Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Transformative Materials for High-Efficiency Thermochemical Production of Solar Fuels

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Northwestern University
April 29, 2019

Project ID 167
DE-EE0008089

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NREL NATIONAL RENEWABLE ENERGY LABORATORY
BERKELEY LAB
Sandia National Laboratories
INL Idaho National Laboratory
Lawrence Livermore National Laboratory
SRNL

Project Overview

Project Partners

Chris Wolverton, Northwestern University
Sossina Haile, Northwestern University

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

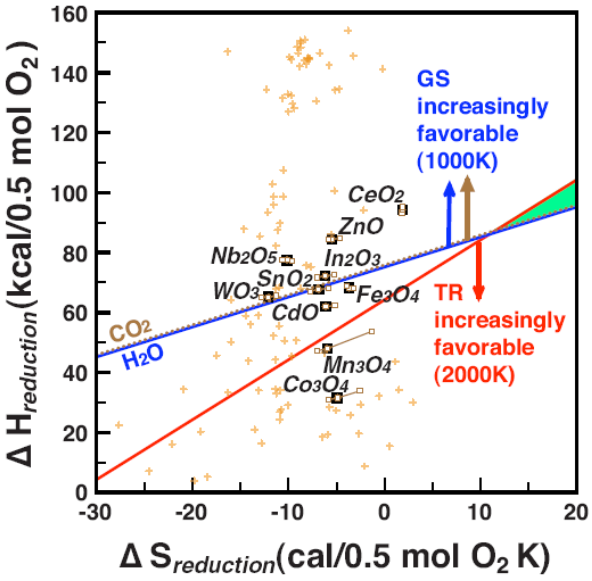
** this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

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.



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) synthesizeability, b) thermodynamics favorable for <1400°C reduction and c) thermodynamics favorable for facile water splitting. State-of-the-art currently CeO_2 and SLMA perovskite.

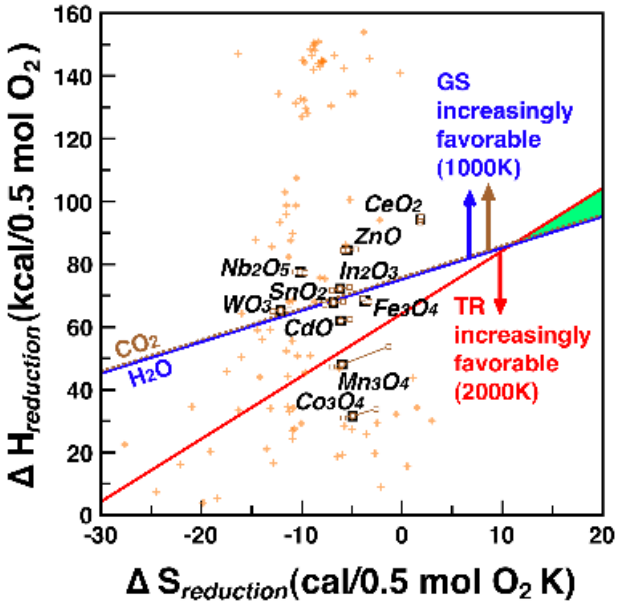
Partnerships

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) – (Sr,Ce)2MnO4 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)

Approach- Innovation

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
$LuFeO_3$	Perovskite	Orthorhombic	Pbnm
$HoFeO_3$	Perovskite	Orthorhombic	Pbnm
$YFeO_3$	Perovskite	Orthorhombic	Pnma
$LuCrO_3$	Perovskite	Orthorhombic	Pbnm
$ErCrO_3$	Perovskite	Orthorhombic	Pbnm
$HoCrO_3$	Perovskite	Orthorhombic	Pbnm
$PrCoO_3$	Perovskite	Orthorhombic	Pbnm
$SmCoO_3$	Perovskite	Orthorhombic	Pbnm
$LaCoO_3$	Perovskite	Rhombohedral	R-3c
$LaNiO_3$	Perovskite	Rhombohedral	R-3c
$YMnO_3$	"$LuMnO_3$"	Hexagonal	$P6_3mc$
$LuMnO_3$	"$LuMnO_3$"	Hexagonal	$P6_3mc$
$HoMnO_3$	"$LuMnO_3$"	Hexagonal	$P6_3mc$
$SrMnO_3$	"$BaMnO_3$"	Hexagonal	$P6_3/mmc$
$BaMnO_3$	"$BaNiO_3$"	Hexagonal	$P6_3/mmc$
$CaMnO_3$	Perovskite	Cubic/Ortho	Pm3m/Pnma
$LaMnO_3$	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

Reduction: $\frac{1}{\delta_f - \delta_i} MO_{x-\delta_i} \rightarrow \frac{1}{\delta_f - \delta_i} MO_{x-\delta_f} + \frac{1}{2} O_2(g)$

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

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

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

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

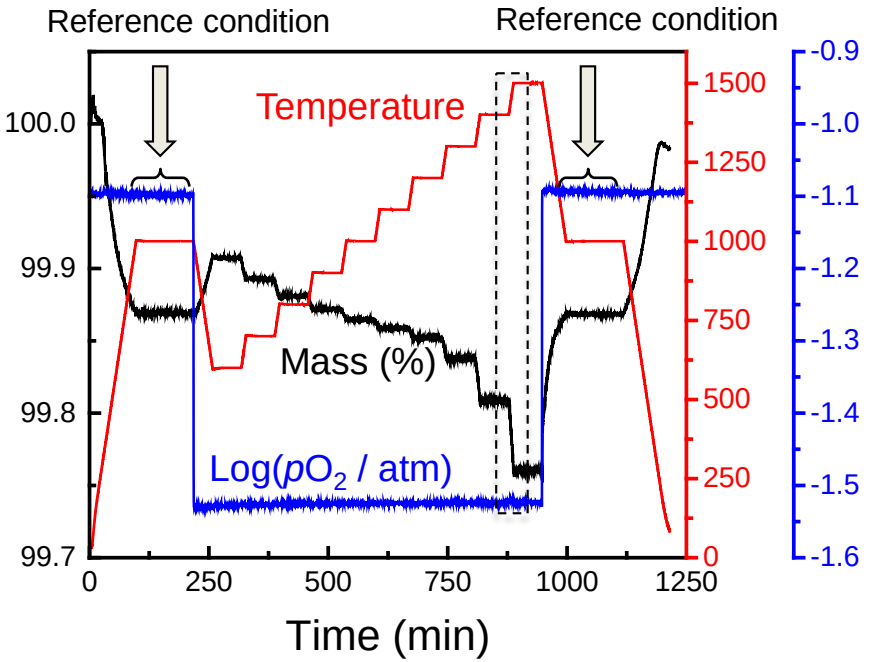
Stepwise heating profile

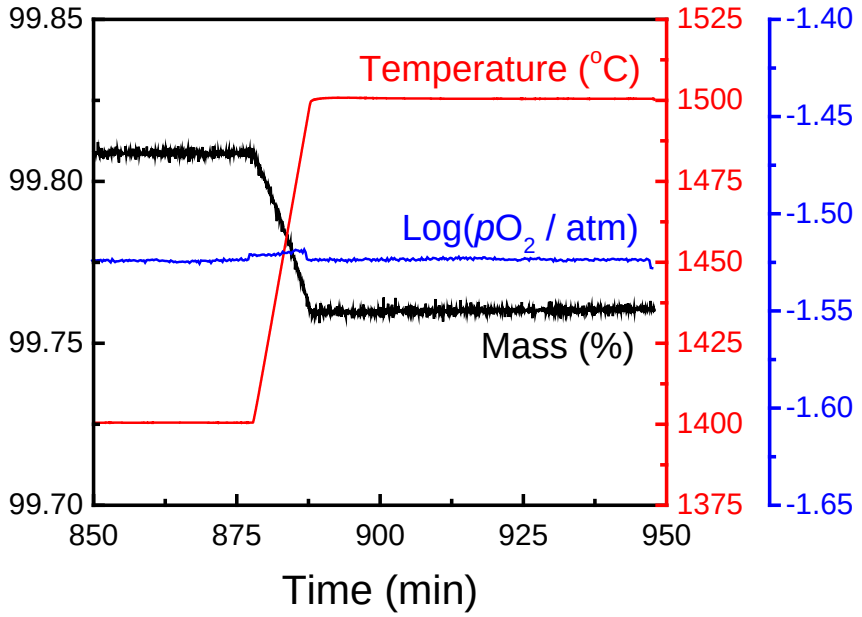
10 °C/min ramp + 1 h hold

Example: $YMnO_3$

Mass change on heating

10 °C/min: 1400 → 1500 °C





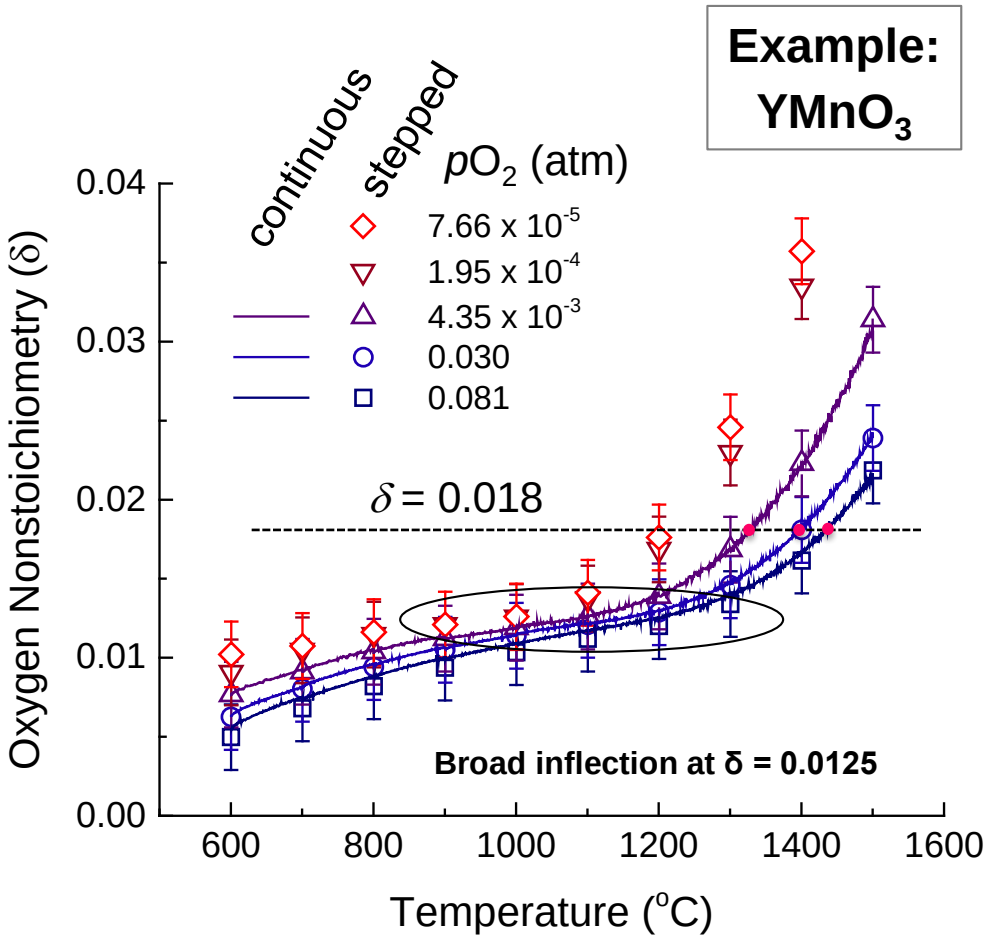
Measure under 5 different pO_2 conditions (0.030 atm shown)

Return to reference mass at end of cycle

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

Sample was equilibrated throughout heating

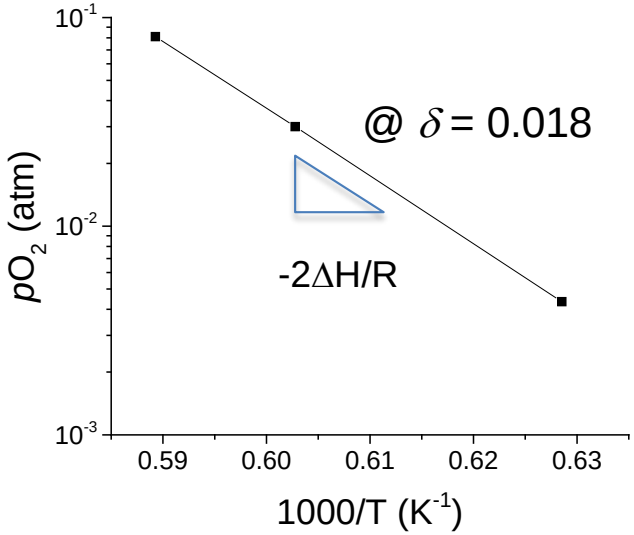
Accomplishments – Measurement Procedure



At a given δ

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

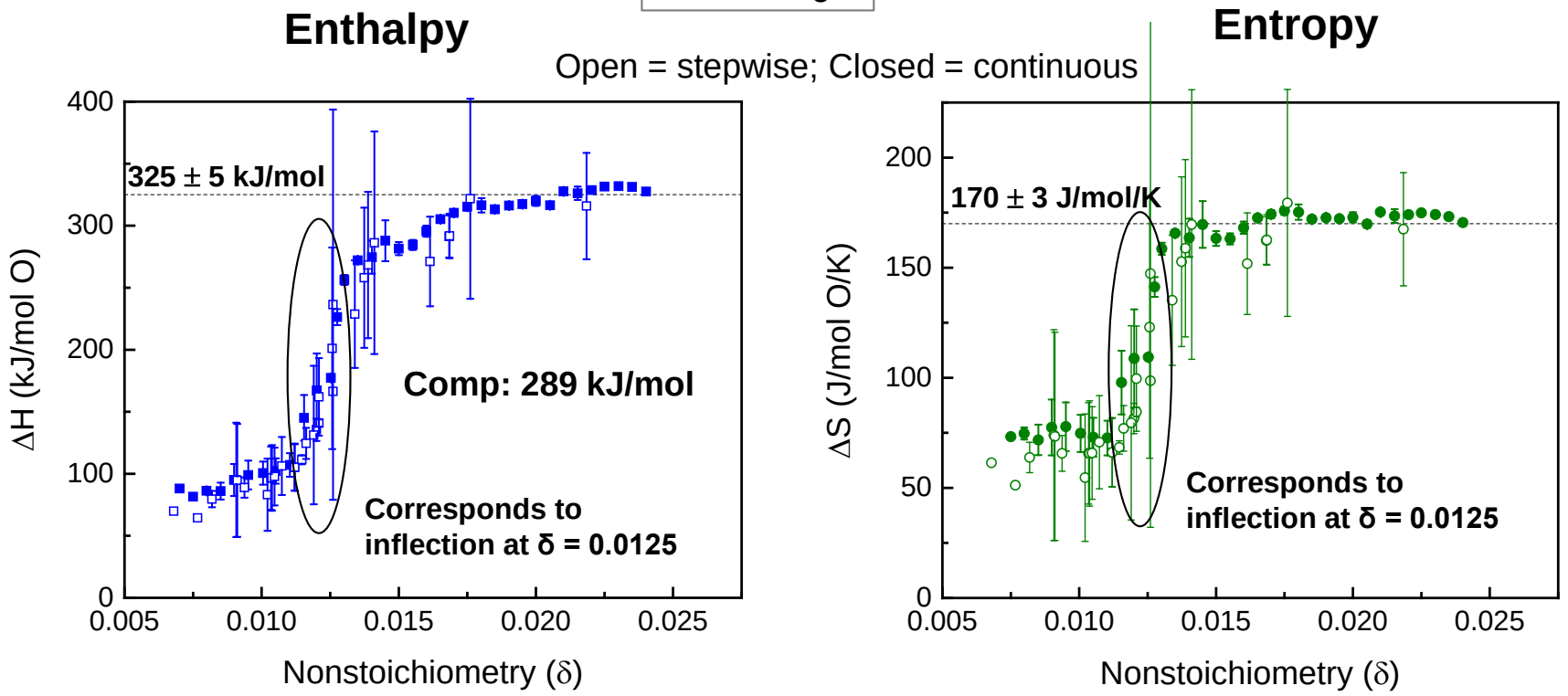
Intercept = 2ΔS/R



Analysis inherently smoother using data from continuous profile

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

Example: $YMnO_3$

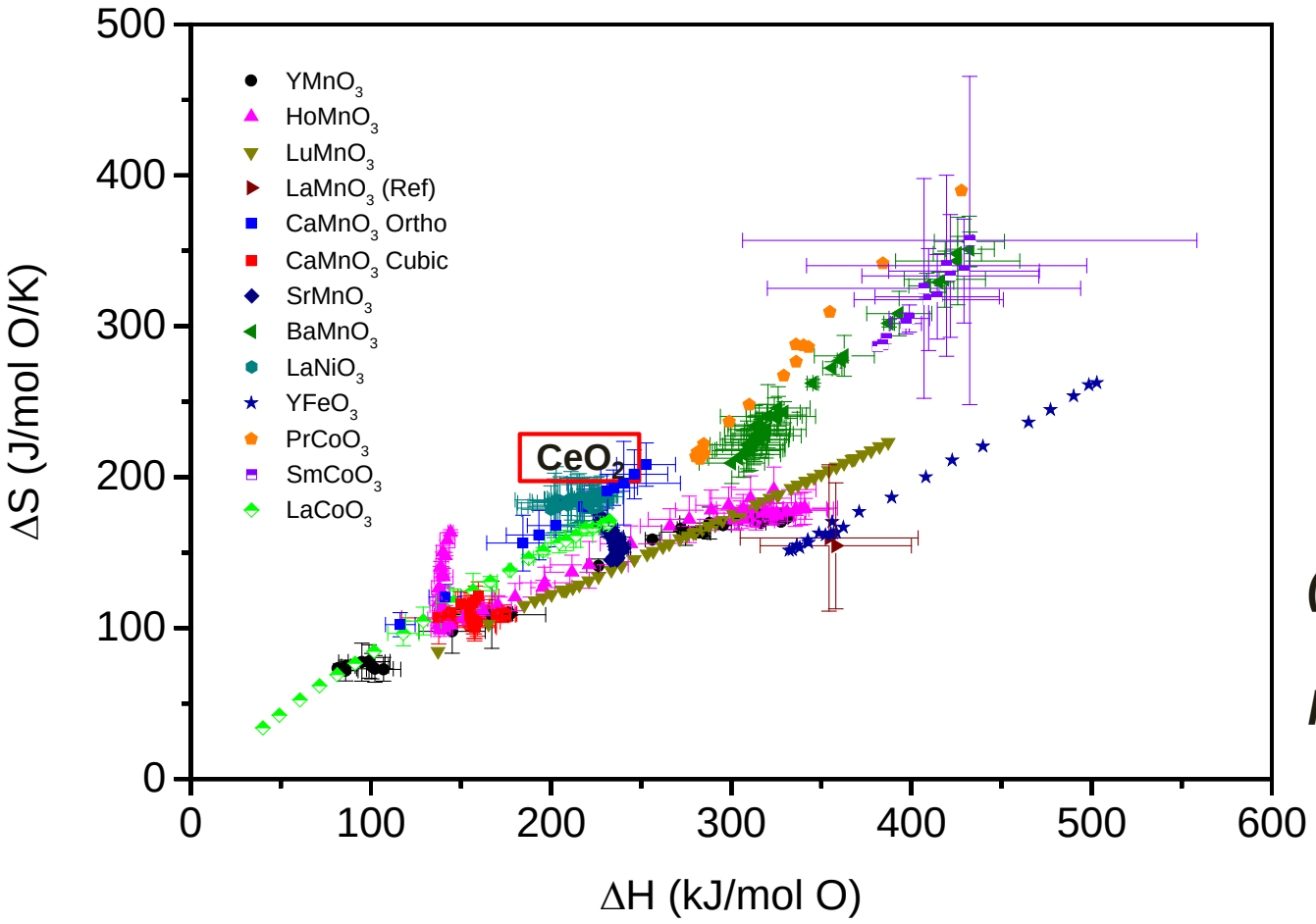


- Data collected in *the same* experiment
- Continuous heating/cooling preferred, so long as equilibration is ensured
- Below inflection δ, access oxygen interstitial sites (?), mechanistic transition (?)

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

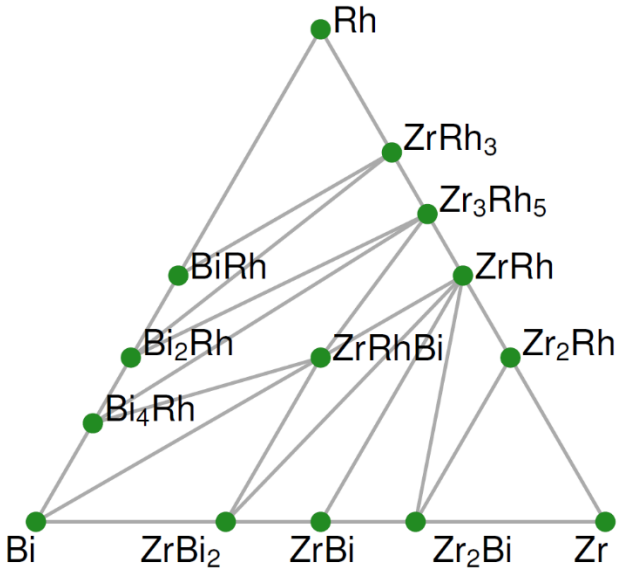
The OQMD is a database of DFT-calculated thermodynamic and structural properties. This online interface is for convenient, small-scale access; for a more powerful utilization of the data, we recommend downloading the entire database and the API for interfacing with it, from the link below.

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!

Current status

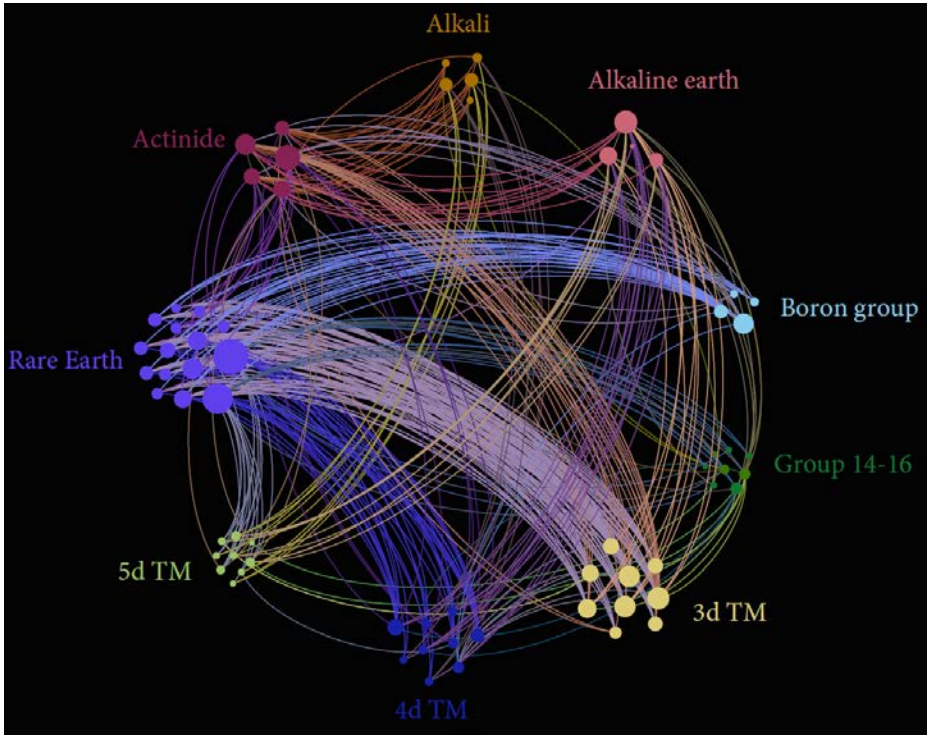
OQMD v1.1 has been released! Download it here.
The database now contains **471857** entries. In addition, calculations of new structures are constantly ongoing!
Recently added compounds include: EuPaBe PrPaFe PaReHg AcLaPa KPaMo

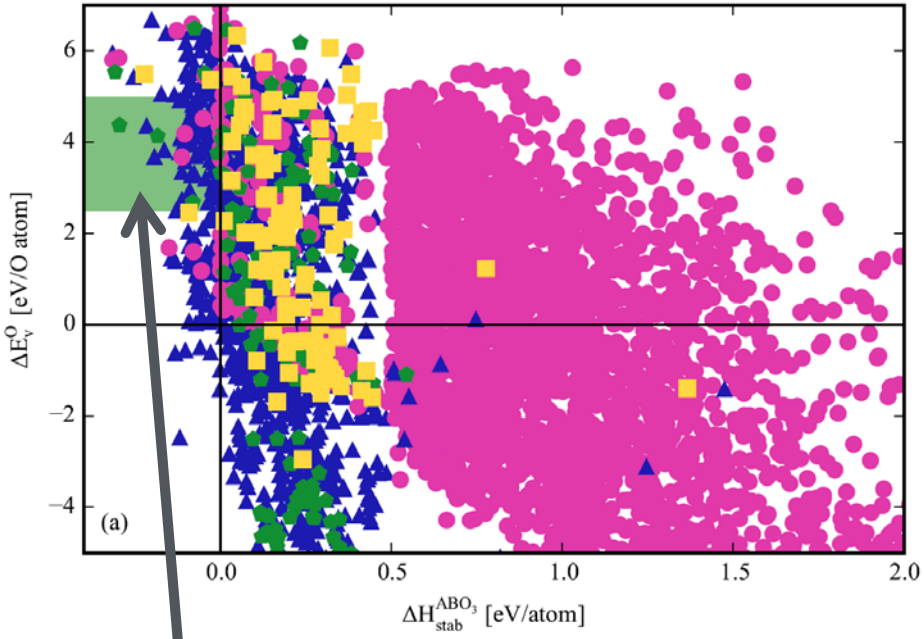


S. Kirklin, J.E. Saal, B. Meredig, A. Thompson, J.W. Doak, M. Aykol, S. Ruehl and C. Wolverton, npj Computational Materials (2015) 1, 15010

Accomplishments: High-throughput DFT Screening of STCH Materials

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



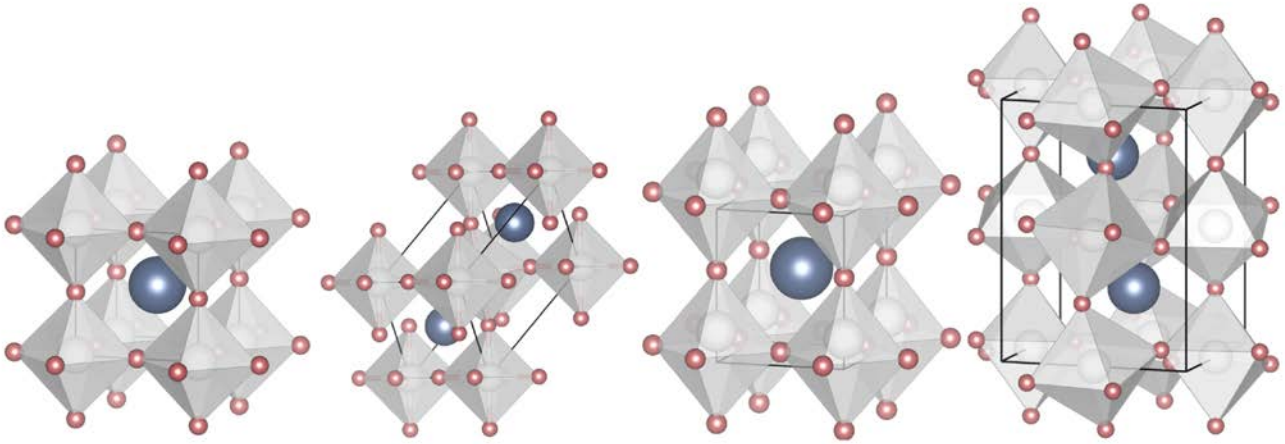


Targeted space: Stable (x<0) and Reduction Suitable for Water Splitting (y between 2.5 to 5 eV)

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

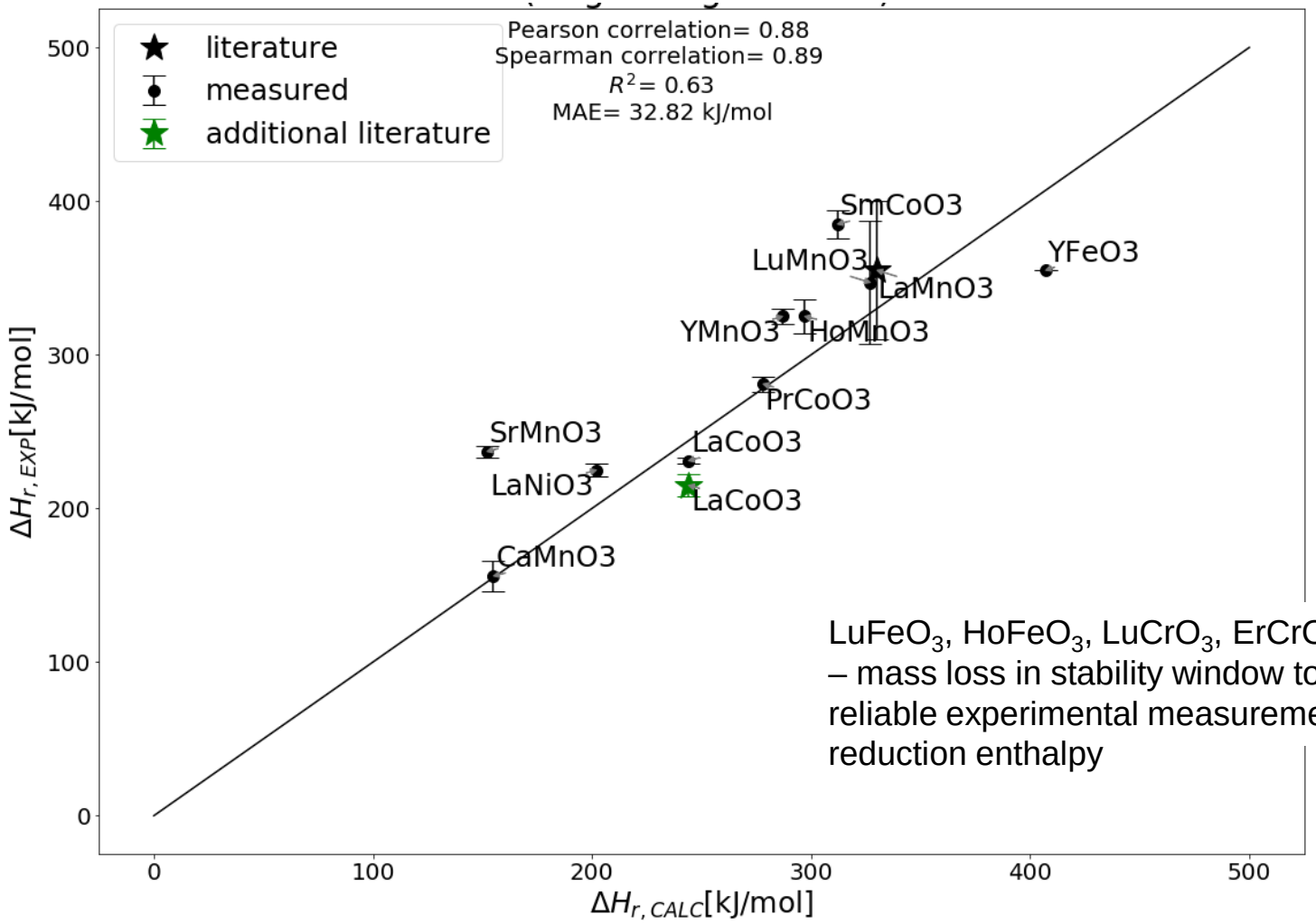
Vacancy Formation Energy in **distorted vs. cubic** perovskite = **4.22eV vs. 3.20 eV**

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

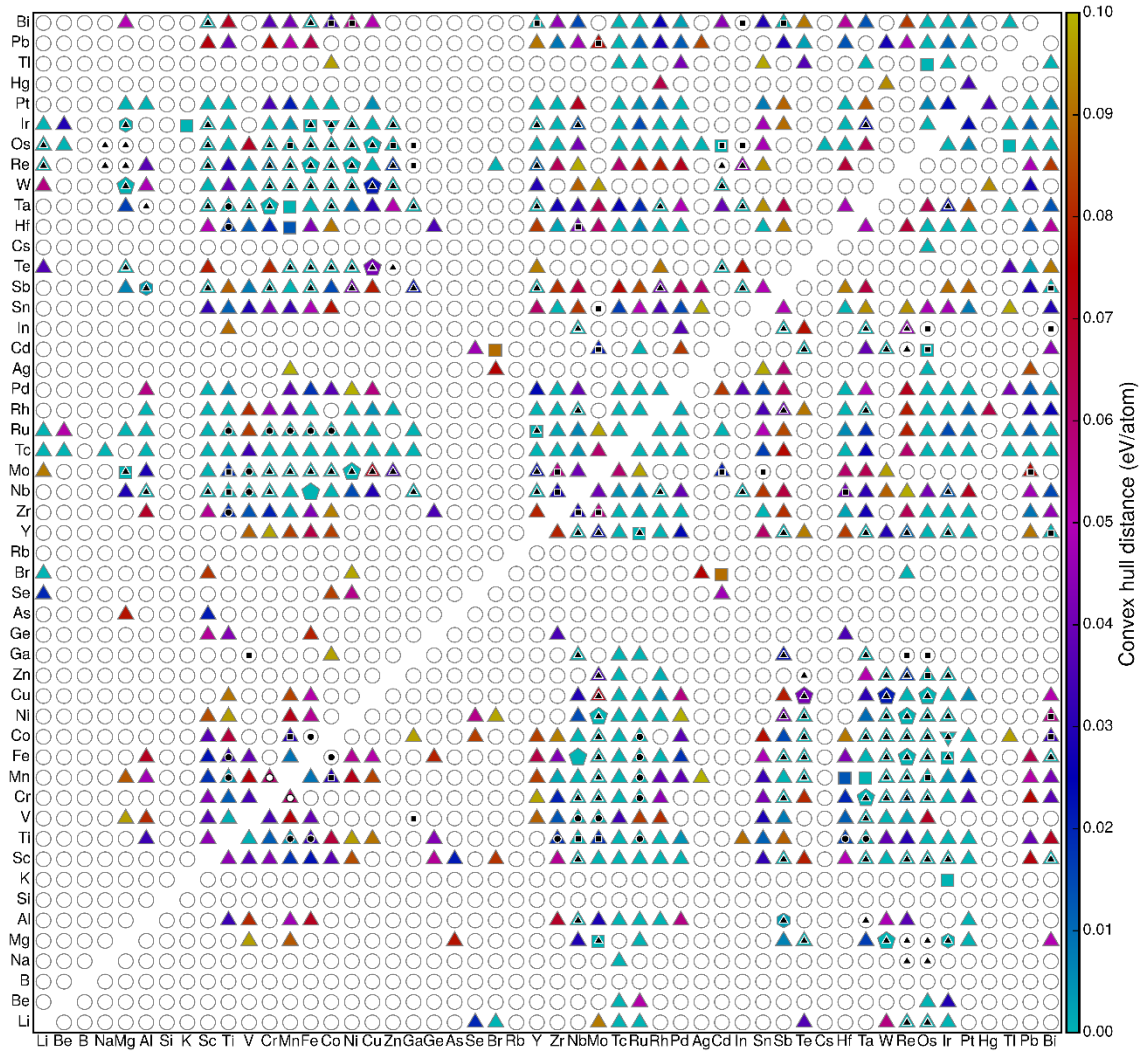
Comparison of Experimental and DFT Calculated Reduction Enthalpies (Key factor for both reduction and water splitting reactions)



$LuFeO_3$, $HoFeO_3$, $LuCrO_3$, $ErCrO_3$, $HoCrO_3$ – mass loss in stability window too small for reliable experimental measurement of reduction enthalpy

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

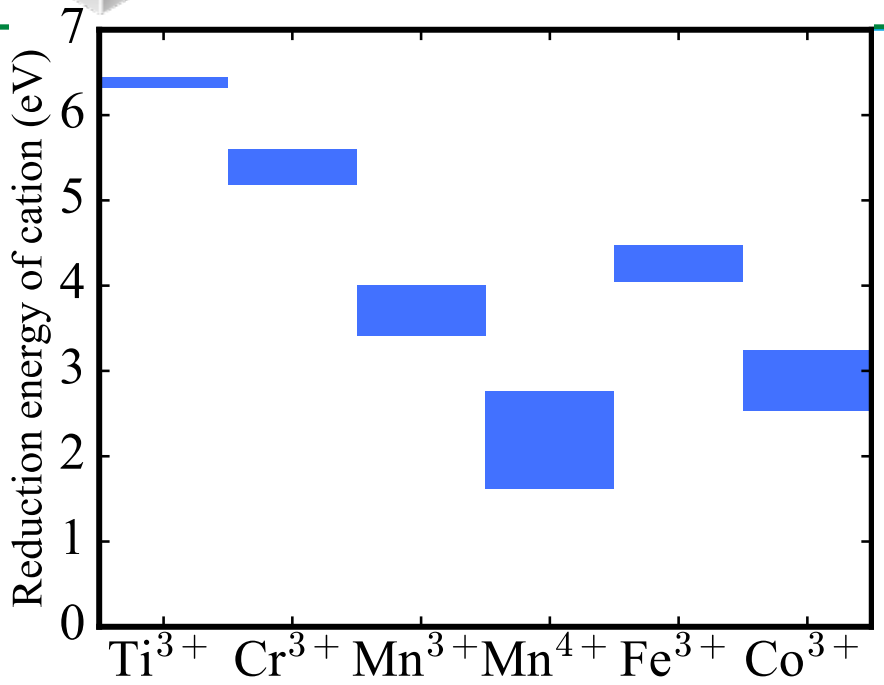
B-site ordered $Ba_2BB'O_6$



- HT calculations on ~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^O (eV/vacancy)
Sr_2TiMnO_6	P21/c	2.190
La_2CuMnO_6	P21/c	2.892
La_2ZnMnO_6	P21/c	3.031
Sr_2CuWO_6	Fm-3m	3.071
Sr_2CuWO_6	I4/m	3.111
Sr_2ZrMnO_6	Fm-3m	3.270
La_2NiMnO_6	P21/c	3.438

- **Key finding: B-site Mn^{4+} is much easier to reduce than other cations. Provides a chemical target for our search - double-perovskites with B-site Mn^{4+}.** (The spread of the value is mainly from the effects of octahedral distortion.)

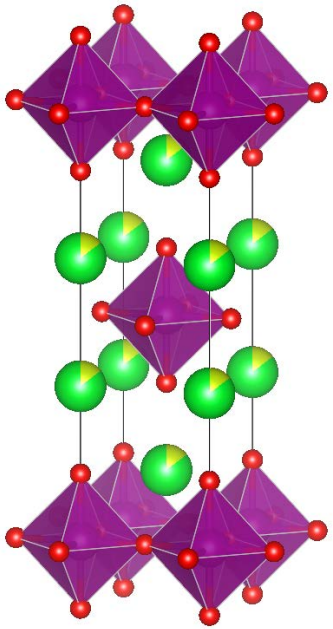
- Therefore, we performed DFT calculations on known Mn^{4+} containing double perovskites, and found the oxygen vacancy formation energy varies from 2.2 to 3.4 eV/vacancy.

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~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

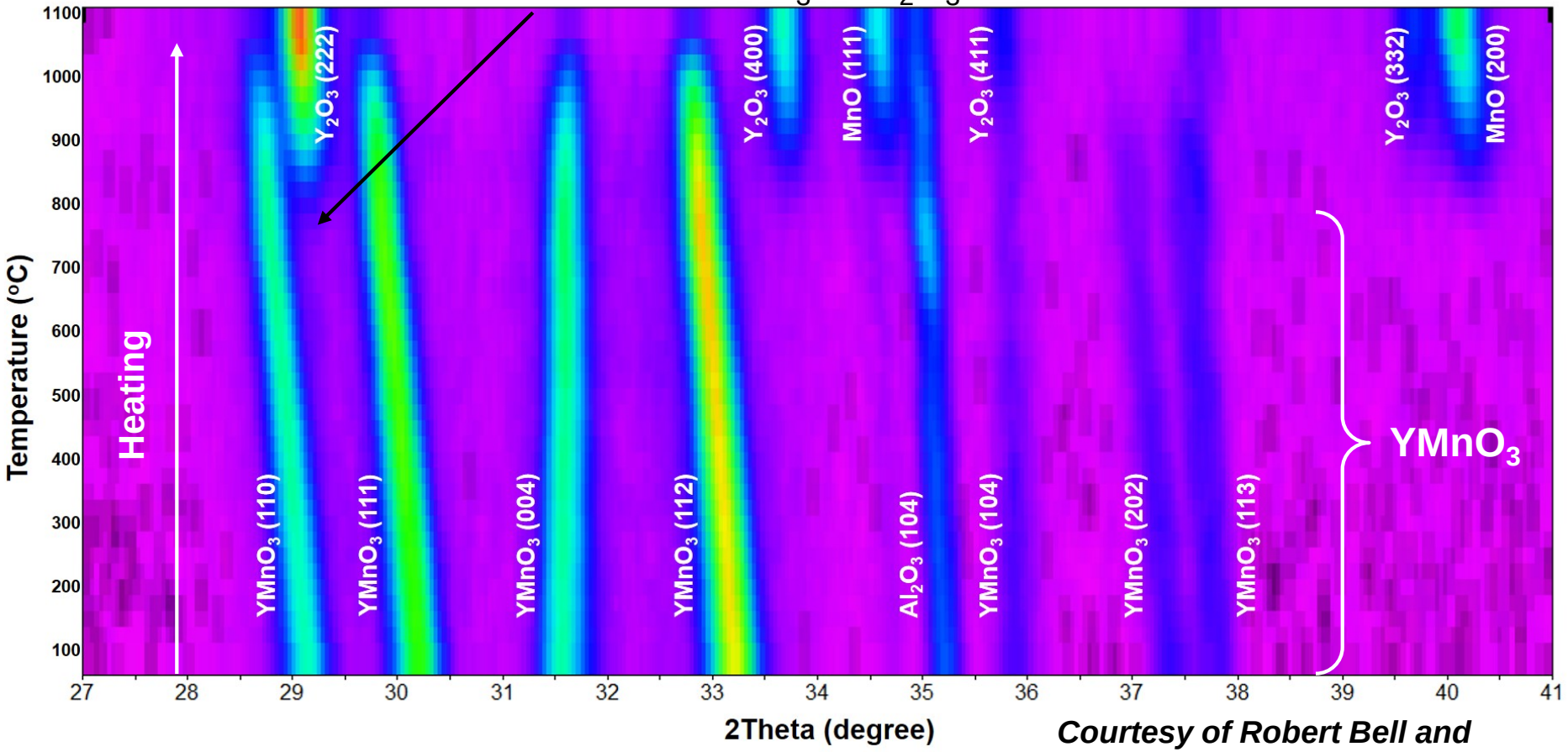
Collaboration with HydroGEN, data collected at SNL

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

825°C: $YMnO_3 \rightarrow Y_2O_3 + MnO$



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., $BaMn_xCe_{1-x}O_3$; 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.