Transformative Materials for High-Efficiency Thermochemical Production of Solar Fuels

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Project ID
PD167

Project Overview

Project Partners

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Sossina Haile, Northwestern University

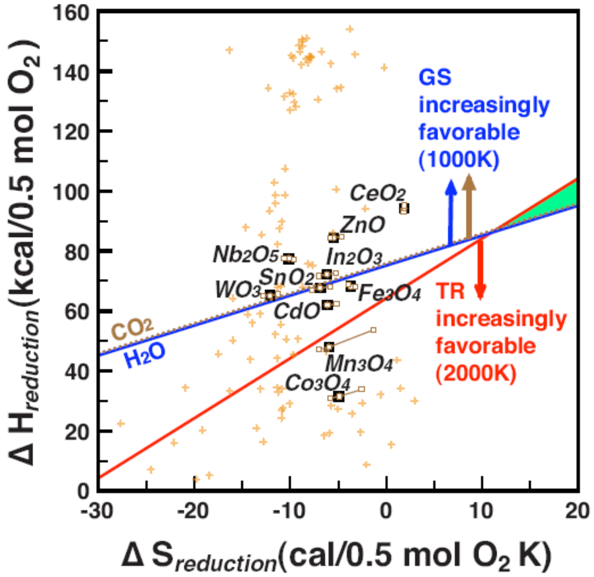
Award #	EE0008089
Start Date Yr 1 End Date Project End Date	10/01/2017 09/30/2018 TBD
Total DOE Share Total Cost Share Year 1 DOE Funding*	\$1,000,000 \$111,117 \$250K

Project Vision

Combine high-throughput computation and experiment to study the properties of novel, predicted 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

Key Impact

Identify promising compounds which show: a) ground state stability/synthesizeability of compound, 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.

Barriers

Risk mitigated by exploring two approaches to novel STCH materials: 1) Doped perovskite oxide materials, 2) Phase transformation materials, allowing combination of excellent thermodynamics and high-capacity

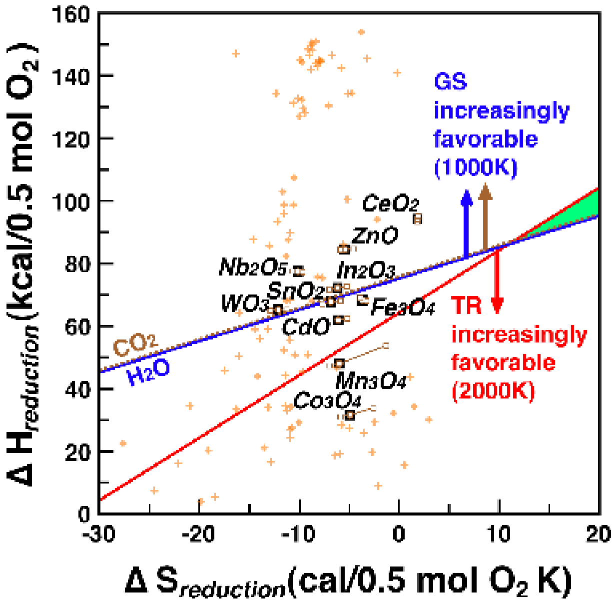
Partnerships

Productive collaborations with several HydroGEN nodes initiated: Lany (NREL) – computational materials science, Wood (Sandia) – mesoscale modeling capabilities, Ginley (NREL) – in-situ XRD and materials synthesis.

Approach- Innovation

A Design Map for Materials:

Thermodynamics very challenging for <u>stoichiometric</u> 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,** Open Quantum Materials Database (OQMD) [3]
- ✓ 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

Previous materials typically either:

(a) oxides that exhibit phase transformations during reduction, or
(b) oxides that exhibit off-stoichiometry during reduction but do not undergo a phase transformation.

Dichotomy:

- Off-stoichiometric materials exhibit better kinetics, due to the large quantities of oxygen vacancies in the material,
- Phase transforming materials exhibit a large degree of reduction, and hence a large resultant amount of fuel.

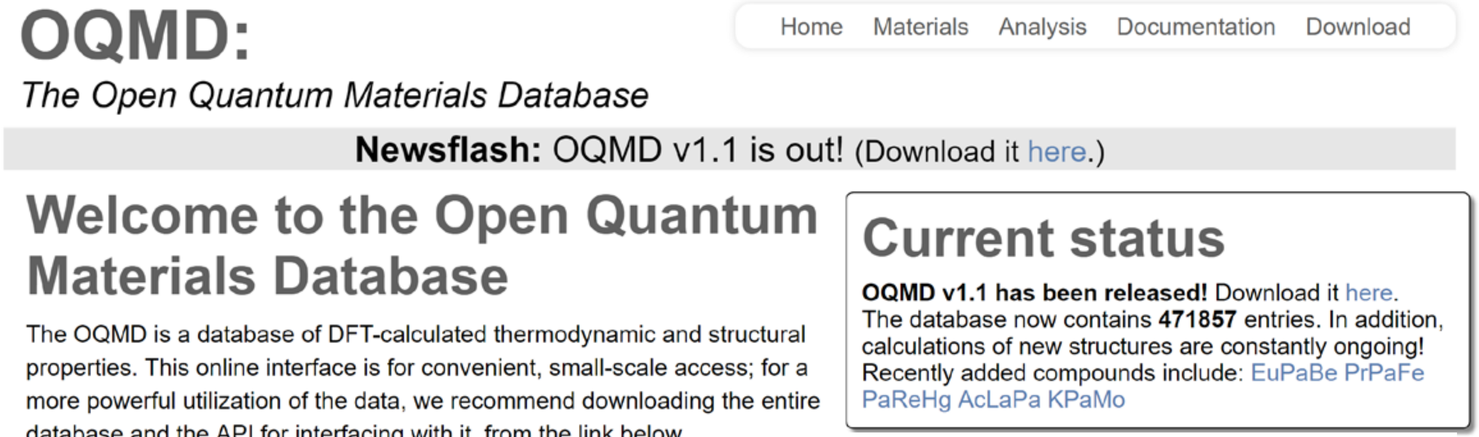
We break this false dichotomy by designing a new set of materials and reactions:

Phase transformation, but with *specifically tuned off-stoichiometric composition in both phases*. The former allows a large capacity of fuel, whereas the latter allows for fast kinetics. Perovskites ABO_3 or $AA'BB'O_6$ are potential materials.

Approach - Innovation

The Open Quantum Materials Database (OQMD) oqmd.org

Large-scale materials database of ~600,000 compounds



OQMD:

The Open Quantum Materials Database

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.

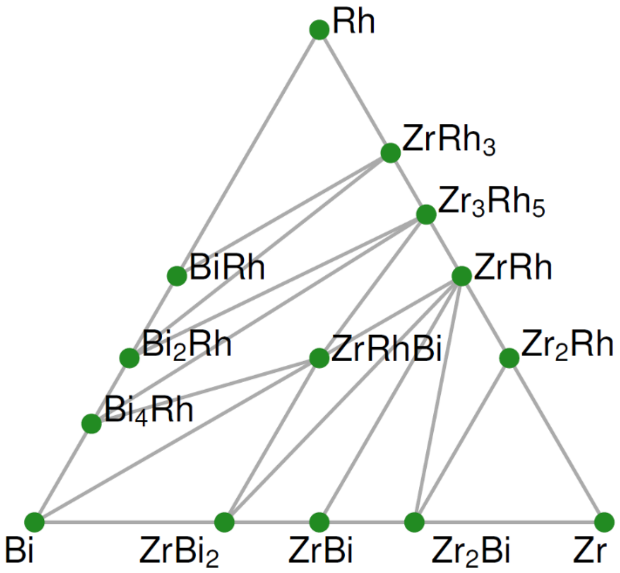
You can...

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

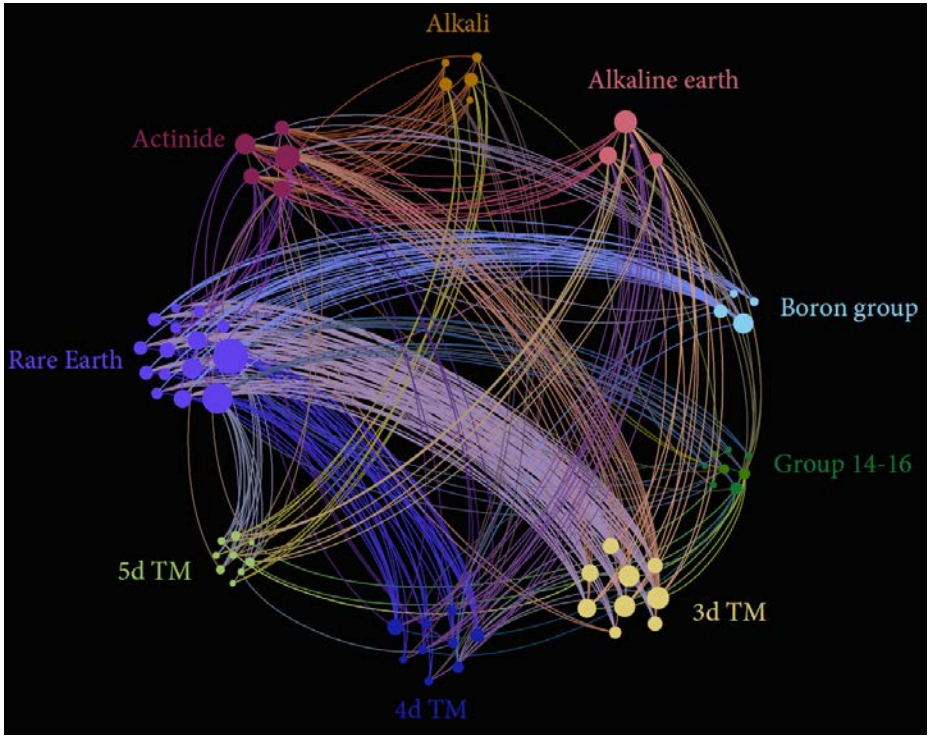
OQMD v1.1 has been released! Download it here.
The database now contains **471857** entries. In addition, calculations of new structures are constantly ongoing!
Recently added compounds include: EuPaBe PrPaFe PaReHg AcLaPa KPaMo

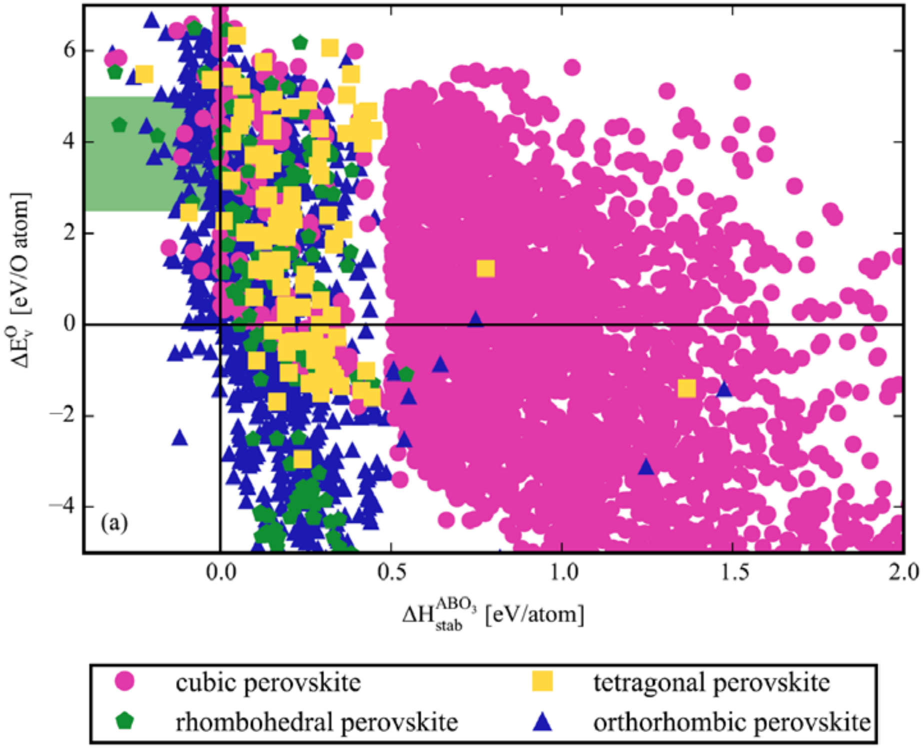
S. Kirklin, J.E. Saal, B. Meredig, A. Thompson, J.W. Doak, M. Aykol, S. Ruehl and C. Wolverton, npj Computational Materials (2015) 1, 15010



Approach – Innovation - High-throughput DFT

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





Provides initial targeted compounds for experimental exploration

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

Approach- Innovation

Summary of Year-1 Scope of Work

(a) Experimentally measure the reduction enthalpy and entropy of nine predicted 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

- 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 CeO2 and SLMA perovskite.

- Discovery of new, higher-efficiency materials is critical towards the practical use of STCH for H2 production (and solar fuels, more generally). ***Our combined high-throughput computation + experimental approach will greatly accelerate this materials discovery effort.***

- Our project involves discovery of phase-change material, STC hydrogen production evaluation, modeling and computation, collaborations with NREL, SNL, LLNL definitely will help facilitate the research progress.

Accomplishments

Go/No-Go Milestone

Validation and successful demonstration of our combined experimental/computational approach for the accelerated discovery of novel oxides for STC hydrogen production. This validation will be accomplished via comparison of computed (a) stability and (b) thermal reduction screening strategies:

Stability will be assessed in terms of the computed convex hull distances for all experimentally synthesized generation 1 perovskites. *Criteria 1: >90% of all experimentally synthesized perovskite materials should fall within 100 meV/atom of the computed convex hull, thus strongly demonstrating the accuracy of our approach to predict novel, synthesizeable compounds.*

Thermal reduction will be assessed in terms of a comparison of computed vacancy formation energies with experimental reduction enthalpies, measured by thermogravimetric analysis, for all generation 1 perovskites studied. Target enthalpy values are between 260 and 405 kJ/mol atom, potentially enabling up to five times the fuel productivity of ceria (ml H_2/g oxide) at a thermal cycle of 1400C reduction/800C oxidation. Both computational/experimental data will be ranked ordered, and Spearman rank correlation coefficient computed. *Criteria 2: A Spearman correlation >0.8 will indicate a successful validation of our methodology to predict materials capable of thermal reduction at any targeted temperature/pressure condition.*

Accomplishments

Thermodynamics Measurements

- $LuFeO_3$/$YFeO_3$/$HoFeO_3$/$YMnO_3$ were synthesized via the 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: $\Delta G = \Delta G^0 + RT\ln(K^{eq}) = 0$

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

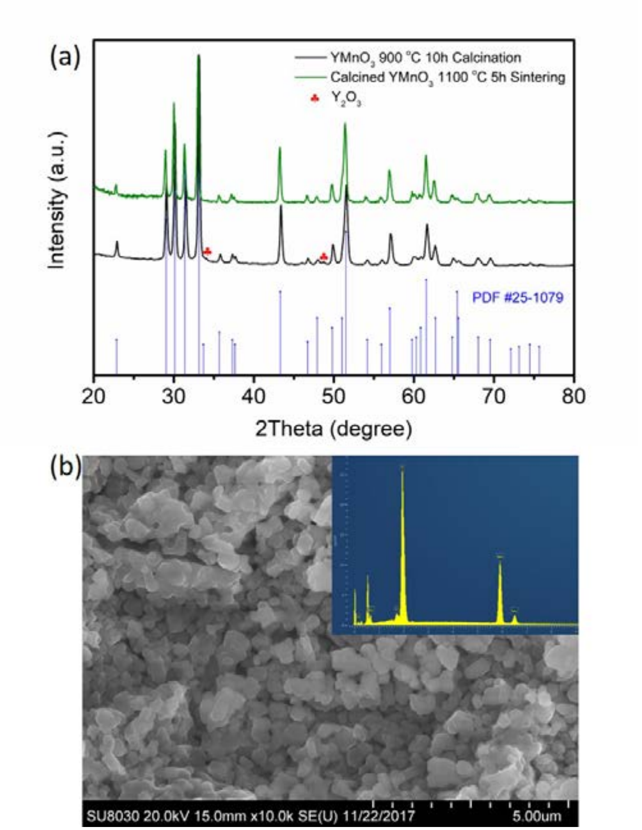
$$\frac{R}{2}\ln(pO_2) = -\frac{\Delta H^0}{T} + \Delta S^0$$

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

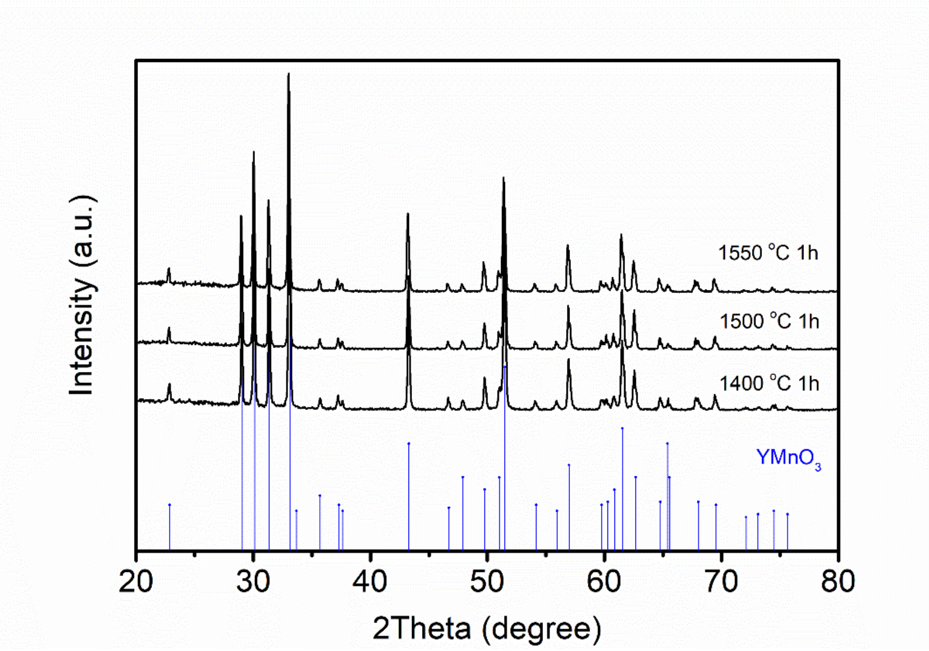
Accomplishments

$YMnO_3$

Synthesis and Characterization



900 °C 10h calcination + 1100 °C 5h Sintering
yield single phase $YMnO_3$, atomic ratio Y:Mn=50.9 : 49.1



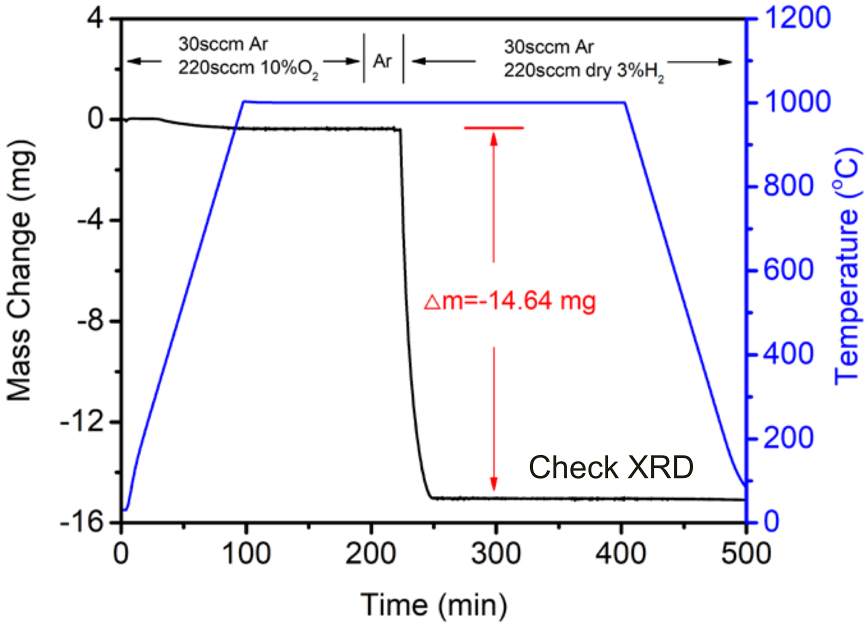
✓ $YMnO_3$ remains single phase until melting at 1600 °C

Synthesis and high-temperature stability of $YMnO_3$

Accomplishments

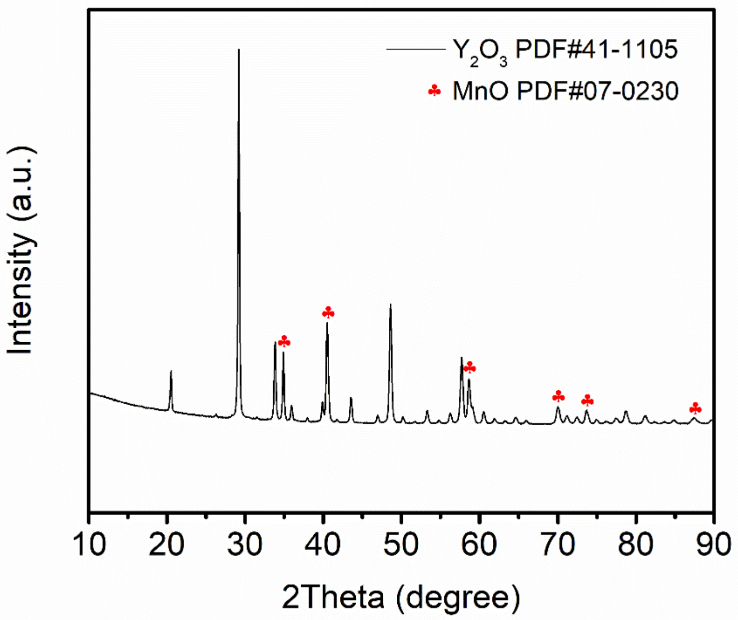
$YMnO_3$

Reference State Nonstoichiometry



Initial mass m_0 = 358.94 mg

Reference State: 1000 °C, pO_2=0.081 atm



XRD of fully reduced material

$YMnO_3$ was reduced to Y_2O_3 and MnO

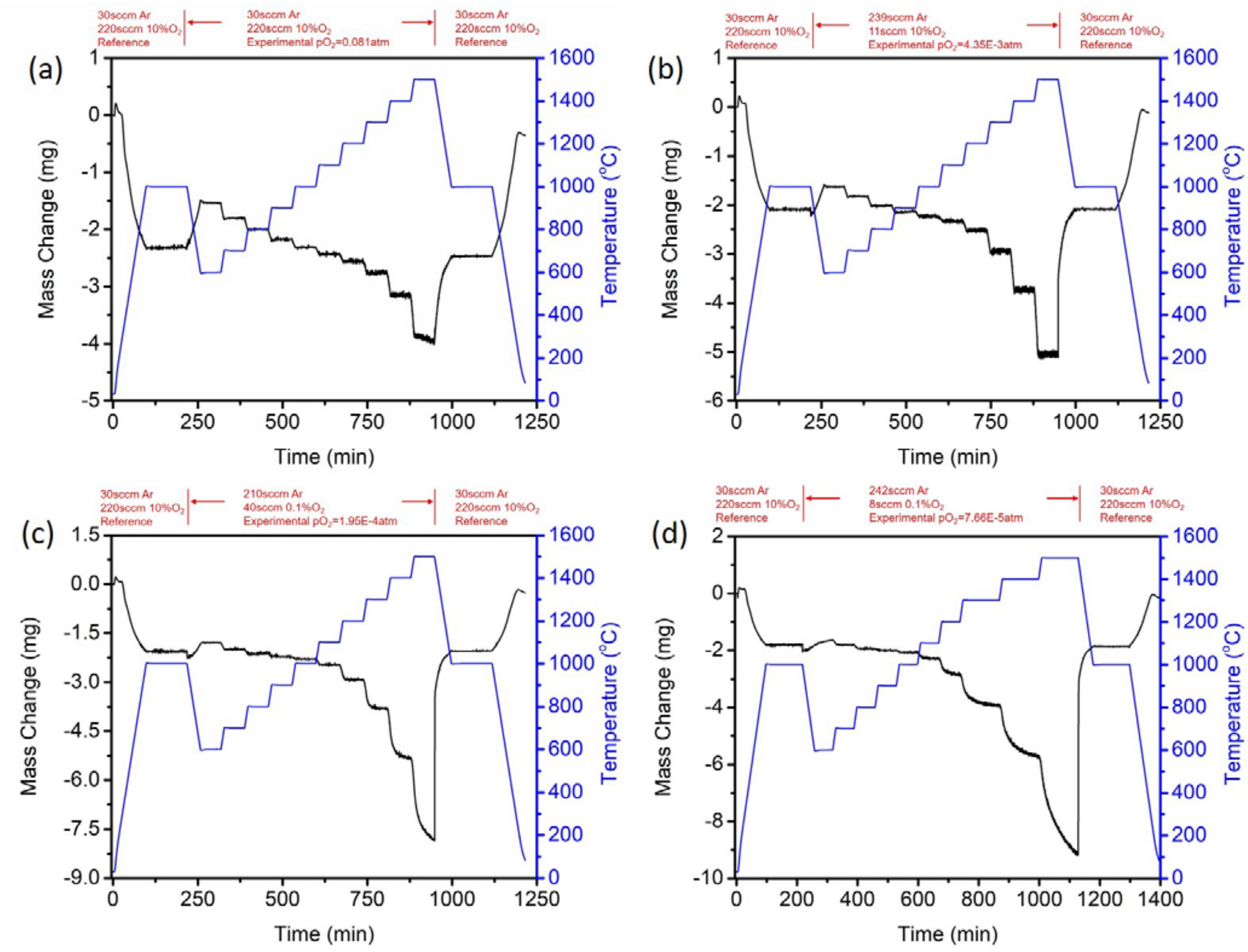
→ $\delta_0 = 0.0109$

Thermal reduction and non-stoichiometry of $YMnO_3$

Accomplishments

$YMnO_3$

TG measurements in Oxidizing Condition



(a) pO_2=0.081 atm, m_0=1735.19 mg;
(b) pO_2=4.35E-3 atm, m_0=1731.70 mg;
(c) pO_2=1.95E-4 atm, m_0=1731.30 mg;
(d) pO_2=7.66E-5 atm, m_0=1730.70 mg;

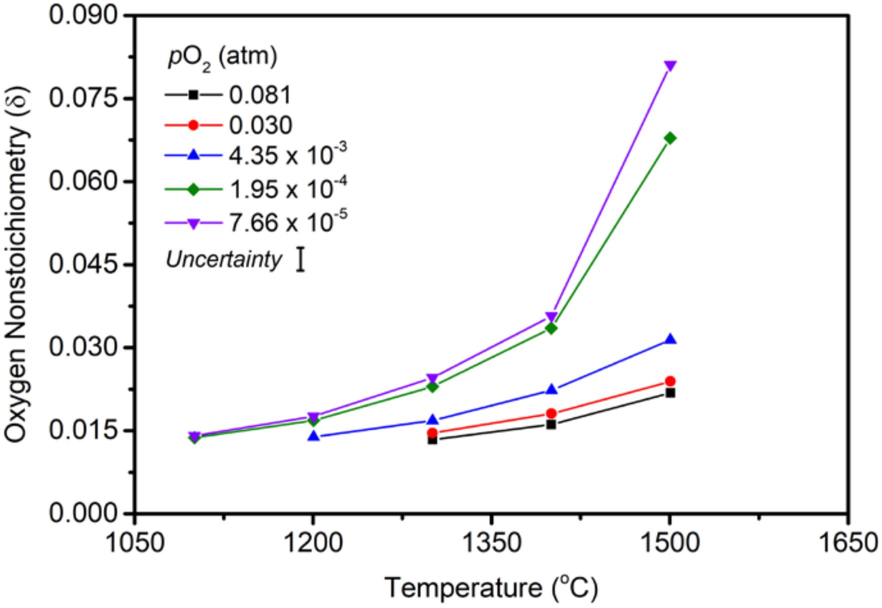
Observable mass loss under different oxygen partial pressure, mass recovers when return to reference state

Thermal Reduction of $YMnO_3$ as a function of p_{O2}

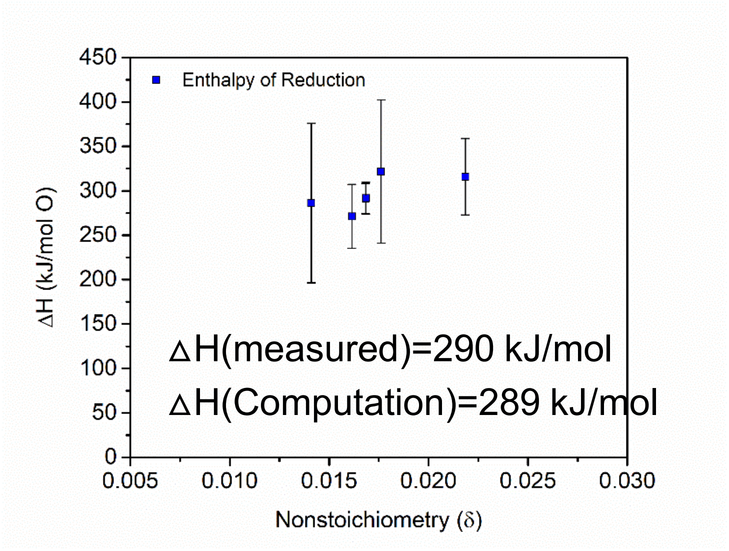
Accomplishments

$YMnO_3$

Redox Thermodynamics in Oxidizing Condition

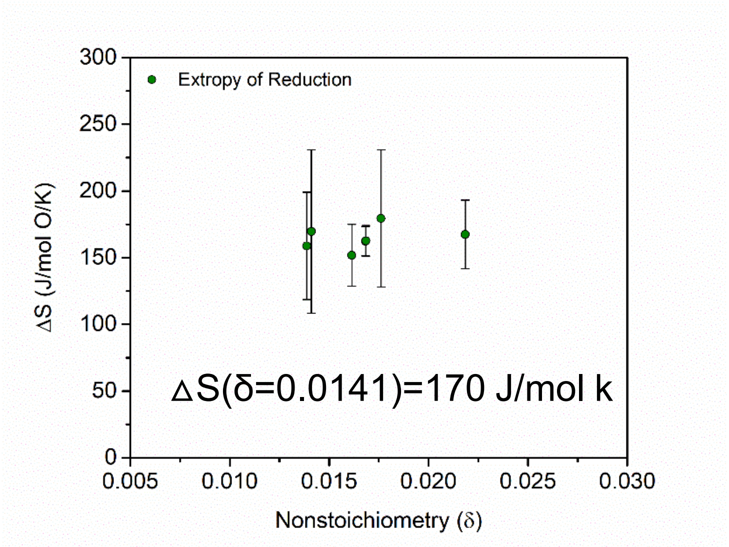


Oxygen nonstoichiometry at various pO_2



ΔH(measured)=290 kJ/mol

ΔH(Computation)=289 kJ/mol



$\Delta S(\delta=0.0141)$=170 J/mol k

Measured ΔH of reduction from non-stoichiometries; DFT calculations in excellent agreement!

Accomplishments

Other Perovskites: Synthesized, Reduced, and Comparison with DFT

Material	**Structure Information**				**Computational Predicted ΔH from cubic phase**	**Experimental temperature (°C) and pO_2 (atm)**	**Measured Oxygen Nonstoichiometry**
	Crystal Structure	Space Group	Lattice Constant (Å) ICSD	Lattice Constant (Å) Refined			
$LuFeO_3$	Orthorhombic	Pnma(62)	a = 5.5532 b = 7.5602 c = 5.2121	a = 5.55353 ± 0.00097 b = 7.56064 ± 0.00138 c = 5.21233 ± 0.00094	4.29 eV/atom or 413 kJ/mol	1000, 0.081 1200, 4.6×10^{-3} 800, 1.3×10^{-18}	0.0000 0.0026 0.0075
$YFeO_3$	Orthorhombic	Pnma(62)	a = 5.5930 b = 7.6033 c = 5.2804	a = 5.59302 ± 0.00064 b = 7.60330 ± 0.00085 c = 5.28044 ± 0.00061	4.20 eV/atom or 405 kJ/mol	1000, 0.081 1300, 4.6×10^{-3} 800, 1.3×10^{-18}	0.0000 0.0000 0.0000
$HoFeO_3$	Orthorhombic	Pnma(62)	a = 5.5915 b = 7.6060 c = 5.2800	a = 5.59153 ± 0.00052 b = 7.60603 ± 0.00068 c = 5.27999 ± 0.00049	4.26 eV/atom or 410 kJ/mol	1000, 0.081 1100, 4.6×10^{-3} 800, 1.2×10^{-16}	0.0000 0.0009 0.0000

Due to the high oxygen vacancy formation energy of $LuFeO_3$ / $YFeO_3$ / $HoFeO_3$, extremely small mass loss at reasonable temperature and pO_2 in TGA, resulting in nearly zero oxygen nonstoichiometry.

Three perovskites synthesized, but much more difficult to reduce (in agreement with DFT calculations)

Accomplishments

Comparing computational oxygen vacancy energies with experimentally measured reduction enthalpy

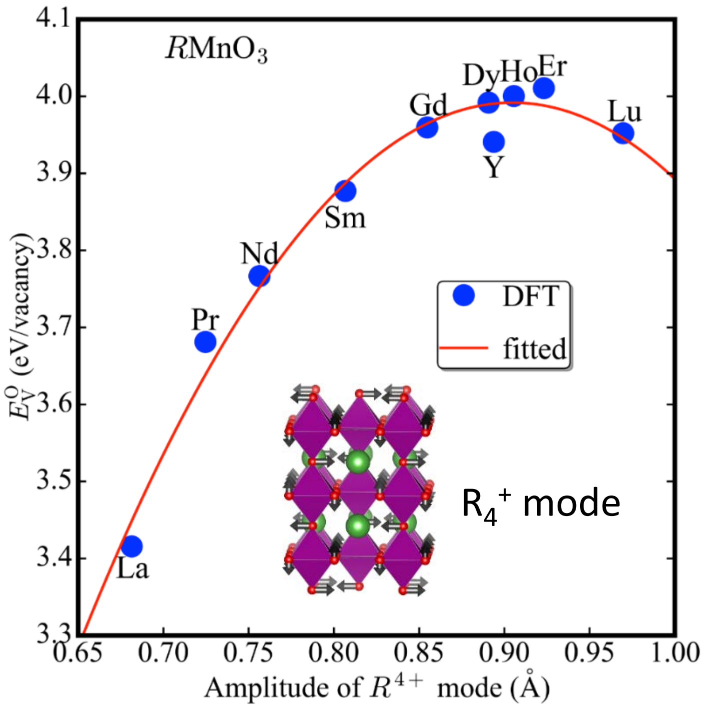
Reducibility (from easiest to hardest)	Measured Reduction Enthalpy	Predicted Oxygen Vacancy Formation Energy
$YMnO_3$	Easy	3.00 eV (289 kJ/mol)
$LuFeO_3$	Very hard	4.29 eV (413 kJ/mol)
$YFeO_3$	Hardest	4.20 eV (405 kJ/mol)

- The calculated oxygen vacancy formation energy of $YMnO_3$ (289 kJ/mol) agrees quantitatively with the measured reduction enthalpy (290 kJ/mol) very well.
- We find $LuFeO_3$ is slightly easier to reduce than $YFeO_3$, perhaps due to the formation of $Lu_3Fe_5O_{12}$ phase during reduction of $LuFeO_3$.
- We did not find an analogous $Y_3Fe_5O_{12}$ phase during reduction of $YFeO_3$ sample.
- We are currently working on characterizing the phase transformations during reduction.

Overall, good correlation between computational prediction of reduction and experimental measurements

Accomplishments

Engineering the Reduction Enthalpy of RMnO$_3$ Perovskites

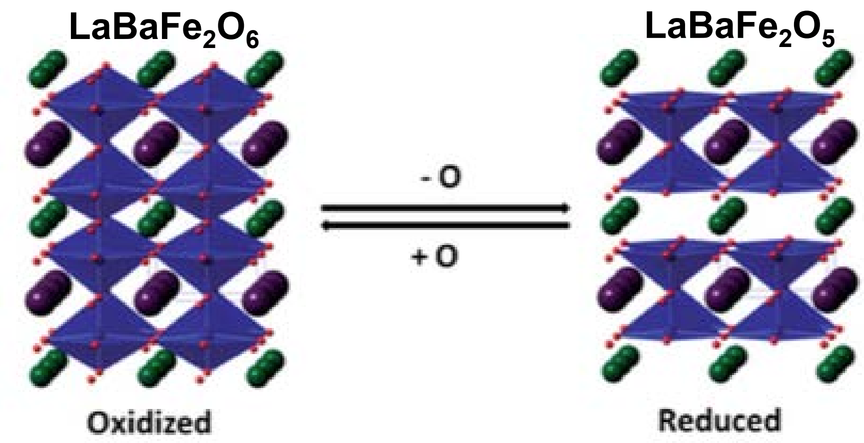


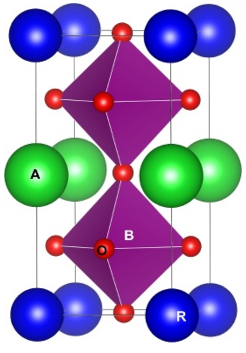
- DFT calculations of the oxygen vacancy formation energies (E_V^O) of RMnO$_3$ series in the Pnma structure.
- The Pnma crystal structure has two important octahedral distortion modes, R_4^+ and M_3^+.
- We find a strong correlation between amplitude of the R_4^+ mode, A-site cation size, and vacancy formation energy.
- This correlation allows us to engineer E_V^O by tuning the size of A-site cation.

Correlation between perovskite distortion and vacancy formation energy allows us to engineer reduction enthalpy by tuning the size of A-site cation.

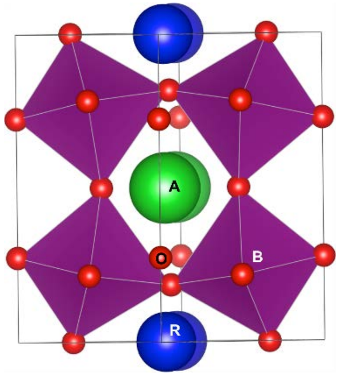
Accomplishments

Expanding the Materials Search: Double Perovskites





P4/mmm



Cmmm

- **Double perovskites** Ba*RM*$_2$O$_6$ (R=La and Y; M=Mn, Fe, and Co) can tolerate a large amount of oxygen vacancies, and **are candidates for high-capacity STCH reactions**.

- We perform **high throughput DFT screening to discover new, previously-unknown stable and metastable double perovskites *RAM*$_2$O$_6$** (*R*=rare earth; *A*=alkaline earth metal; *M*=transition metal).

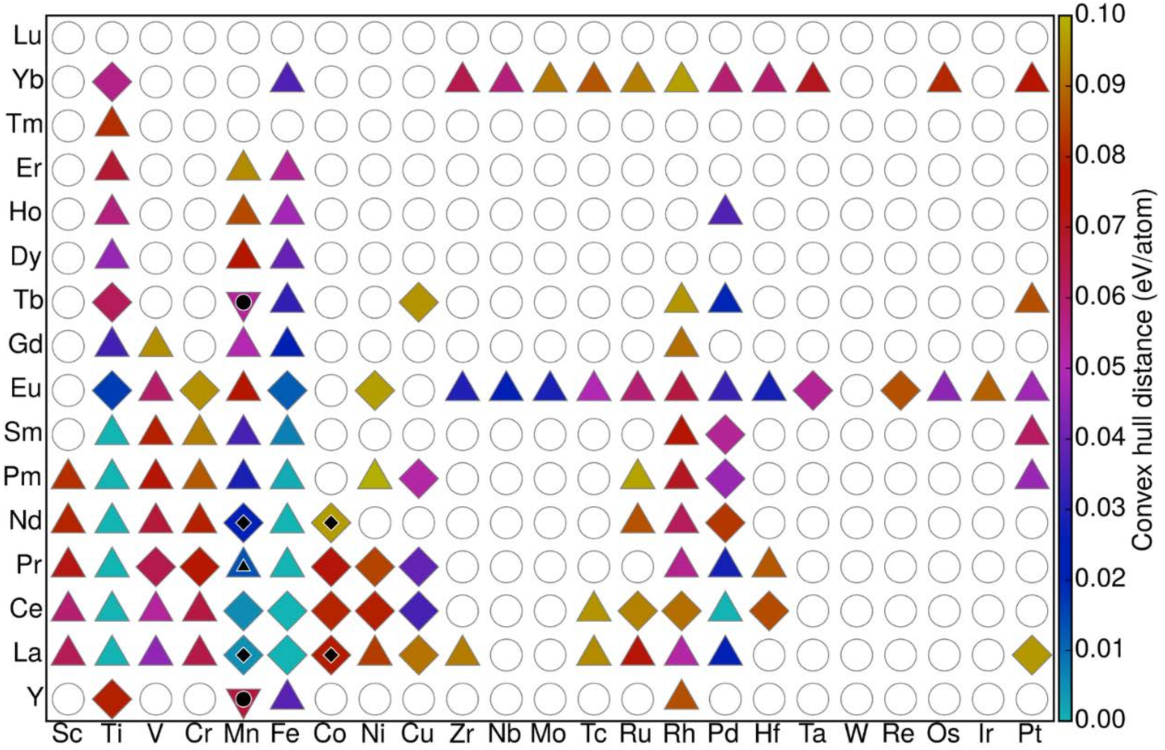
- We perform high-throughput calculations of a large space of *RAM*$_2$O$_6$ substitutions using two commonly-observed crystal structures (P4/mmm and Cmmm), .

Can we find new, previously undiscovered STCH materials using high-throughput computations?

Accomplishments

High-Throughput Discovery of BaRM_2O_6 double perovskites (A-site ordering)

- High throughput DFT calculations of BaRM_2O_6 (*R*=rare earth; *A*=alkaline earth metal; *M*=transition metal) compounds.
- All experimentally known compounds reported in ICSD (black diamond or triangle) are stable or metastable, confirming our screening approach.



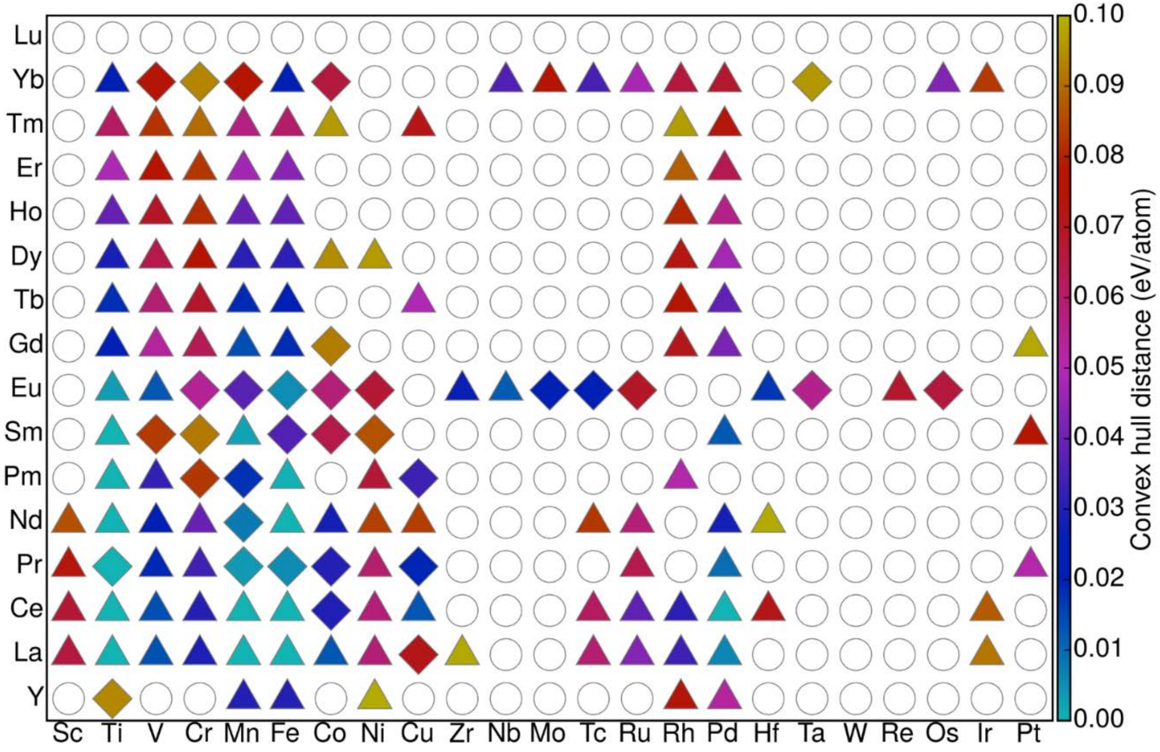
Many new stable double perovskites found!

Next step: Compute reduction enthalpies to target promising STCH materials.

Accomplishments

High-Throughput Discovery of SrRM_2O_6 double perovskites (A-site ordering)

- High throughput DFT calculations of SrRM_2O_6 (R=rare earth; A=alkaline earth metal; M=transition metal) compounds.
- No experimentally known compounds in this class reported in ICSD, hence all stable compounds represent new predictions.



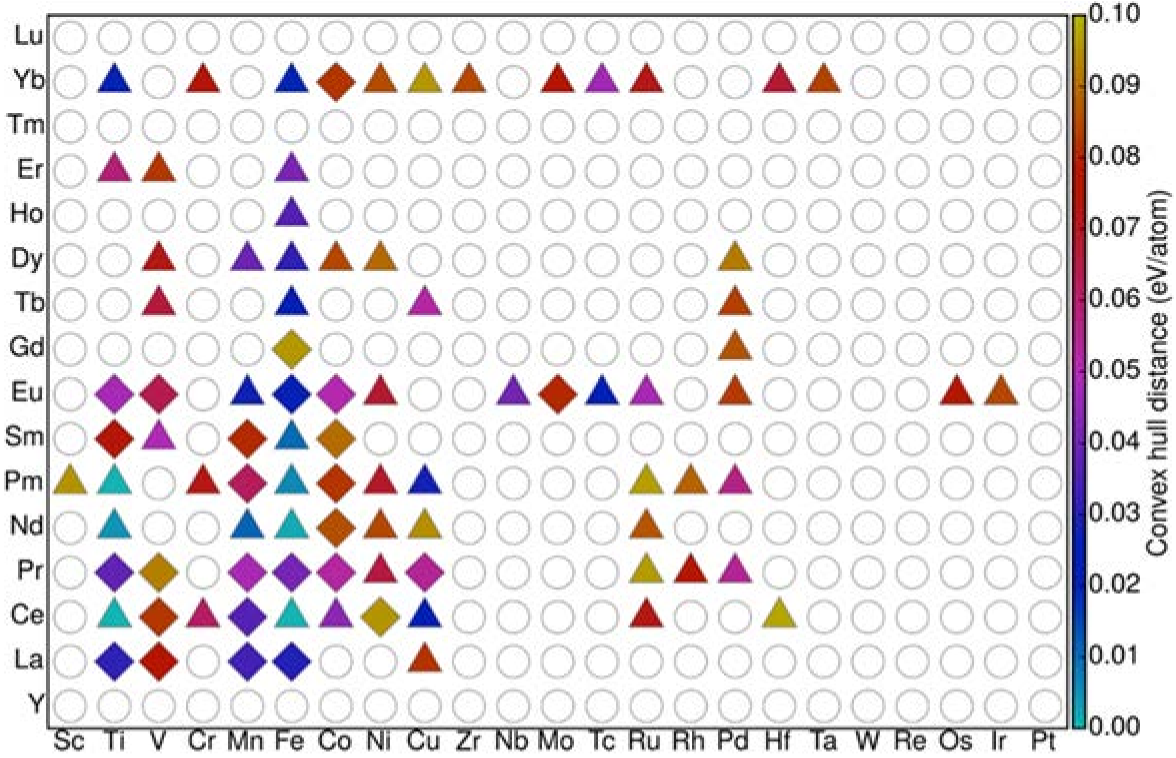
Many new stable double perovskites found!

Next step: Compute reduction enthalpies to target promising STCH materials.

Accomplishments

High-Throughput Discovery of $CaRM_2O_6$ double perovskites (A-site ordering)

- High throughput DFT calculations of $CaRM_2O_6$ (*R*=rare earth; *A*=alkaline earth metal; *M*=transition metal) compounds.
- No experimentally known compounds in this class reported in ICSD, hence all stable compounds represent new predictions.

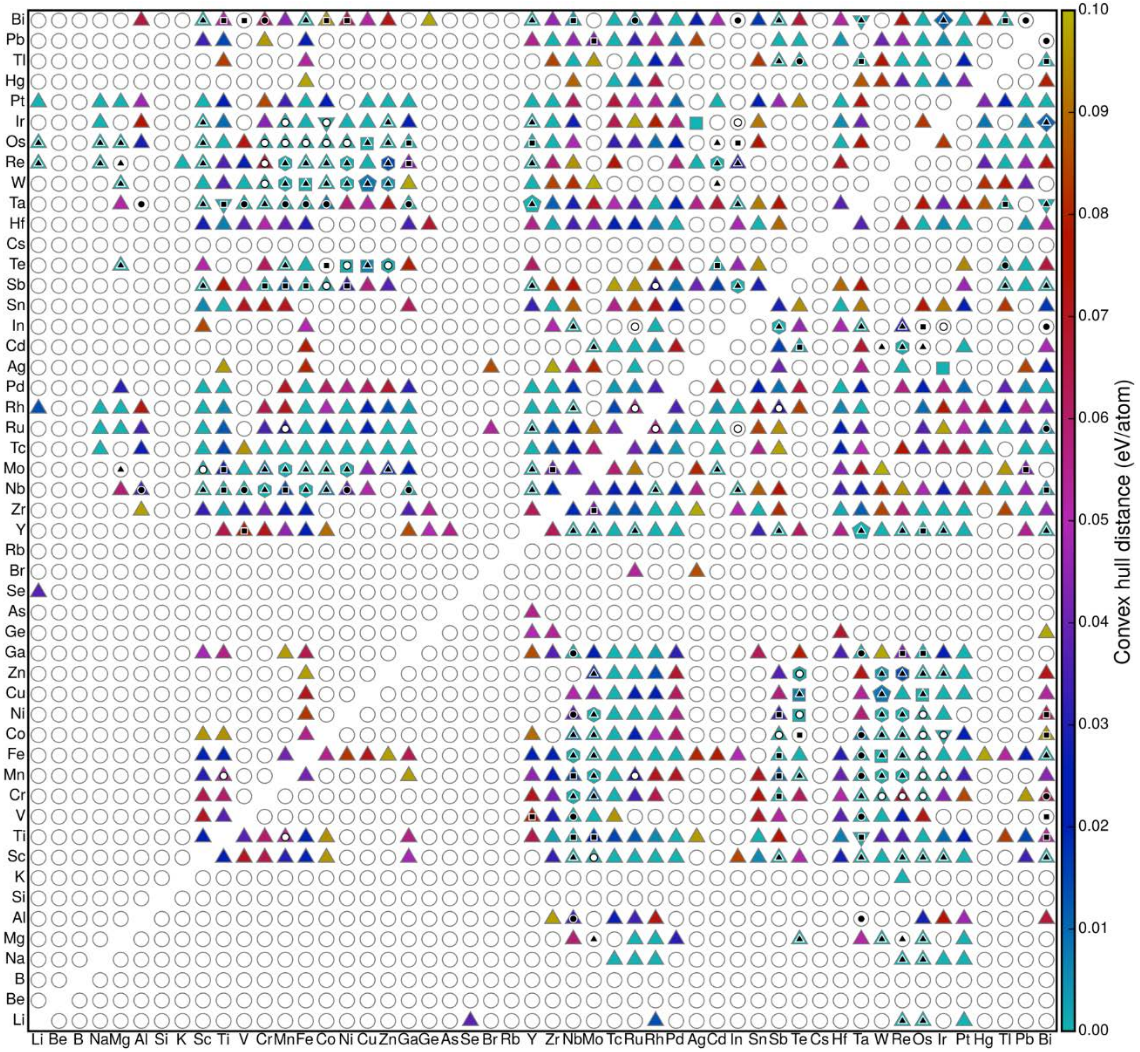


Many new stable double perovskites found!

Next step: Compute reduction enthalpies to target promising STCH materials.

Accomplishments

High-Throughput Discovery of $Ba_2MM'O_6$ double perovskites (B-site ordering)



- High throughput DFT screening has validated almost all the synthesized compounds (indicated by small symbols inside of the structure symbols).
- Strong validation of our high-throughput screening approach

321 new stable/metastable double perovskites are predicted using our strategy!

Collaboration: Effectiveness

- **Productive collaboration with EMN nodes initiated on several fronts, both computational and experimental:**
- **Brandon Wood (Sandia)** SNL group performing phase transformation/microstructure modeling based on our first-principles calculations, i.e., lattice constants, bulk modulus, and elastic constants.
- **Stephan Lany (NREL)** NREL group collaborating on accurate electronic structure calculations. NREL found that the charged defect can cause a large electronic entropy, which can have a large contribution to solar thermochemical hydrogen production. NREL group also working on FERE (fitted elemental-phase energies) corrections that will enable our high-throughput searches with higher accuracy to discover new compounds.
- **Dave Ginley (NREL)** Plan to conduct high-temperature in-situ X-ray diffraction under reducing atmosphere (humidified 3%H_2) either at CHESS or APS to understand the phase evolution of $LuFeO_3$ and $Lu_3Fe_5O_{12}$. NREL group can perform accurate measurements of the crystal structure at different temperatures and the amount of second phase in sample; effect of thermal expansion on oxygen vacancy formation. Knowledge of the phase distribution is essential for extracting thermodynamic data from thermogravimetric measurements. The latter reveal mass changes, but directly distinguish between nonstoichiometric oxygen loss and stoichiometric phase change.

Proposed Future Work

- Year 2 Objectives: The experimental work will test site-substituted versions of the most promising materials found in Year 1, and will also test double perovskite compounds predicted by computation in Year 1. Computational work in Year 2 will significantly expand range of chemistries consider for potential double-perovskites, will use experimental data from Year 1 to validate more refined thermodynamic models, and will expand range of reactions to consider phase-transformation reactions with excellent thermodynamic properties.
- Year 3 Objectives: The experimental work will focus on the morphological stability of the most promising reactions identified to date in the project, and will also focus on measuring the properties of double-perovskites predicted in Year 2. Computational work will use the more refined, validated thermodynamic models for final screening studies, and will focus computations on kinetic properties of the most promising compounds.

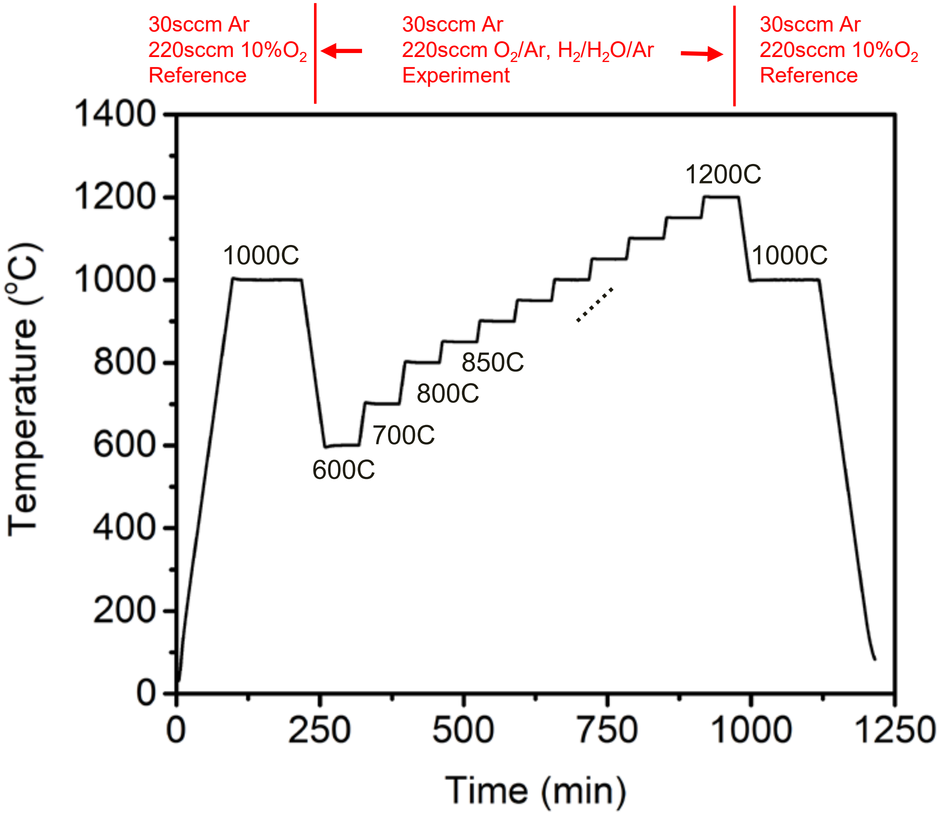
Project Summary

- High-throughput DFT has produced screening of tens of thousands of perovskite and double-perovskite materials. These calculations have largely been validated to date by comparison with experimental enthalpies of reduction. **This serves as a very effective strategy to accelerate experimental discovery of novel materials and reactions**.
- Computationally predicted $LuFeO_3$/$YFeO_3$/$HoFeO_3$/$YMnO_3$ were measured by TG at various oxidizing and reducing conditions, the redox thermodynamics of $YMnO_3$ was extracted while $LuFeO_3$/$YFeO_3$/$HoFeO_3$ have too high oxygen vacancy formation energy to be measurable via TG, consistent with DFT predictions.
- The sharp mass loss accompanied by phase change behavior at moderate temperature under reducing condition was observed in both $LuFeO_3$ and $YMnO_3$, both materials showed rapid mass recovery during reoxidation which reveals fast reaction kinetics, making them potential phase-change materials.

Technical Back-Up Slides

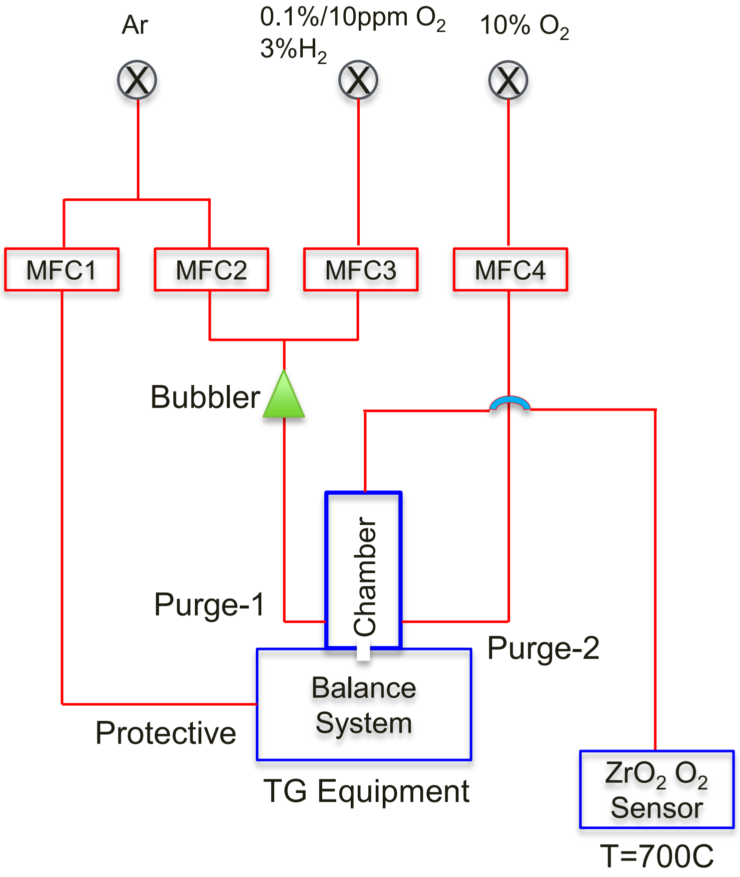
TG Measurement

Experimental setup



Step-wise Measurement

need internal reference δ_0, determine δ_0 separately



Automated gas switch