Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Mixed Ionic Electronic Conducting Quaternary Perovskites: Materials by Design for STCH H_2

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Project ID # p168

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

Project Overview

Project Partners

PI, Arizona State University

Co-PI, Princeton University

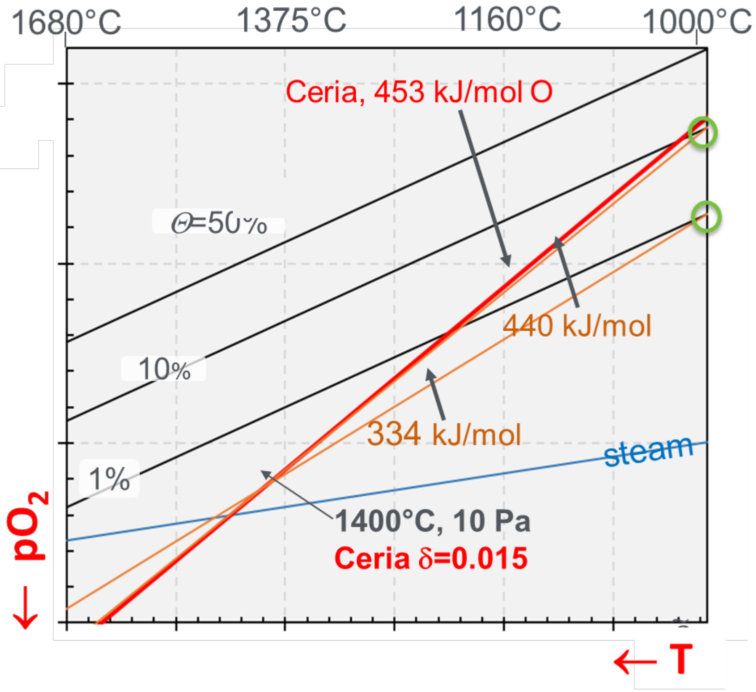
Award #	EE0008090
Start/End Date	10/01/2017 – 3/31/2021
Total Project Value*	$702,200
Cost Share %	10.30%

Project Vision

We are solving the challenge of computing the solid state oxygen chemical potential for complex mixed ionic electronic (off-stoichiometric) perovskite solid solutions by using a sublattice model formalism and accurate zero temperature first principles calculations, from which we can extract off-stoichiometry as a function of gas phase conditions (temperature, pO_2, steam/H_2 mix) and provide inverse design principles and at least one candidate material following the inverse design criteria.

Project Impact

We expect to contribute to materials discovery for improved STCH materials. We expect to offer strategies and candidates that if able to be synthesized will boost solar to hydrogen thermal efficiency. This theoretical guidance will provide experimentalists with crucial input by determining best possible, thermodynamically consistent targets depending on operating conditions and guide systems design.



Approach- Summary

Project Motivation

In order to optimize the search for better materials for STCH, the field needs inverse design criteria, hence we see a need to determine the optimum reduction enthalpy (ΔH) that balances degree of reduction, hydrogen yield, and temperature swing and given that strategies to tune the ΔH and ΔS.

Metric	State of the Art	Proposed
Reduction Temperature	> 1500°C	< 1450°C
Reduction Capacity ($\Delta\delta$ per atom)	**0.01**	**0.04**
Reduction Enthalpy	~450 kJ/mol	~375-400 kJ/mol
Accuracy of modeled chemical potentials over relevant operating window	N/A	±20%

Barriers

- Direct comparison theory & experiment is difficult
- Open shells and disorder, difficult to calculate.
- Calculating sublattice models without experimental input is very difficult.
- Calculating the "equation of state" **off-stoichiometry δ as a function of the oxygen chemical potential** from 1st principles has never been attempted.
- Inverse design problem poorly defined because of wide range of possible operating conditions.

Partnerships

Prof. Emily Carter, Dr. Sai Gopalakrishnan, and Dr. Robert Wexler, Princeton University

NREL and Sandia National Laboratories

Expertise: Developing new DFT capabilities, complex oxides, calculating chemical potentials in complex disordered materials
Materials synthesis and characterization
Uncertainty quantification

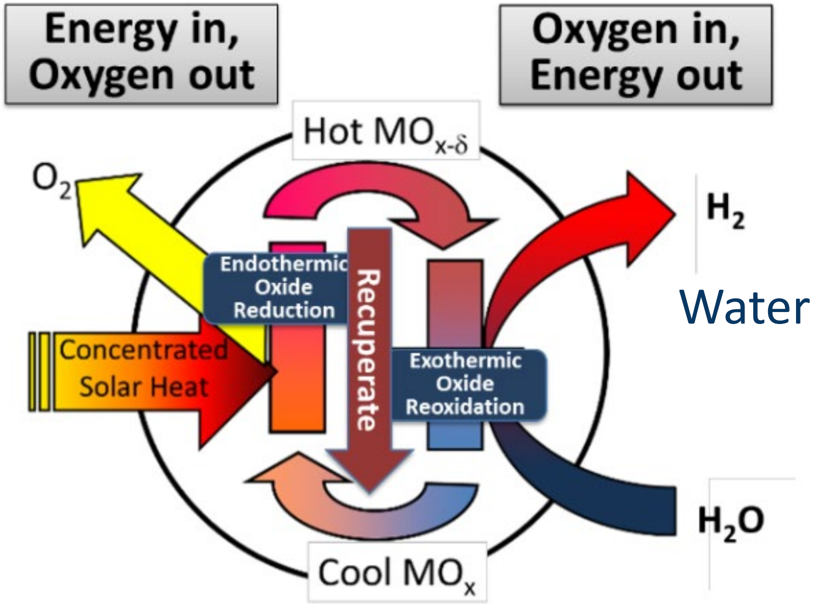
Specific capabilities: DFT functionals (SCAN+U), Computational Sublattice Model Formulation, Machine learning, Rigorous thermodynamic constraints.

Approach- Summary

Four interrelated pillars

1. Methodology that can calculate the off-stoichiometry and the solid state oxygen chemical potential from first principles
   - Based on the sublattice model formulation (aka Calphad, compound energy formulation)
   - Zero temperature DFT (using SCAN + U energy functional)
   - Validated using Zinkevich and Grundy Calphad models for ceria and $La_{1-x}Sr_xMnO_3$ – derived the general functional form from this approach to fit experimental data
2. Using insights gained from the sublattice model formulation to suggest new candidates
   - Validate with experimental synthesis and characterization
3. Identify rigorous thermodynamic relationships to determine target reduction enthalpy/entropy
   - Given constraints on practicalities to define (1) minimum yield (10%), (2) minimum oxidation temperature (600°C), (3) minimum partial pressure of O_2 (10 Pa), and (4) maximum reduction temperature (1450°C)
4. Identify and quantify model uncertainty to answer a key question
   - How accurate is accurate enough? How unique are fits to experimental data

Approach: Innovation
Background



Thermal reduction (TR): High T, low pO$_2$

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

Endothermic

Water splitting (WS): “Low” T, high (pH$_2$O/pH$_2$)

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

Exothermic

TR and WS reactions are thermodynamically feasible, if,

$$\Delta G_{TR} = \frac{1}{d\delta} G_{MO_{x-d\delta}} + ½\, G_{O_2} - \frac{1}{d\delta} G_{MO_x} \leq 0$$

$$\Delta G_{WS} = \frac{1}{d\delta} G_{MO_x} + G_{H_2} - \frac{1}{d\delta} G_{MO_{x-d\delta}} - G_{H_2O} \leq 0$$

Both expressions have solid and gas phase energetics.

We decouple the solid from the gas-phase thermodynamics

Approach: Innovation

Oxygen chemical potential in the Metal Oxide

$\frac{1}{d\delta}MO_{x-\delta} \rightarrow \frac{1}{d\delta}MO_{x-\delta-d\delta} + \frac{1}{2}O_2$ ***At equilibrium*** $\Delta G=0$

Rearranging and taking the limit $d\delta \rightarrow 0$

$$\frac{1}{d\delta}G(MO_{x-\delta}) - \frac{1}{d\delta}G(MO_{x-\delta-d\delta}) = -\frac{1}{2}G(O_2)$$

$$-\frac{dG(T,\delta)}{d\delta} \equiv \mu_{oxide} = \frac{1}{2}\mu_{O_2}(T_{TR}, pO_2\ ) = \mu_{H_2O}(T_{WS}, pH_2O)\text{-}\ \mu_{H_2}(T_{WS}, pH_2)$$

O chemical potential

Reduction

Re-oxidation

Changing the chemical potential of oxygen in the gas phase affects the oxygen stoichiometry to equilibrate the chemical potential of oxygen in the metal oxide

Rigorous relationships between enthalpy **δH**$\equiv \frac{d\Delta H_{reduction}}{d\delta}$, **$T_{TR}$**, **$p_{O2}$**, yield **θ** related to product ratio **pH_2O/pH_2**, and **$\Delta T=T_{TR}-T_{WS}$** have not previous been quantified.

Approach: Innovation

Calculate oxygen chemical potential (μ_O)

- μ_O of gas phase components (H_2O, H_2, and O_2) is well known and available

$$\mu_O^{H_2O/H_2,gas} = \mu_{H_2O} - \mu_{H_2}$$

  - e.g., from National Institute of Standards and Technology (NIST) or HSC

- μ_O of the solid phase requires calculating the Gibbs energy as a function of temperature and δ and differentiating wrt δ
  - Density functional theory (DFT) based approaches can yield good estimates for enthalpy, but estimating entropy is non-trivial
  - We aim to construct “simple” thermodynamic models based on the sublattice model formulation to get an “accurate enough” estimate of Gibbs energies and the solid state oxygen chemical potential

- Validated models with available data
  - For CeO_2, $(Ce,Zr)O_2$ (first year) and $La_{1-x}Sr_xMnO_3$ (last year) –demonstrate that the functional form works for perovskites more generally

- Devise thermodynamic target criteria
  - Strategy to increase reduction entropy and target for enthalpy of reduction
  - Suggest candidate material, synthesize, and characterize

Approach Innovation:
Comprehensive uncertainty management

- Overall goal is to predict thermodynamic efficiency given the thermodynamics of a material and a fixed operating cycle subject to thermodynamic constraints and specify uncertainty.
- SNL UQ (Uncertainty Quantification) node determines confidence needed on fitting to the sub-lattice model (a.k.a. compound energy formalism)
  - Bayesian model inference for thermodynamic behavior (oxygen chemical potential) of the redox active materials
  - Bayesian model comparison for fundamental equation for the off-stoichiometry as a function of gas composition, temperature, and/or partial pressure of oxygen.
  - Propagation of parametric uncertainty into thermodynamic properties is ongoing

Relevance & Impact

- **Efficiency** of the hydrogen production pathway is of critical importance to achieving **< $2/kg**.
  - This project makes a direct connection between computational thermodynamics, the potential efficiency, and management of key uncertainties.
- "**Good fit**" with the HydroGEN Consortium R&D model
  - **Uncertainty Quantification** in Computational Models of Phys. Sys.
    - ✓ Facilitate answering the question how accurate in measurements or computation is accurate enough to meaningfully inform materials discovery
  - Controlled **Materials Synthesis** and Defect Engineering
    - ✓ Facilitate validation of DFT predictions and further testing of candidates
  - **HT-XRD** and Complementary **Thermal Analysis**
    - ✓ Facilitate experimental determination of the oxygen chemical potential, μ_O
- Enhances the broader consortium by providing a missing link between computation, experiment, efficiency, and cost of H_2

Accomplishments & Progress

- Go/No-Go was provide 6/30/2019
  - **Goal: Identify candidate material with promise to perform better at lower temperature and/or higher partial pressure when compared to ceria.**
  - Synthesize, in collaboration with NREL STCH Node, up to two candidates Determine structure, phase purity, and lattice constants compare to theory
    - ✓ **Goal: 20% agreement between derived thermodynamics; i.e., chemical potential inferred from measurements and theory**
    - ✓ **Enthalpy & entropy of reaction rigorously from derivatives of μ_O**
- Significance: Direct comparison between theory and experiment through one function (the chemical potential), which can be directly inferred from experiment and calculated with zero temperature DFT.
  - Using a realistic operating cycle **connects materials discovery to technology**.
  - Uncertainty Quantification goal is to answer the question how good do measurements or computation have to be to differentiate between materials.
- We have derived rigorous theory for functional representation of the chemical potential, which can be used to extract the chemical potential from experiments or to use density functional theory
  - We have derived rigorous constraints relating yield to the thermodynamics and chosen operating conditions

Accomplishments & Progress

Higher entropy of reduction = higher capacity

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 ~0.034 (mol of O)/(mol atom ABO_3) higher than B-reduction only

- Equivalent to ~76 cm^3 O_2/(mol atom ABO_3)
- 0.01 (mol of O) off-stoichiometry in CeO_2 ~ 37cm^3 O_2/(mol atom CeO_2)

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

O_2(gas, 1473K, 10Pa)

Assuming ideal solution of mixing, large increase in ΔS_{red} possible if both A and B cations reduce simultaneously in ABO_3

Fixed ΔH_{red}, higher $\Delta S_{red} \rightarrow$ higher yield

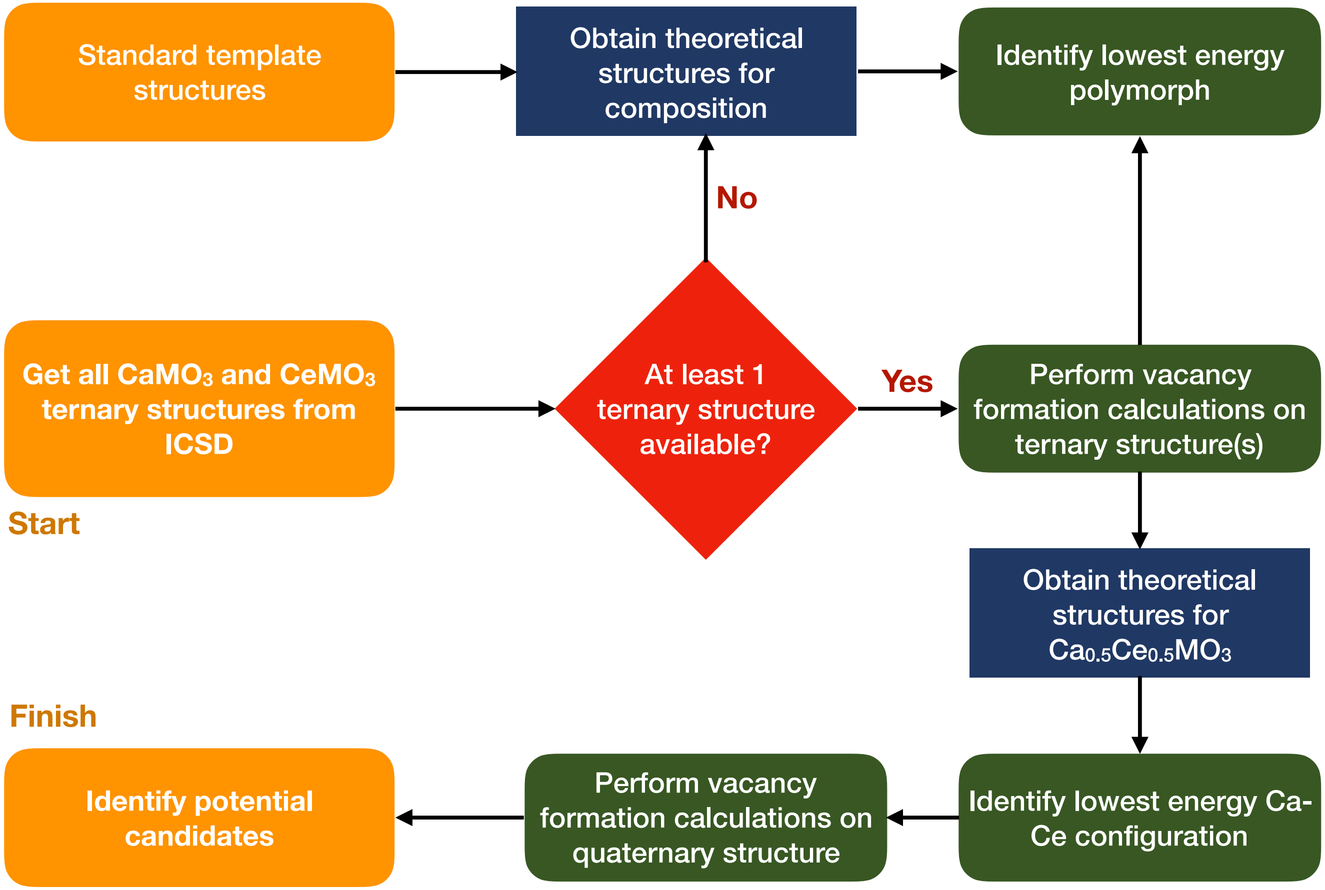
Potential simultaneously redox active ABO_3 perovskites?

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

Accomplishments & Progress

No experimental $Ca_{0.5}Ce_{0.5}MO_3$ structures available



Start

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

At least 1 ternary structure available?

No

Standard template structures

Obtain theoretical structures for composition

Identify lowest energy polymorph

Yes

Perform vacancy formation calculations on ternary structure(s)

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

Identify lowest energy Ca-Ce configuration

Perform vacancy formation calculations on quaternary structure

Finish

Identify potential candidates

High ΔH_{red}: no oxygen off-stoichiometry

Low ΔH_{red}: no water/CO_2 splitting

Candidates need to show optimal ΔH_{red}: use a 3.5-4. eV range

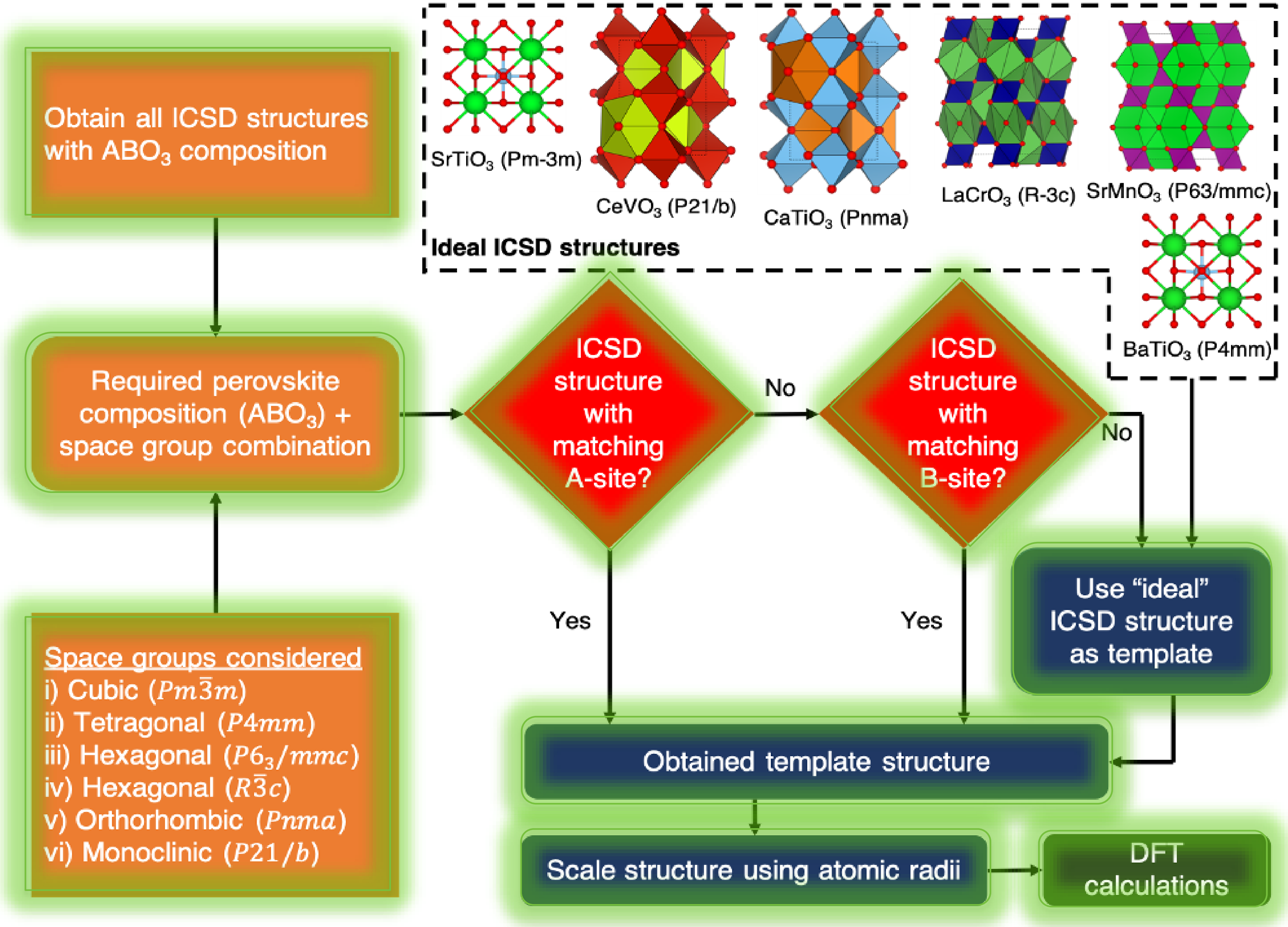
Density functional theory engine: strongly constrained and appropriately normed (SCAN) functional, corrected with optimal Hubbard *U* correction[1]

- $\Delta H_{red} \approx \mathrm{E_F}[\mathrm{Va_O}]$ (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.** *in press* **(2020)**

Accomplishments & Progress

Framework to obtain theoretical structures: Template matching



Obtain all ICSD structures with ABO_3 composition

Required perovskite composition (ABO_3) + space group combination

Space groups considered
- i) Cubic ($Pm\bar{3}m$)
- ii) Tetragonal ($P4mm$)
- iii) Hexagonal ($P6_3/mmc$)
- iv) Hexagonal ($R\bar{3}c$)
- v) Orthorhombic ($Pnma$)
- vi) Monoclinic ($P21/b$)

ICSD structure with matching A-site?

No

ICSD structure with matching B-site?

No

Yes

Yes

Use “ideal” ICSD structure as template

Obtained template structure

Scale structure using atomic radii

DFT calculations

Ideal ICSD structures

$SrTiO_3$ (Pm-3m)

$CeVO_3$ (P21/b)

$CaTiO_3$ (Pnma)

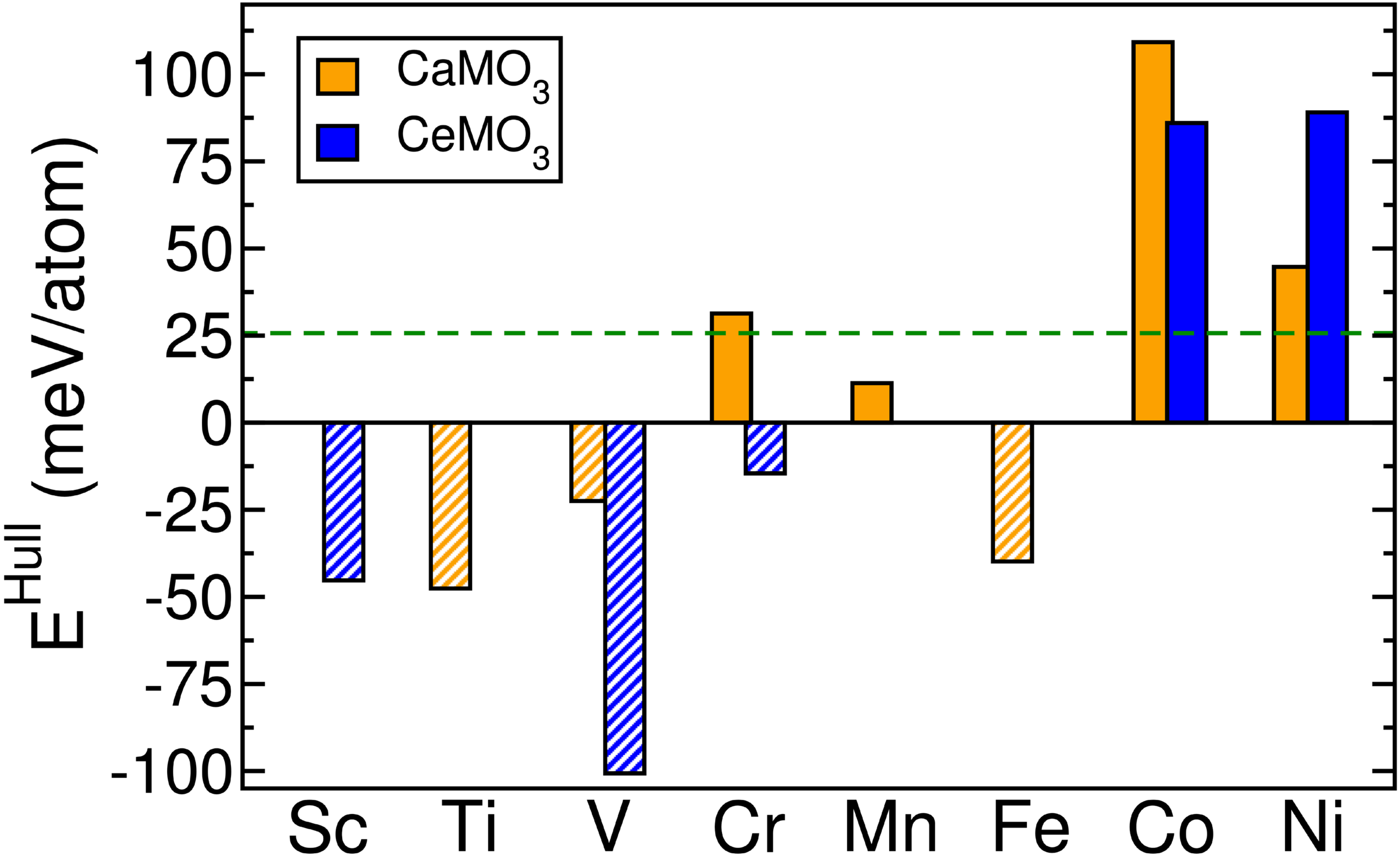
$LaCrO_3$ (R-3c)

$SrMnO_3$ (P63/mmc)

$BaTiO_3$ (P4mm)

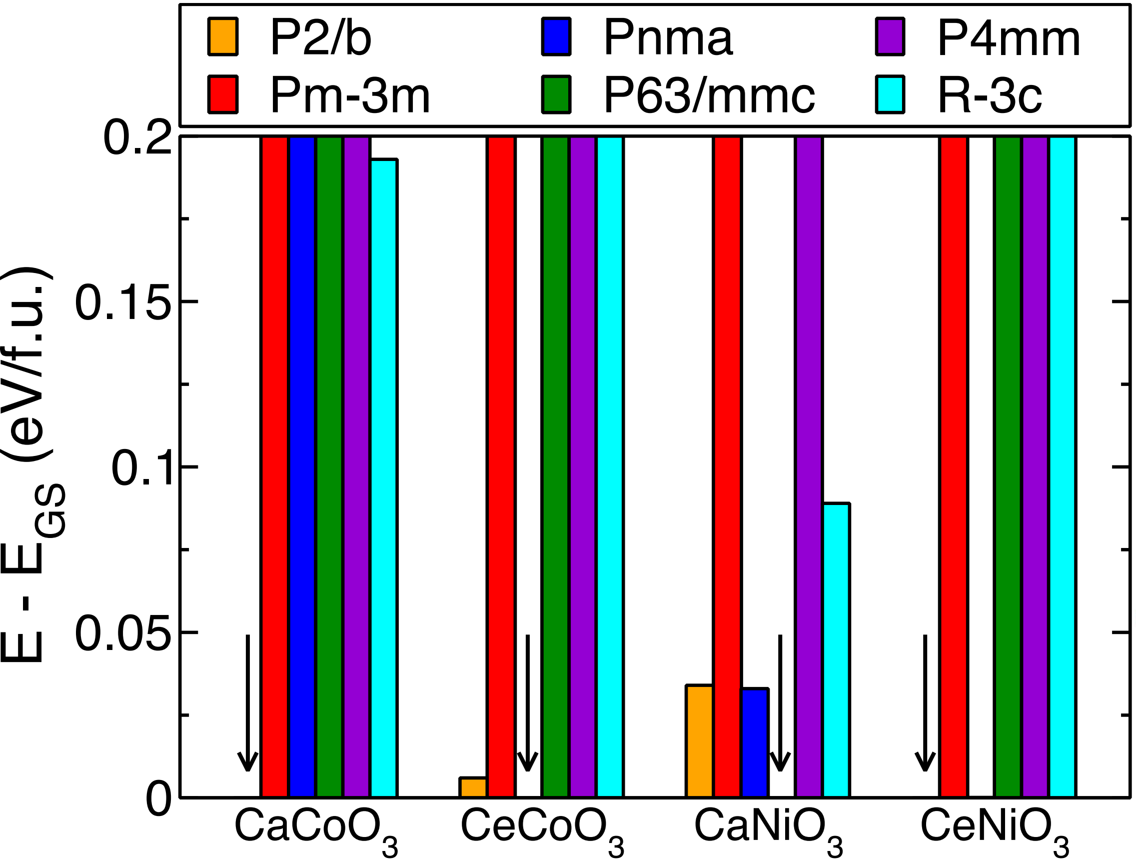
Accomplishments & Progress

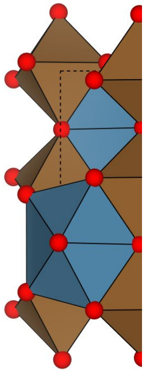
Ternary $CaMO_3$ and $CeMO_3$: 0 K stability



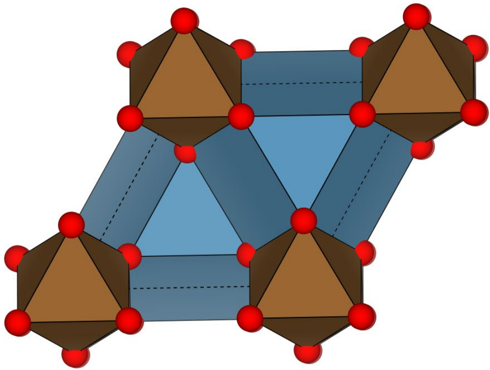
Accomplishments & Progress

Stable structures of Co and Ni perovskites



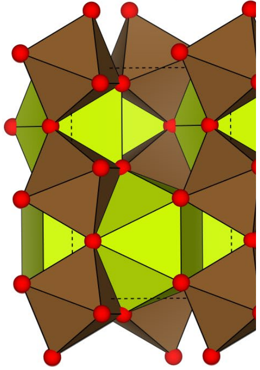


CaCoO$_3$ (P2/b)

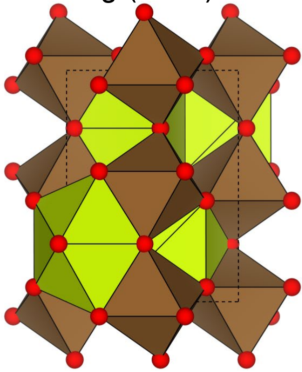


CaNiO$_3$ (P63/mmc)

CeCoO$_3$ (Pnma)

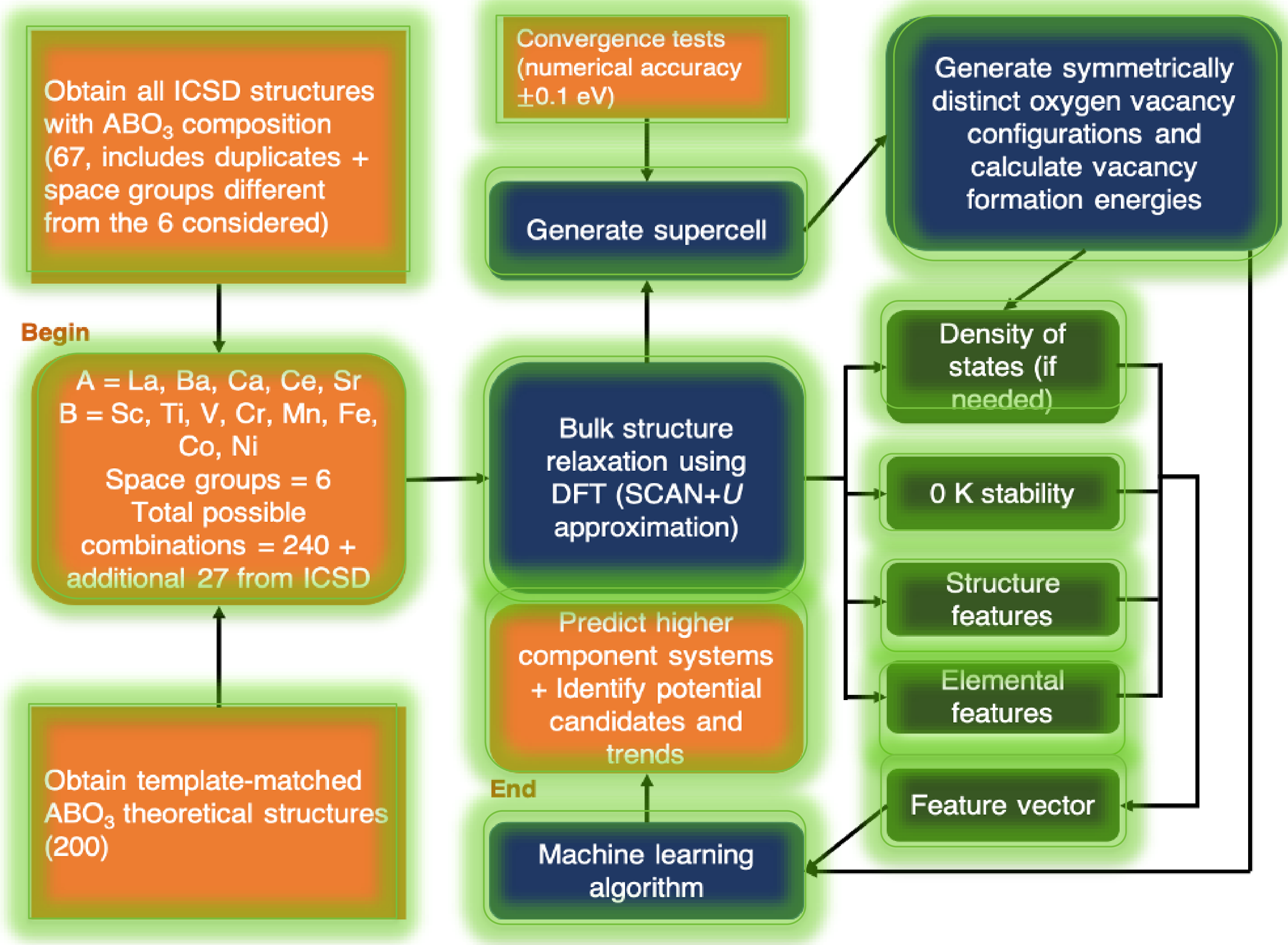


CeNiO$_3$ (P2/b)



Accomplishments & Progress

Framework to generate a Machine Learning model



Obtain all ICSD structures with ABO_3 composition (67, includes duplicates + space groups different from the 6 considered)

Convergence tests (numerical accuracy ±0.1 eV)

Generate supercell

Generate symmetrically distinct oxygen vacancy configurations and calculate vacancy formation energies

Begin

A = La, Ba, Ca, Ce, Sr
B = Sc, Ti, V, Cr, Mn, Fe, Co, Ni
Space groups = 6
Total possible combinations = 240 + additional 27 from ICSD

Bulk structure relaxation using DFT (SCAN+*U* approximation)

Density of states (if needed)

0 K stability

Structure features

Elemental features

Feature vector

Obtain template-matched ABO_3 theoretical structures (200)

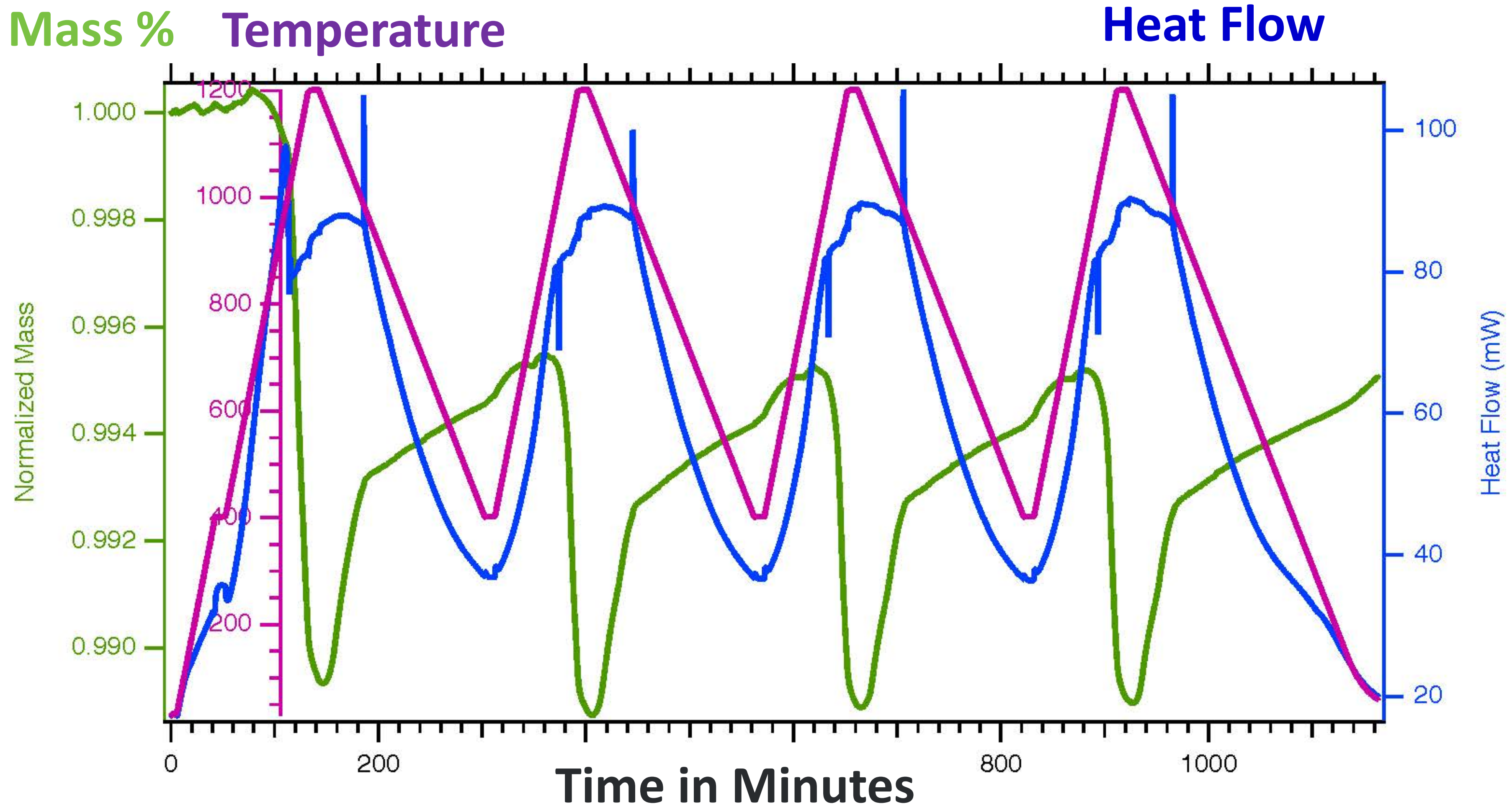
Predict higher component systems + Identify potential candidates and trends

End

Machine learning algorithm

Accomplishments & Progress

$(Ca,Ce)VO_3$ cycles repeatedly

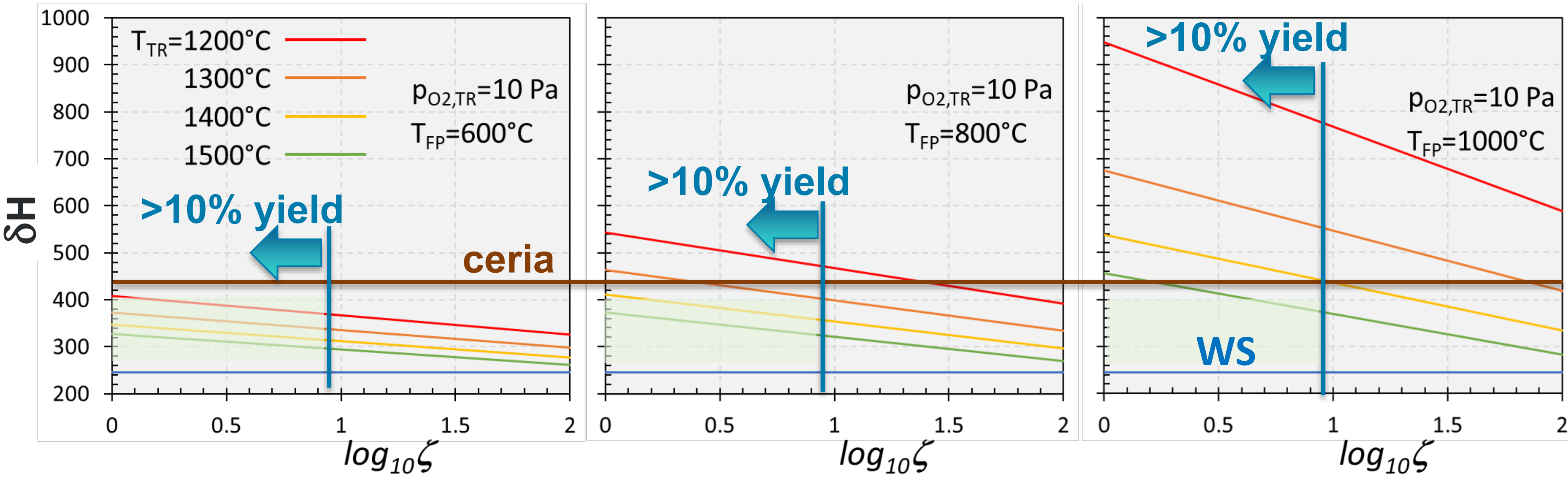


Thermogravimetic Analysis; Measured at NREL

Note Reversible Phase Transition

Accomplishments & Progress
Yield & Reduction Enthalpy: Relationship

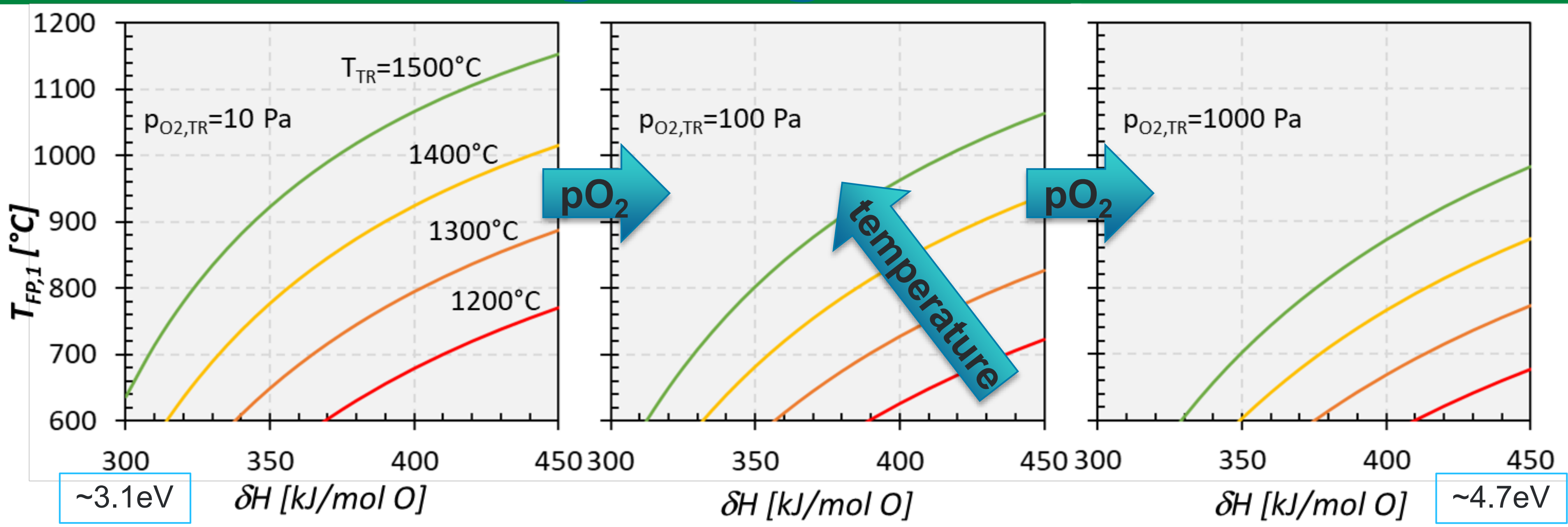
Yield and Steam Overflow: $\theta = \frac{1}{\zeta + 1}$ $\zeta \equiv \frac{pH_2O}{pH_2}$



- **At fixed reduction pressure, yield decreases with decreasing reduction temperature**
- **To compensate:**
  - **Decrease oxidation temperature (i.e. increase ΔT)**
  - **Increase δH (i.e. generally decreases productivity; increases reaction exotherm during re-oxidation)**

Accomplishments & Progress

Determining a target for δH



~3.1eV

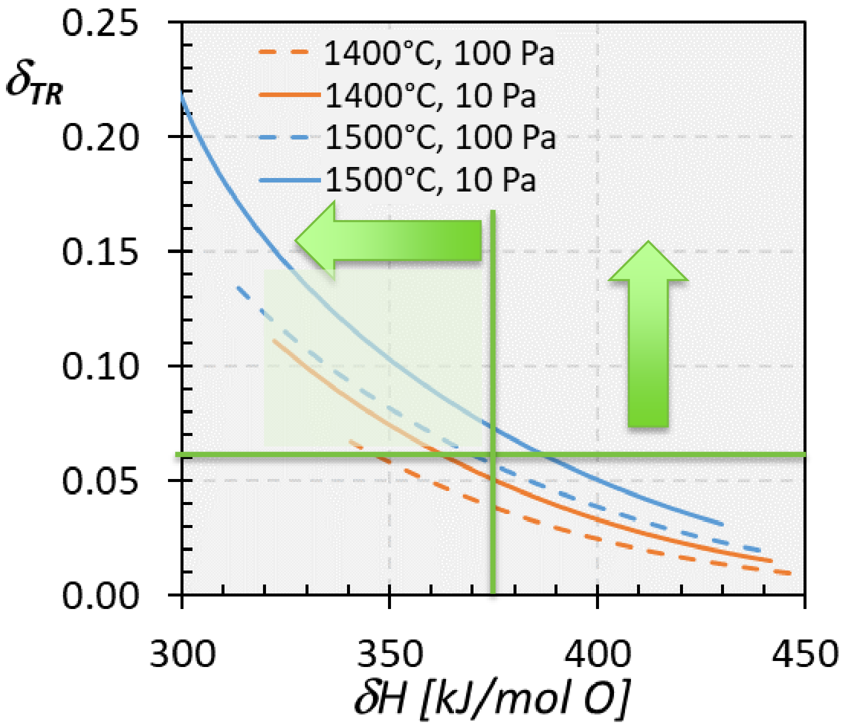
~4.7eV

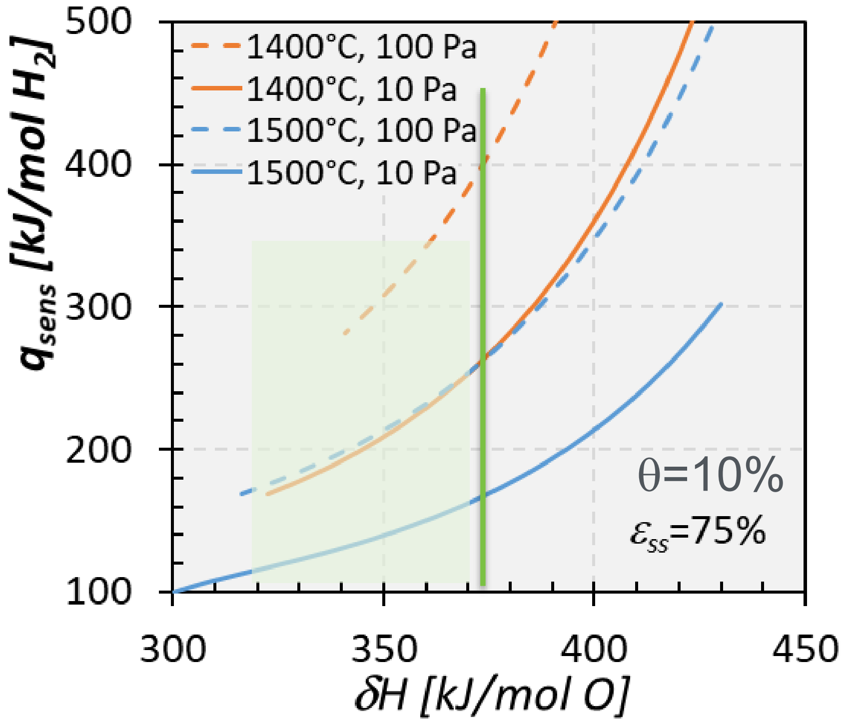
On the premise that, all else equal, lower δH is better:

- **Optimal δH follows directly from T_{TR}, pO_2, Θ, and T_{FP} (solid in, gas out)**
- **At 1200°C reduction and 800°C water splitting (or fuel production in general), and $pO_2 \geq 10$ Pa there is no solution for δH lower than ceria;**
- **Higher T_{TR} and lower pO_2 are a win-win: more productivity from operating conditions AND from possibility of using low δH materials**

Accomplishments & Progress

Modified Zinkevich CEF: Full Cycle Insights



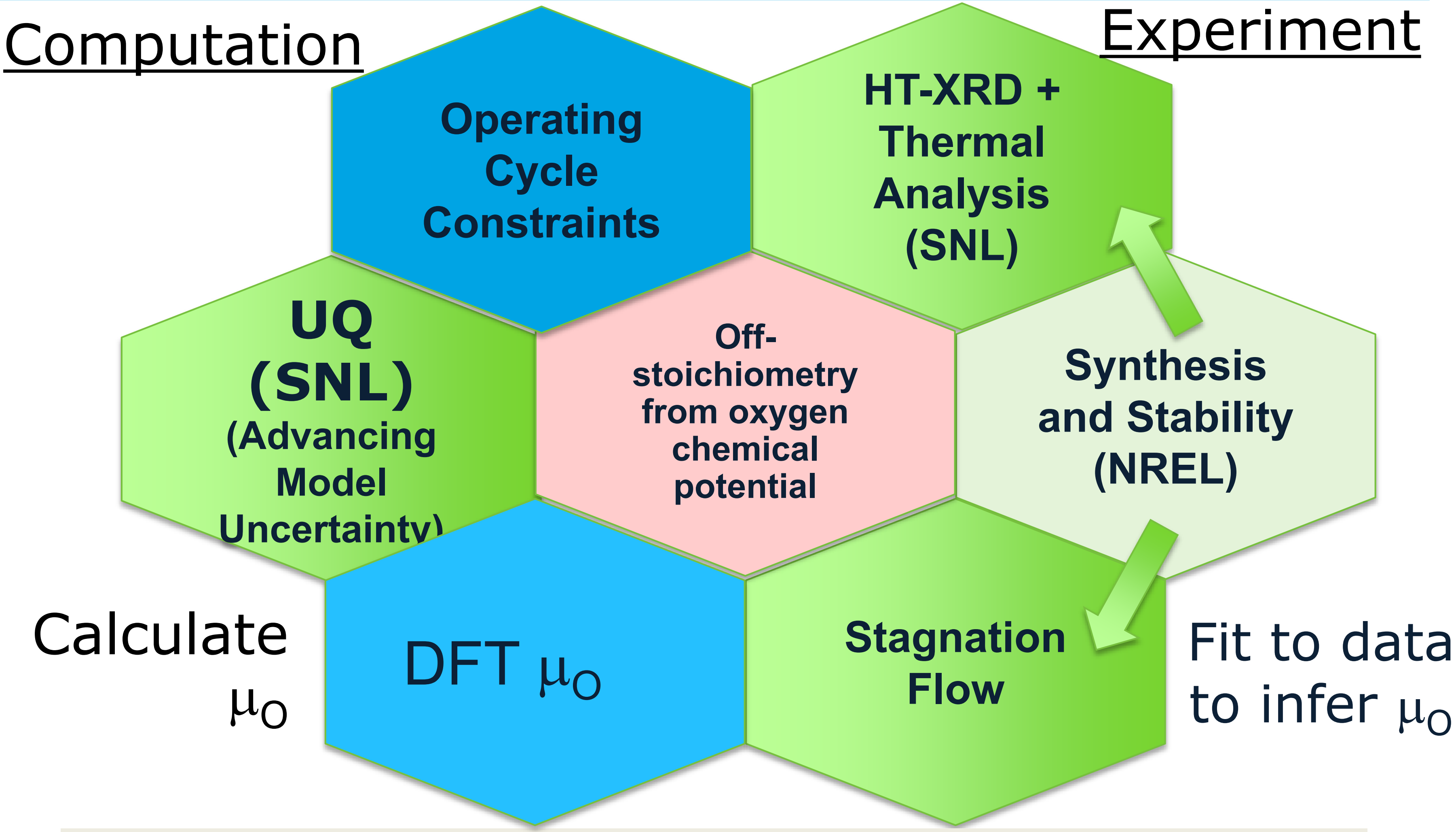


Zinkevich, et al Solid State Ionics 177 (2006) 989–1001; we artificially reduced the ΔH between $^{F}Ce_2O_3$ (meta-stable, 25% vacancies) and Ce_2O_4

- **Meaningful δ_{TR} reached only for δH < ~374 kJ/mol O (~3.9 eV)**
- **$Q_{sens} \sim {}^{\Delta T(1-\varepsilon_{ss})}\!/\!_{\varepsilon_{ss}\Delta\delta}$ (50%, is 3x 75% ε_{ss} and 25% is 9x)**
- **Relaxing T_{TR} or pO_2 sharply increases sensible heat input**
- **Larger Δδ wins – implication: should accept the increased ΔT**

Collaboration: Effectiveness

It takes a "village"



Computation

Experiment

Operating Cycle Constraints

HT-XRD + Thermal Analysis (SNL)

UQ (SNL)
(Advancing Model Uncertainty)

Off-stoichiometry from oxygen chemical potential

Synthesis and Stability (NREL)

Calculate μ_O

DFT μ_O

Stagnation Flow

Fit to data to infer μ_O

All the important thermodynamics is encompassed in the oxygen chemical potential: gas phase known – solid phase modeled with sub-lattice formalism (either from experiment, computation, or combination)

Collaboration: Effectiveness

- Specific interactions
  - Working very closely with the SNL Uncertainty Quantification Node (Dr. Bert Debusschere and a student)
  - Working closely with the NREL Synthesis and Characterization Node (Drs. Dave Ginley, Robert Bell, and Phil Parilla) on synthesizing candidate materials
  - Working with SNL Thermal Analysis Nodes (Dr. Eric Coker) to measure equilibrium off-stoichiometry as function of temperature and pO_2
  - Regular conversations with SNL STCH lead and Node Owner for Stagnation Flow (Dr. Tony McDaniel)
  - Phase 2 has a strong focus on verifying candidate recommendation derived from theory and computation and verifying general utility of the compound energy formalism representation of the solid state oxygen chemical potential
- This project has a close association with the 2B team as PI (Prof. Stechel) here is co-PI on the 2B project
- Expected benefits will derive from a closer relationship between what experimentalists measure and theorists calculation with defined protocols
  - Standardization and defined protocols will lower the barrier to entry
  - Determining rigorous thermodynamic constraints on the relationship between reduction enthalpy and operating conditions will help guide the experimental community in its search for at least one material with better performance than ceria.

Proposed Future Work

Remaining Challenges and Barriers

- Build sub-lattice models for $(A,A')(B,B')O_3$ quinary perovskites, with both A' and B simultaneously redox active
  - Predict oxygen off-stoichiometries and validate with experimental data
  - Predict oxygen vacancy formation energies using machine learning
- Nodes: NREL developing synthesis routes and synthesizing newly proposed candidates
  - Two SNL nodes will measure off-stoichiometry and we will infer enthalpy and entropy using our sub-lattice formalism (as opposed to Van't Hoff and linear fits/extrapolation)
- Uncertainty Quantification
  - Characterization of model error– tradeoff between accuracy and simplicity
  - Refine propagation of model error into thermodynamic properties
- Port computational sublattice formalism up through quinary perovskites to prime (ASU) and develop protocol with the 2B team and NREL computational node for DFT sublattice model formulation for estimating the off-stoichiometry.
  - Compute solid state oxygen chemical potential as function of δ and T for a range of redox active materials – identify best trade-offs between yield, ΔT, reduction temperature/pO_2, and enthalpy of reduction
  - Methodology for in silico materials discovery verified and validated and improved materials identified.

Project Summary

- Construction of chemical potential maps is useful to decouple the energetic contributions of the gas and solid phases in a thermochemical cycle
  - Equilibrium δ comes from equating solid state and gas phase oxygen chemical potentials – sub-lattice model provides unique functional form for the oxygen chemical potential (previously not recognized)
- Prediction of chemical potentials in solid phases is not trivial
  - Construction of sub-lattice models, with energy values from DFT, is proving to be a promising approach – not high-throughput but reasonable number of zero-temperature DFT (SCAN+U is proving good accuracy) calculations
  - Machine learning will provide a faster screening approach
- We have identified a promising pathway to improve capacities (modest increase in entropy, without compromising kinetics from phase transitions)
  - Redox (cation) couples for $(A,A')(B,B')O_3$ quinary perovskites with A' and B simultaneously redox active.

Thank you for your attention