemical impedance approach to extract redox thermodynamics by using gradient film.
- Initiated the evaluation of predicted double perovskites and doped perovskites.