Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

Accelerated Discovery of STCH Hydrogen Production Materials via High-Throughput Computational and Experimental Methods

Ryan O'Hayre and Michael Sanders
Colorado School of Mines
05/20/2020

P165

This presentation does not contain any proprietary, confidential, or otherwise restricted information

NREL · BERKELEY LAB · Sandia National Laboratories · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

Project Overview

Project Partners

Ryan O'Hayre and Michael Sanders
Colorado School of Mines

Award #	EE0008087
Start/End Date	10/01/2017 – 12/31/2020
Year 1 Funding* Year 2 Funding*	$249,990 $265,324

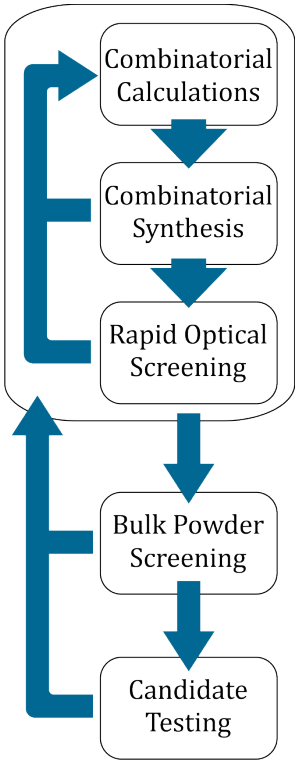
** this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Project Vision

Integrate combinatorial synthesis methods with combinatorial theoretical calculations to rapidly discover new potential materials for use in two-step metal oxide cycles for STCH

Current SOA STCH efficiency (CeO_2): ~2%
Efficiency for optimal STCH material: >60%

Huge opportunity for transformative improvement



Project Impact

Greatly increase number of viable STCH materials candidates

Compositions Studied for Nonstochiometric Redox STCH:

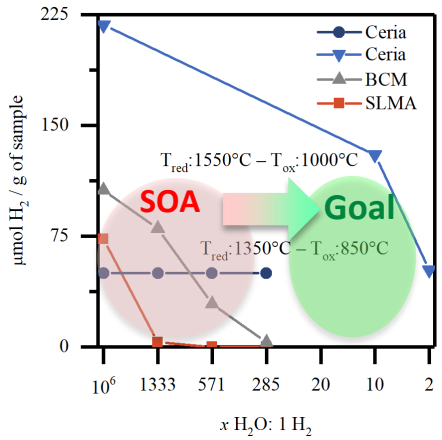
Today: 10's of compositions
Project Goal: 1000's of compositions

100x increase

Approach- Summary

Project Motivation

Builds on prior Sandia/CSM STCH collaboration, which has produced two novel perovskite-based STCH candidate



Key Impact

Metric	State of the Art	Proposed
Reduction Temperature	*1550°C*	*1350°C*
Hydrogen Production	*150 μmol H_2/g sample (@T_{RED}=1550°C)*	*>= (@T_{RED}=1350°C)*

Ultimate goal:

200 °C lower T_R with equal capacity to CeO_2

Comparable Steam-to-Hydrogen Performance

Barriers

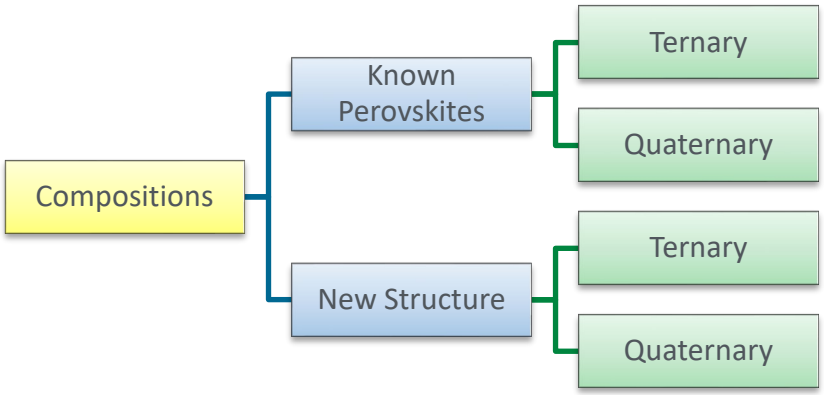
- Secondary defect calculations have not yet reached accuracy necessary
- Optical evaluation failed
- Ex-Situ stoichiometry characterization may be impractical for screening

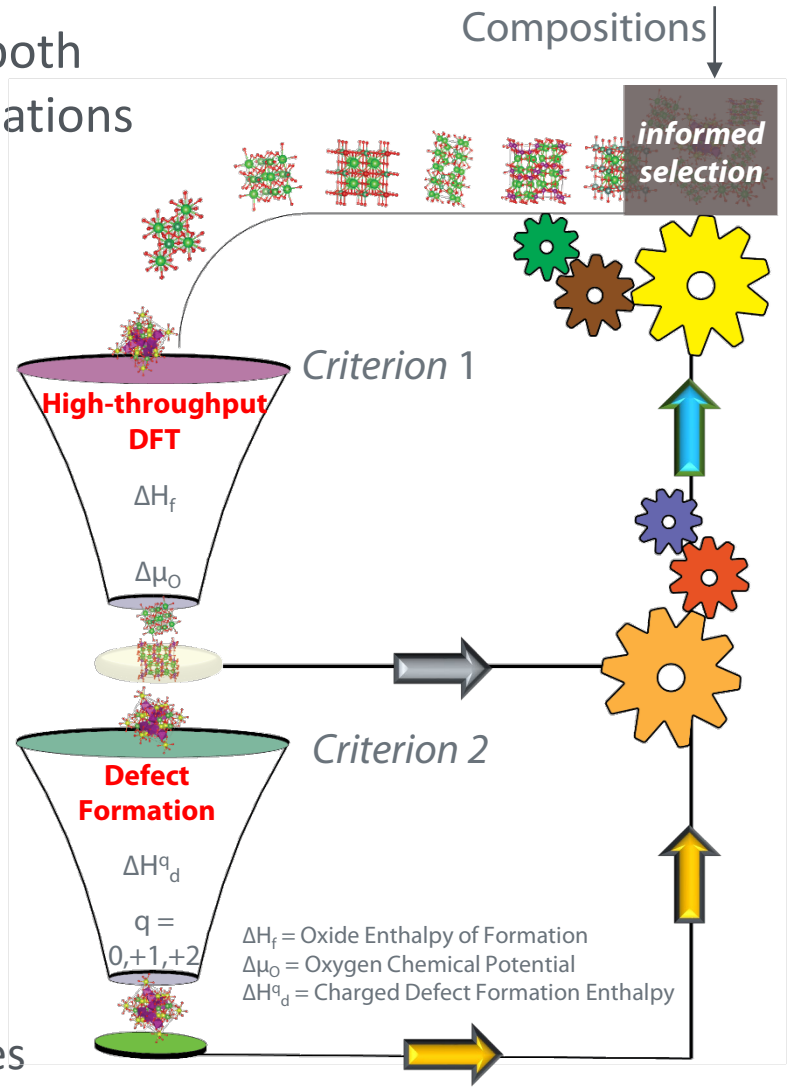
Partnerships

- NREL (Lany): High-throughput DFT calculations
- NREL (Zakutayev): Combinatorial thin-film deposition and characterization
- Sandia (McDaniel): Stagnation Flow Reactor (SFR) for STCH materials validation

Approach- Innovation: DFT Screening

- A two-part screening method to leverage both high-throughput and detailed defect calculations focused on two main search directions:

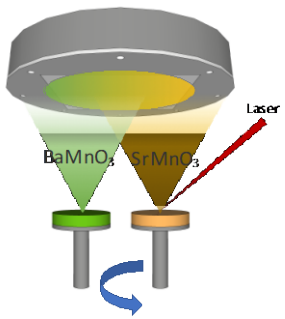




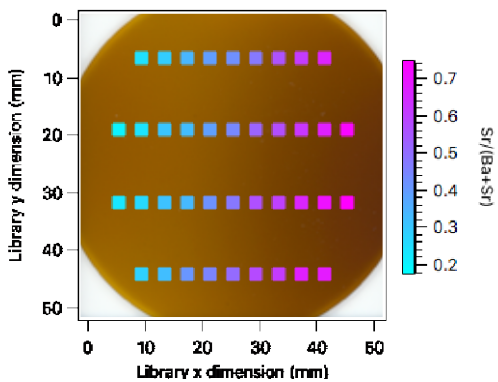
- Initial compositional space:
  - Low cost, earth abundant
  - Non-toxic
  - Ce and Mn present in most good STCH materials
  - Multiple oxidation state accessible to B-sites

Approach- Innovation: Experimental Screening

Combinatorial Pulsed Laser Deposition



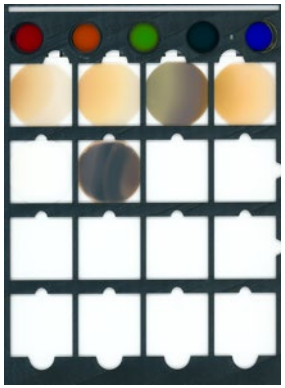
Co-deposition from compound targets



Combinatorial sample library and 44-point grid

High Throughput Colorimetric Screening

Optical Scanner for colorimetry analysis

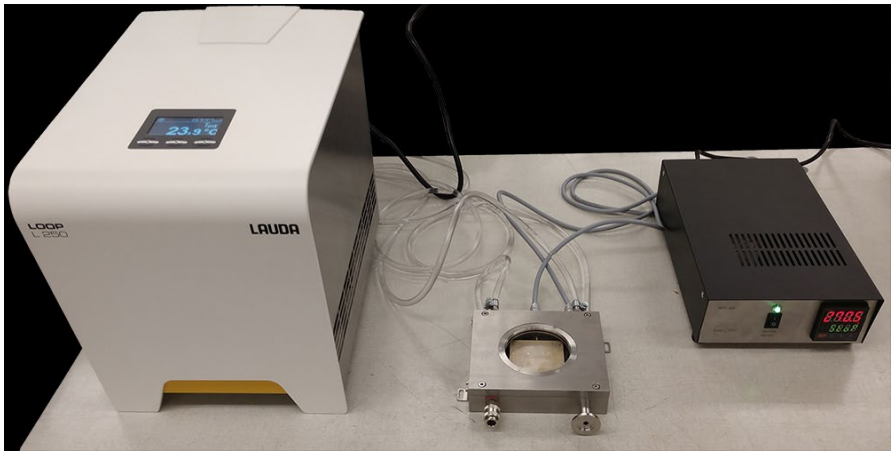


3D-printed holder for 16 libraries, 5 references

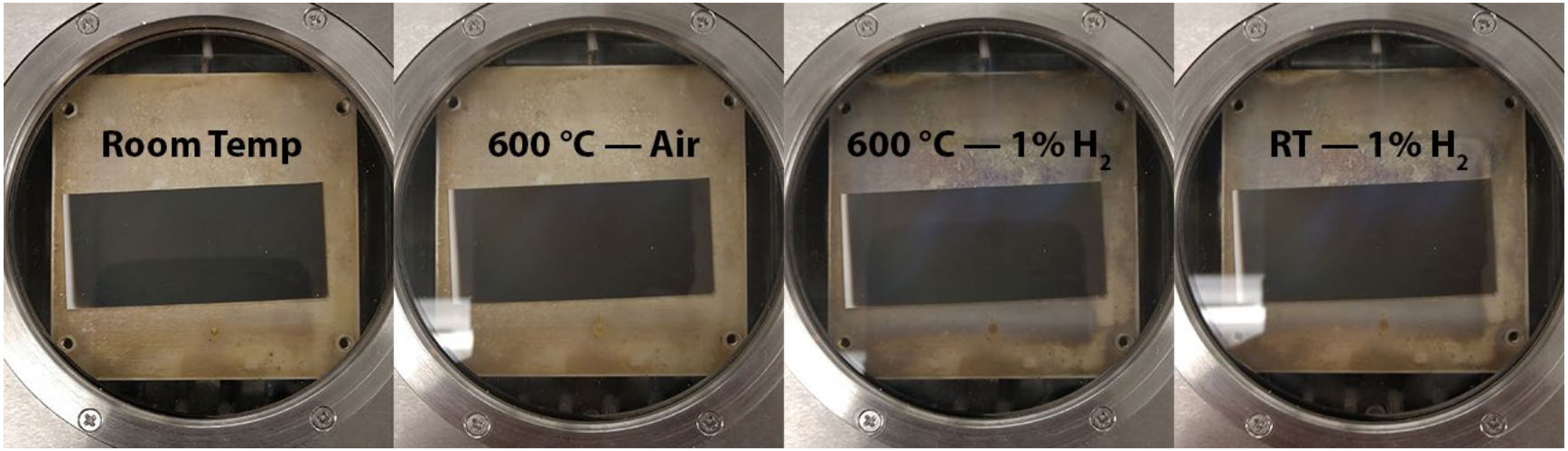
High Throughput XRF and XRD are also used for composition and structure

The combinatorial PLD technique allows for the simultaneous formation of many chemical compositions. These libraries can then be rapidly evaluated for structural and thermochemical behavior.

Approach- Innovation: In-situ color Measurement



- An optical observation hot stage was purchased to facilitate in-situ colorimetry of combinatorial films
  - Max 600°C
  - H_2 reduction to simulate thermal reduction at higher temperature
  - Capable of using steam for reoxidation



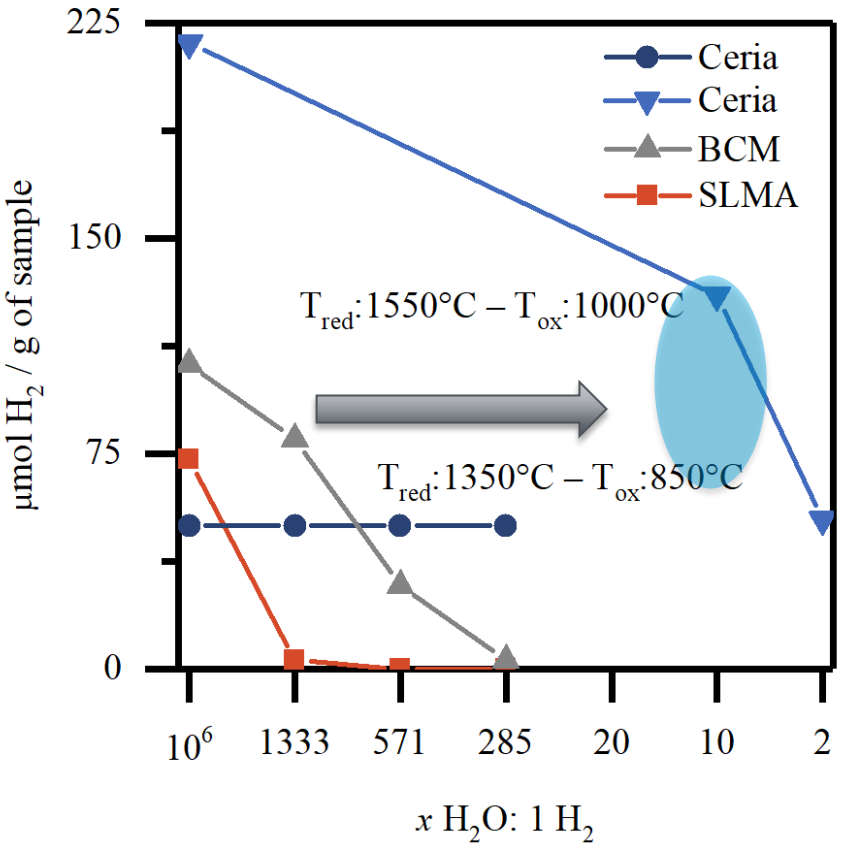
Approach- Innovation: Summary

- Based on Y1 lessons-learned, modifications were made
  - Winnowed the element list down to “most-likely” constituents (Ba, Sr, La, V, Nb, Mn, Mo, Ce) based on Y1 findings due to unanticipated calculation expense.
  - Combinatorial and Optical Screening method required more investigation to determine suitability, before implementation.
- Consortium resources and expertise have proven critical
  - Close relationship with computational team has provided not only access to valuable resources but allowed CSM’s materials insights to inform NREL node’s other computational work.
  - NREL’s Combinatorial PLD system and Sandia’s SFR are capabilities that cannot be easily duplicated in-house.

Relevance & Impact: Support for H2<$2/kg

STCH cost targets require:

- Large improvements in hydrogen production capacity (mmol H_2/g oxide-cycle)
- Lower reduction temperatures
- High conversion capability
- Fast redox reaction kinetics



Achieving these goals requires new materials, as all current STCH candidates fail on at least one criteria

Relevance & Impact: Fitting in with HydroGEN

- This project was developed to explicitly leverage the EMN model of merging high-throughput computational and experimental techniques to accelerate new materials discovery
- Promising new STCH materials candidates as well as the broader structure-property-performance relationships discovered in this project will be shared. These discoveries may assist other water-splitting efforts within the HydroGEN consortium

The calculation and screening techniques developed in this project could have an impact well beyond HydroGEN, with relevance to other broad materials discovery efforts

Accomplishments: Milestone Overview

Year 2 Go/No Go Milestone

Milestone Number	Milestone Type	Milestone Description	Milestone Verification Process
M3.5	Bulk materials testing	Bulk testing demonstrates that at least one material composition splits water under steam-to-hydrogen ratios lower than 10:1 and with a hydrogen capacity under the reduction conditions of 1350°C and oxidation temperatures of 850°C-1000°C at least equal to that of ceria under the reduction conditions of 1450°C and oxidation temperatures of 850°C-1000°C.	Production of at least 150 μmol H_2/g sample at the conditions listed. Results of testing performed at CSM must be repeatable and duplicated by experiments using Sandia's SFR.

- Meeting the Y2 Go/No Go criteria requires the discovery of a game-changing material
  - Secondary milestones include finding three more materials that at least meet Y1 G/NG targets. One has been found to date.

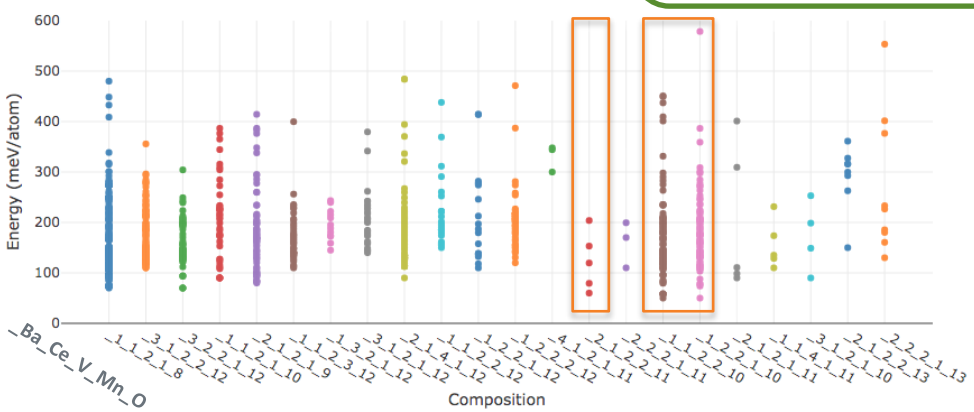
Accomplishments: Key Results

Task 1: Computational Stability Screening

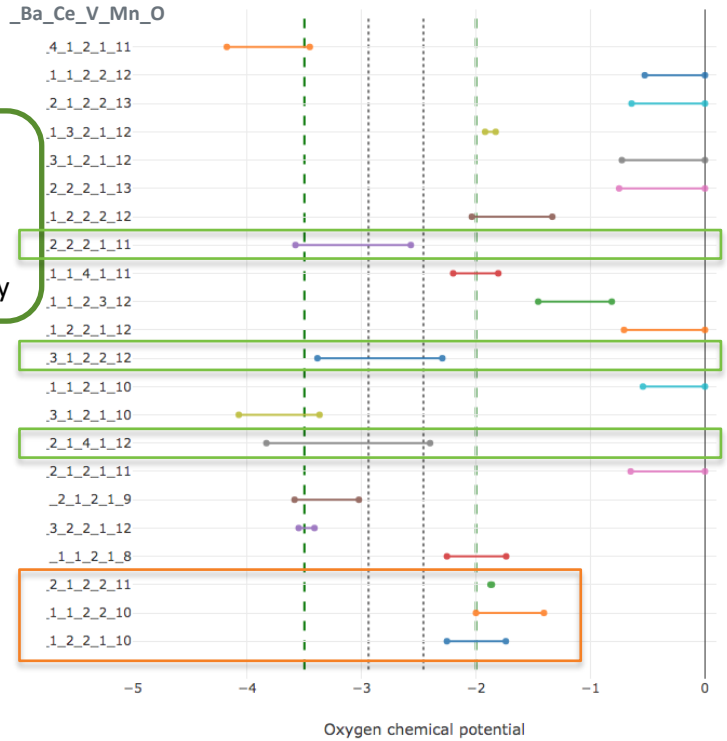
- 22 compositions [Ba, Ce, V, Mn, O]
- Specific stoichiometry under constraints:
  - Ba^{+2}, Ce^{+4}, $V^{+3/+5}$, Mn^{+4}
  - 20 atoms per unit cell
- 1300 DFT calculations

In Collaboration w/First Principles Theory Node (NREL)

Compositions with $\Delta\mu_O$ in correct range do not necessarily correspond to compositions with minimized structural energy



Energetics profile exhibiting distance from convex hull for each composition



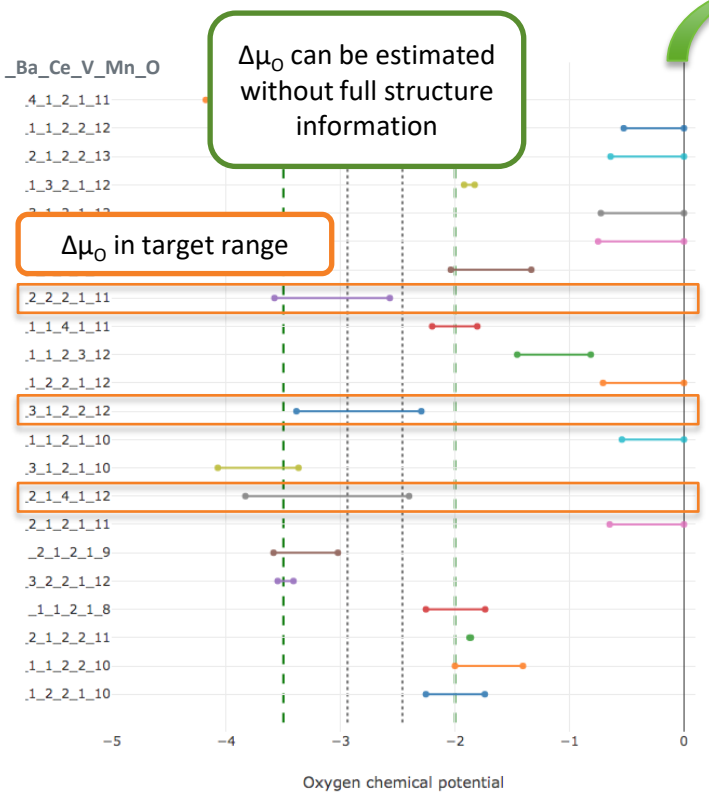
STCH compatible oxygen chemical potential window shown by vertical dotted lines

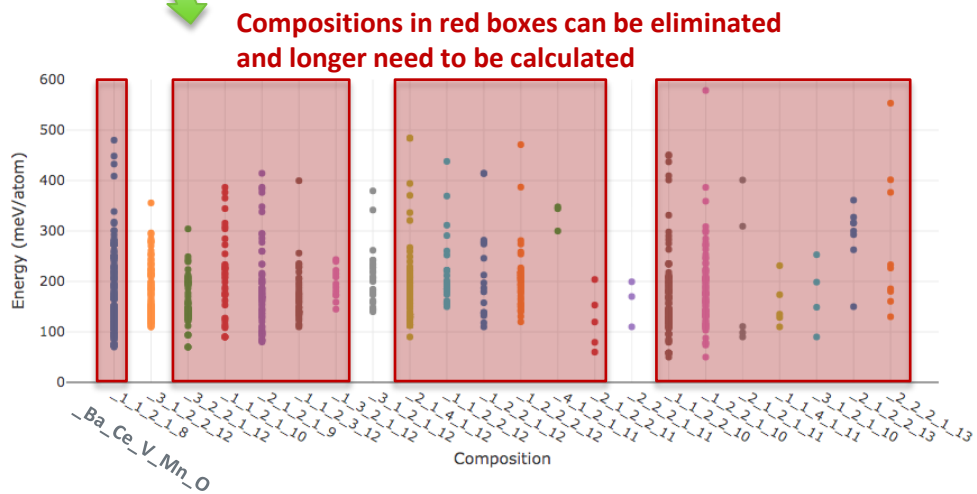
Identified 3 compositions in [Ba,Ce,V,Mn,O] chemical space with suitable STCH $\Delta\mu_O$ along with structures that are within 50-70 meV/atom from convex hull.

Accomplishments: Key Results

Task 1: Computational Stability Screening

In Collaboration w/First Principles Theory Node (NREL)





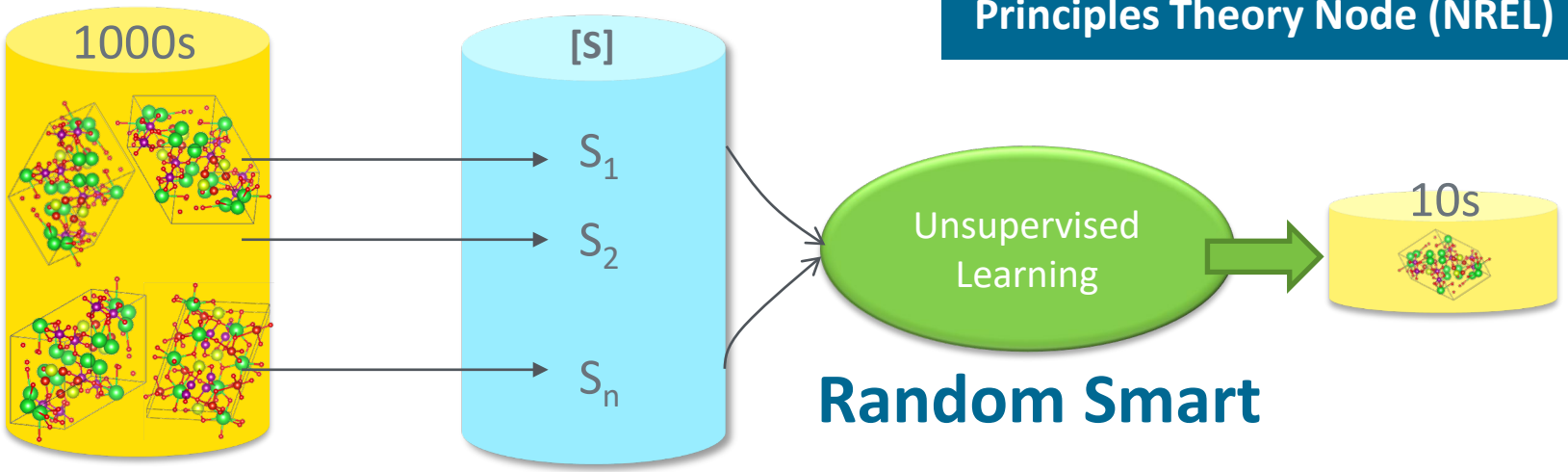
- Regardless of stable structure, only those that have a $\Delta\mu_O$ within the target range have any chance to be a STCH candidate
- More calculation power can be devoted to finding stable structures for candidates

In this example, by estimating Δu_o first, we reduce the number of DFT calculations by 87%. This reduction allows for a dramatic increase the number of compositions we can investigate without additional computational resources.

Accomplishments: Key Results

Task 1: Computational Stability Screening

In Collaboration w/First Principles Theory Node (NREL)



Random Smart

We have developed a new machine learning algorithm that rapidly identifies suitable low energy configurations to accelerate ground state structure search

Method:

- Collection of structures from varying procedures such as random, prototyping, etc.
- Each structure is associated to a fingerprint generated from local coordination environment forming an S-matrix for the complete database.
- Unsupervised learning is performed on the S-matrix to identify representative candidates.

Advantages:

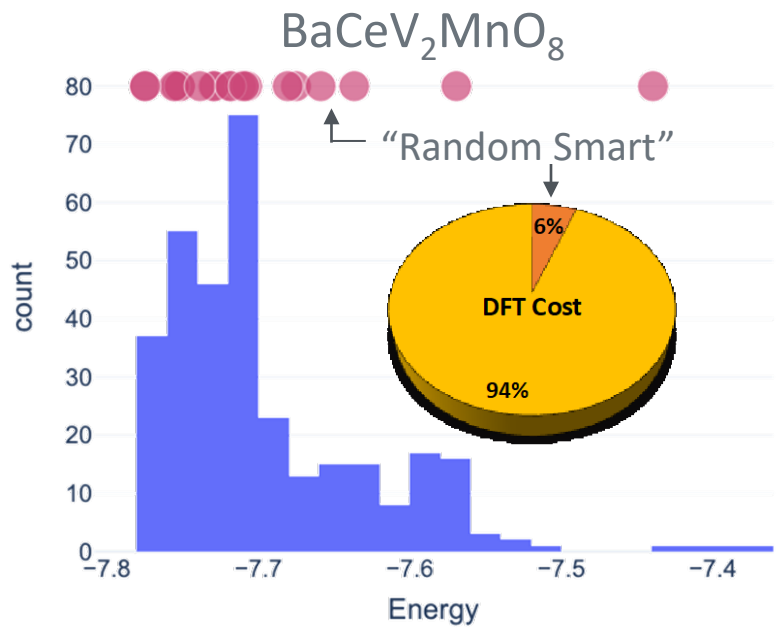
- Significant reduction (~16X) in computation expense.
- Especially useful for complex compositions with large simulation cell sizes.
- Fewer calculations allows for wider compositional search, improving probability of finding candidates with novel combinations.

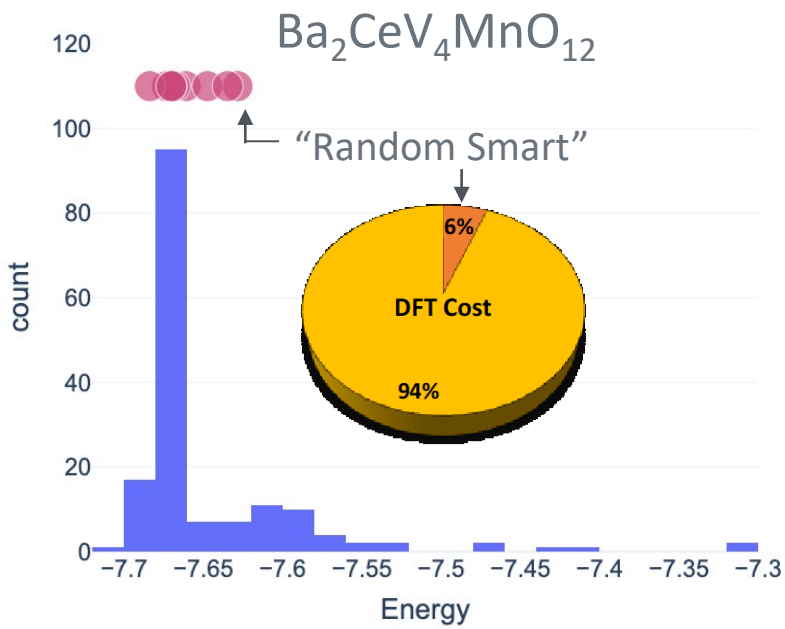
Accomplishments: Key Results

Task 1: Computational Stability Screening

In Collaboration w/First Principles Theory Node (NREL)

- "Random Smart" predicts *suitable* candidates in structure search at much lower computational cost
  - Uses unsupervised ML algorithm
  - Shown to work for large complex quinary oxide compositions with large simulation cells
- Significant speedup: ~16X





NOTE: This method is not intended to obtain the lowest energy structure but built to quickly reach near the neighborhood of stable ground state. These structures can be used as seeds for follow-up calculations using methods such as an evolutionary algorithm.

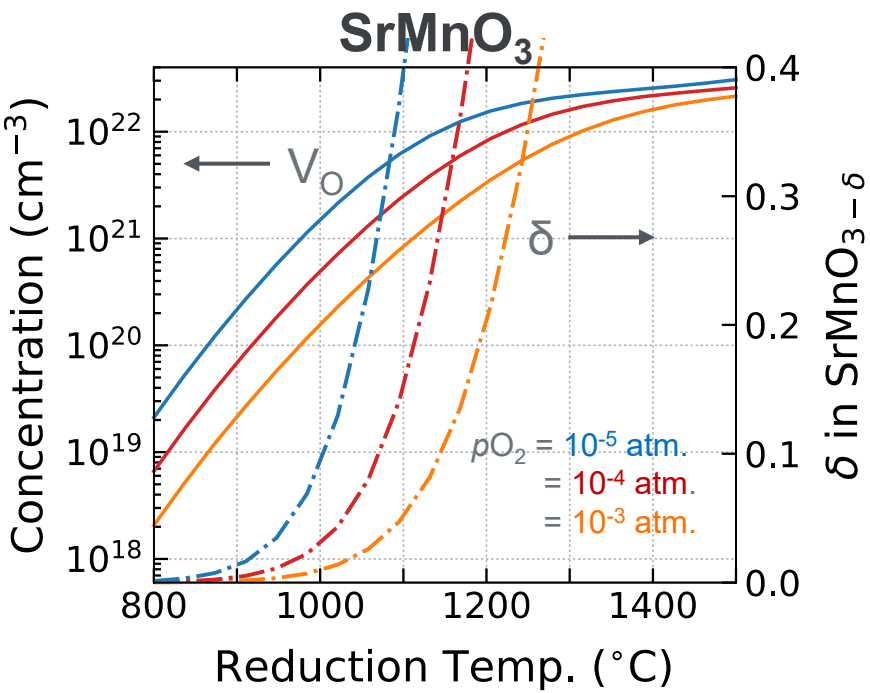
Accomplishments: Key Results

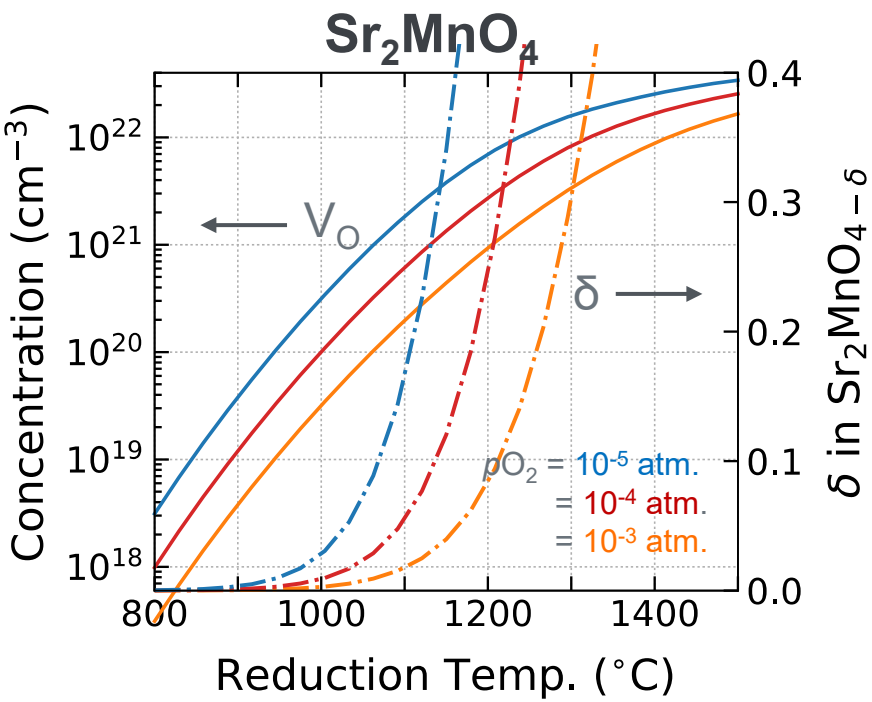
Task 1: Computational Defect-Formation Screening

In Collaboration w/First Principles Theory Node (NREL)

δ off-stoichiometry at the O site during reduction

- Computational modeling captures reduction trends in $SrMnO_3$ and Sr_2MnO_4
- Additional development is necessary to model SCM and CSM
  (see Tech. Back-up Slides for roadmap)



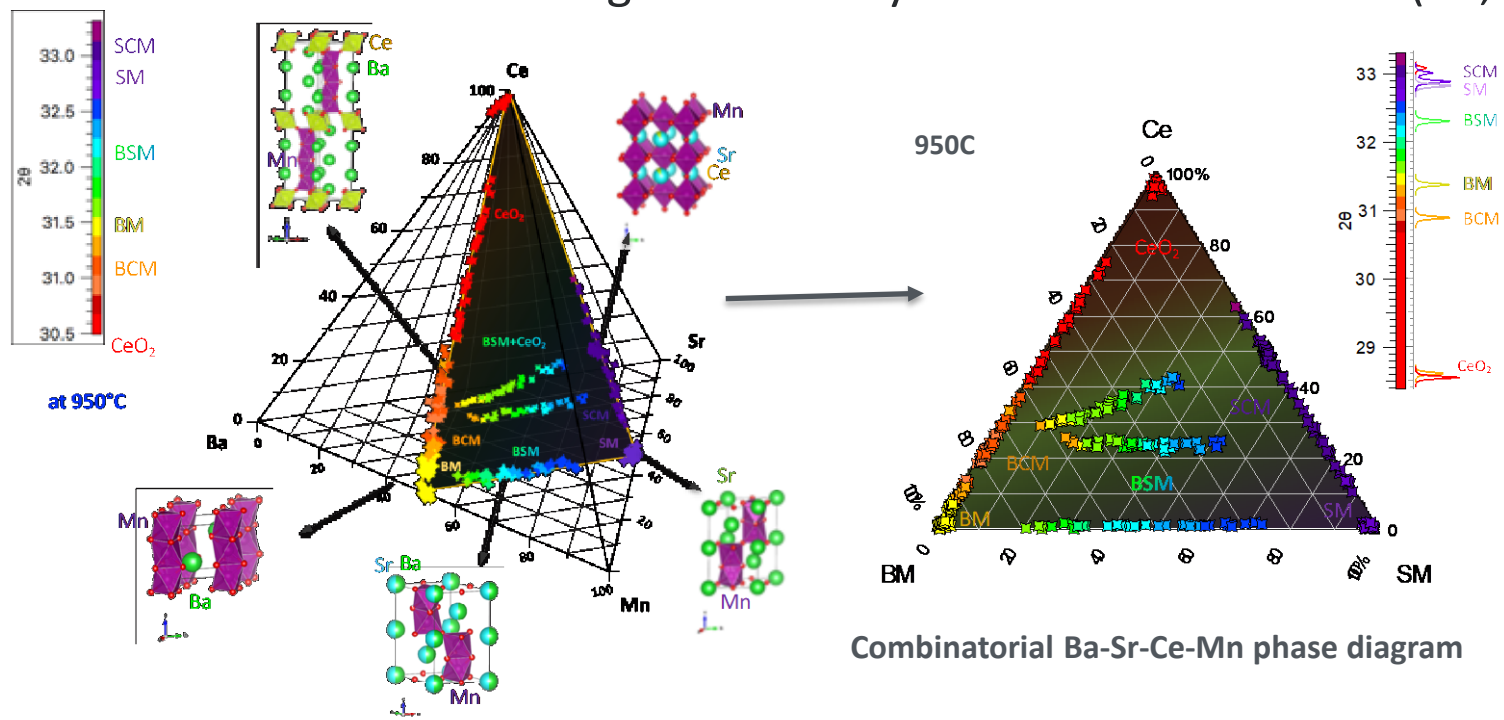


Accomplishments: Key Results

In Collaboration with Combi Node (NREL)

Task 2: Combinatorial

- The combinatorial PLD technique makes many chemical compositions at once
- These "libraries" are screened for for structural and thermochemical behavior
- We used combi PLD to investigate solubility limits of Ce within the $(Ba,Sr)MnO_3$



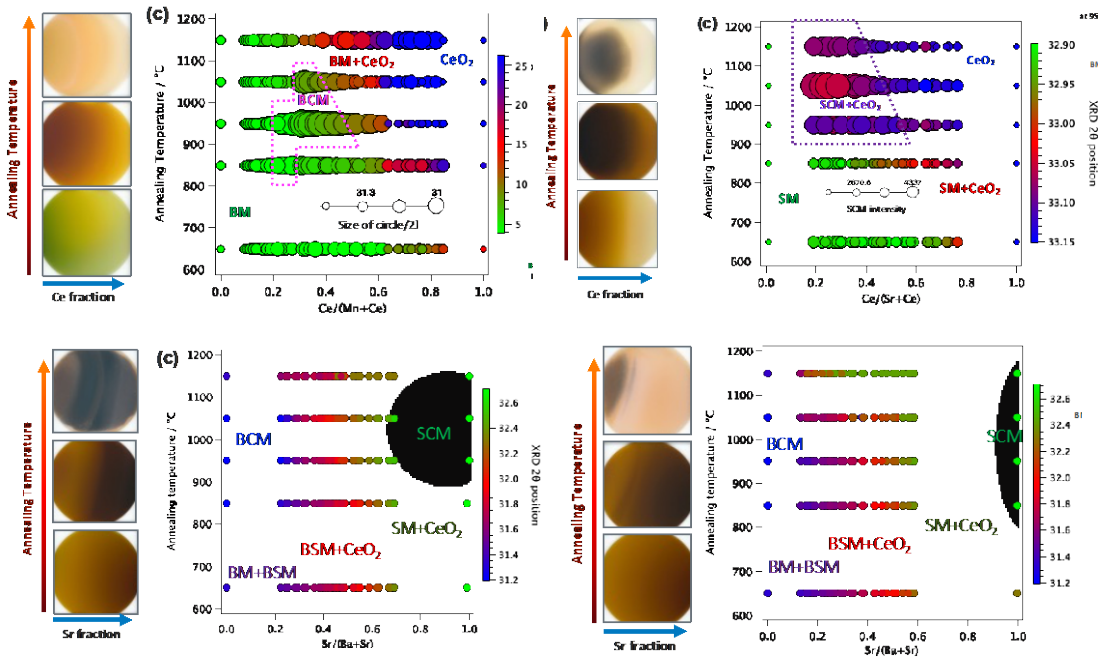
Combinatorial Ba-Sr-Ce-Mn phase diagram

The BMO/SMO system allows for a reasonable amount of Ce alloying around BCM and SCM
The quaternary BSCM alloys do not have higher Ce solubility than the parent compositions

Accomplishments: Key Results

In Collaboration with Combi Node (NREL)

Task 2: Combinatorial



- Films cycled to T and then returned to RT for XRD and optical color scanning
- Below 800°C there is no permanent color change
- Above 1100°C changes due to interaction with substrate
- In the 800-1100°C, color changes due to change in phase
- The observed changes are consistent with bulk samples
- Broader composition range can be studied with thin films

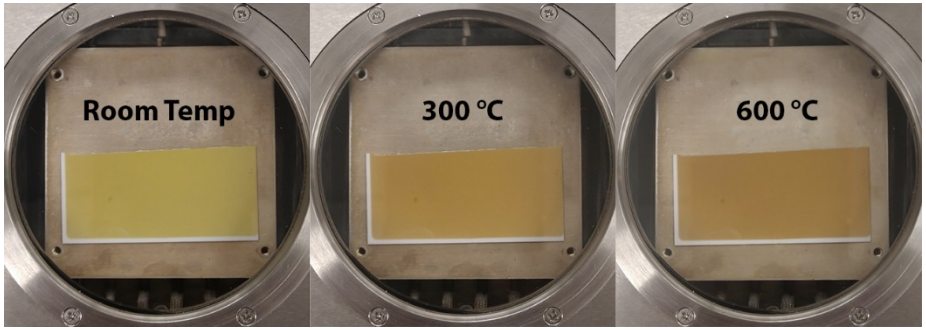
The phase diagrams are consistent with bulk samples, validating thin film screening method
Keeping the testing temperature below 1100°C insures that films don't interact with substrate

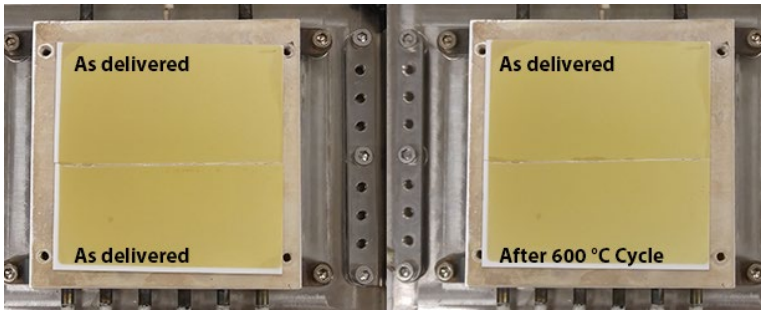
Accomplishments: Key Results

In Collaboration with Combi Node (NREL)

Task 2: Combinatorial

- In-situ testing at 600°C was undertaken, using chemical H2 reduction to simulate thermal reduction at higher temperature
  - Color changes were uniform and reversable at these temperatures
  - Further testing identified color change are likely temperature related, which can be convoluted with change in oxygen stoichiometry
  - More detailed wavelength-resolved analysis of the cycled films are needed to identify and quantify subtle changes in optical absorption spectra





Experiments demonstrate that in-situ screening is complicated due to subtle changes in optical properties
Ex-situ characterization of redox films could be possible due to the uniform heating and gas environment

Accomplishments: Key Results

In Collaboration w/Stagnation Flow Reactor Node (SNL)

- Synthesized and tested SCM40 ($Sr_{0.6}Ce_{0.4}MnO_{3-\delta}$), a simple perovskite allotrope of CSM2
  - SCM40 produced 280 µmol H_2/g sample, a 15% increase over CSM, the highest yield produced on this project
  - Much like other true perovskites, however, the increase in yield comes at the expense of the hydrogen tolerance necessary to split water at lower steam-to-hydrogen ratios
  - While further increasing the Ce content could further enhance performance, experiments indicate that 40% cerium is nearing the saturation limit

The continued improvement of overall yield regardless of "high conversion" performance remains important, as innovations in reactor design could change constraints and provides valuable data in understanding material design trends.

Accomplishments: Outlook

- Computational efforts have identified three new **[Ba,Ce,V,Mn,O]** containing oxide compositions as potential STCH candidates.
- These recently identified candidates will be synthesized and tested for STCH performance once stay-at-home orders expire.
- Latest computational advances allow for a dramatic increase in elemental compositions that can be investigated, leading to new insights into trends
- Use thin-film based combinatorial screening to validate theory-derived structure/stability results. Use small-batch bulk synthesis to validate STCH capability.

Small-batch bulk synthesis of candidate families directly after computational identification will still allow for both rapid screening and informing subsequent rounds of calculations as the computational cycle is significantly shortened.

Collaboration: Effectiveness

Task 1: Computational	
Stephan Lany First Principles Materials Theory for Advanced Water Splitting Pathways	• Assisted in developing the new Y2 strategies to focus the computational materials efforts on more likely constituent elements • Lead work on improving the computational accuracy of defect calculations • Continued assistance to CSM computational team • All new results being introduced to NREL MatDB
Task 2: Combinatorial	
Andriy Zakutayev High-Throughput Experimental Thin Film Combinatorial Capabilities	• Technical guidance on film deposition strategies • Development of color measurement protocols • Input on improvements to Y2 strategies to maximize the benefits of their capabilities and expertise • Spearheaded the investigation into increasing Ce content in BCM/CSM/SCM • Developing strategies to use simple oxide targets to produce ternary and quaternary oxide films, decreasing the barriers to exploring exotic combinations
Task 3: Bulk Testing	
Anthony McDaniel Virtually Accessible Laser Heated Stagnation Flow Reactor	• Assisted in SFR operation for testing of SCM and CSM • All experimental raw data uploaded to HydroGEN Data Hub, analyzed data follows as it is produced • Valuable advice on improving the rapid optical screening method • Main interface between group and pathway-specific Working Group

Proposed Future Work

- Year Two Scope ($265k)
  - Expand computational and combinatorial search to more complex compositions (quaternary perovskites, single-dopant layered perovskites)
  - Discover at least three more quality candidates that split water
  - Discover at least one excellent candidate that produces hydrogen at steam-to-hydrogen ratios lower than 10:1 and, under the reduction conditions of 1350°C and oxidation temperatures of 850°C-1000°C, has a hydrogen capacity at least equal to that of ceria under the reduction conditions of 1450°C and oxidation temperatures of 850°C-1000°C
- Year Three Scope ($252k)
  - Full characterization and advanced study of excellent candidate, including H2A analysis

The identification of an excellent STCH material candidate greatly increases the likelihood that the production of industrial scale quantities of hydrogen using solar thermal energy at <$2/kg becomes technically feasible

Any proposed future work is subject to change based on funding levels

Project Summary

- Computational screening is moving towards original vision of low computational resource screening of compositions from ternary to quinary oxides
- Combinatorial thin-film experiments helpful in validating phase structure/stability. In-situ optical screening of STCH behavior challenging due to subtle changes in optical properties. Ex-situ characterization of redox films/powders could be possible
- SCM40 had highest hydrogen production of tested materials, but does not improve on steam-to-hydrogen ratio performance
- Successful collaboration with three EMN nodes
- Positive reviews from 2019 HPTT & AMR

Budget Period Two Go/No-Go remains challenging, but final quarters will see increase in number of candidates tested

Publications and Presentations

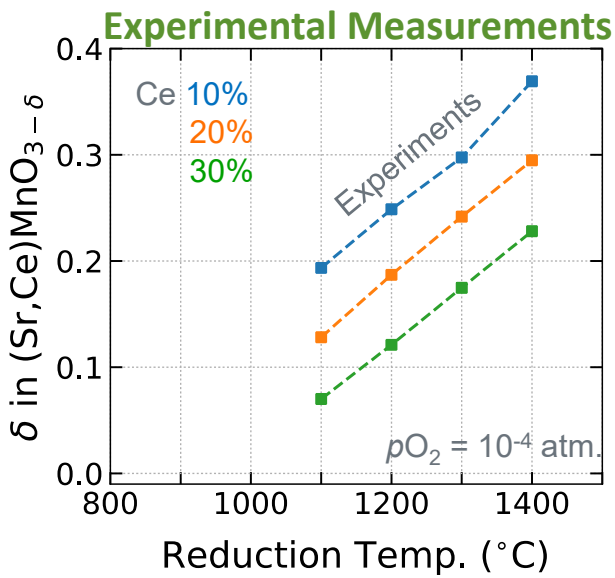
- Barcellos, D.R., et al., *Phase Identification of the Layered Perovskite* $Ce_xSr_{2-x}MnO_4$ *and Application for Solar Thermochemical Water Splitting*. Inorganic Chemistry, 2019. 58(12): p. 7705-7714. DOI: 10.1021/acs.inorgchem.8b03487

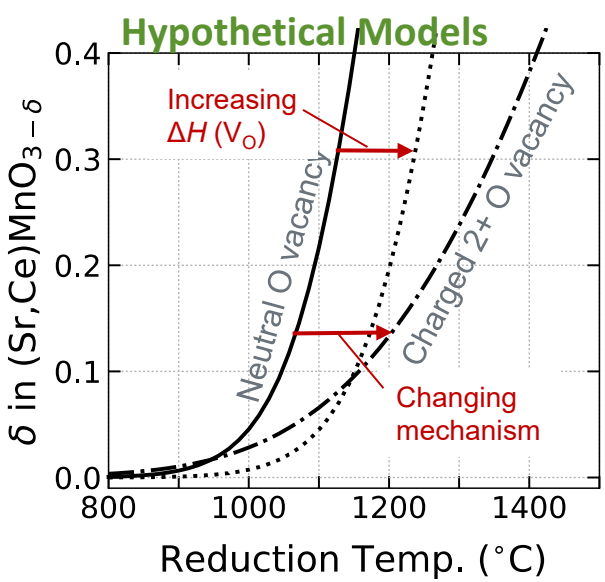
Technical Back-Up Slides

Modeling Reduction Behavior of (Sr,Ce)MnO_3 Alloys

Hypothesis:

- Reduction in alloy systems $Sr_{1-x}Ce_xMnO_{3-\delta}$ and $Sr_{2-x}Ce_xMnO_{4-\delta}$ via O vacancy formation
- $\Delta H(V_O)$ depends on Mn^{3+}/Mn^{4+} ratio, increasing with Ce substitution and off-stoichiometry (δ)
- δ vs T behavior depends on the formation mechanism (neutral vs. 2+ charge state), possibly involving electron polarons ($V_O^{2+} + 2Mn_{Mn}^{-}$)





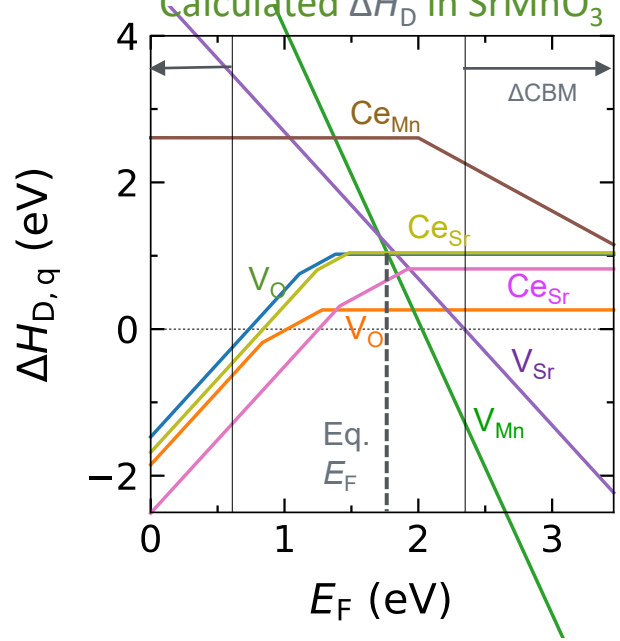
Preliminary Result: Defect Formation Energies

Step 1:

- Calculate defect formation enthalpy ΔH_D and charge transition levels in $SrMnO_3$ and Sr_2MnO_4 from DFT+U (E_g = 1.74 eV) level of theory
- DFT+U band gap corrected (E_g = 3.5 eV) using GW calculations (band edge shifts shown in grey in the defect diagram)
- O-vacancy has the lowest formation energy and stable in the neutral charge state at equilibrium E_F
- Mn atoms neighboring the neutral O-vacancy in Mn^{3+} charge state and spin $3d_+^4$
- O vacancy mechanism (neutral vs. 2+ with localized polaron Mn_{Mn}^-) important to consider
- ΔH_D then help model thermodynamic properties: Concentration, off-stoichiometry as function of T and pO_2

Low $\Delta H(V_O)$ → easy to reduce → large V_O concentration → high δ

Calculated ΔH_D in $SrMnO_3$

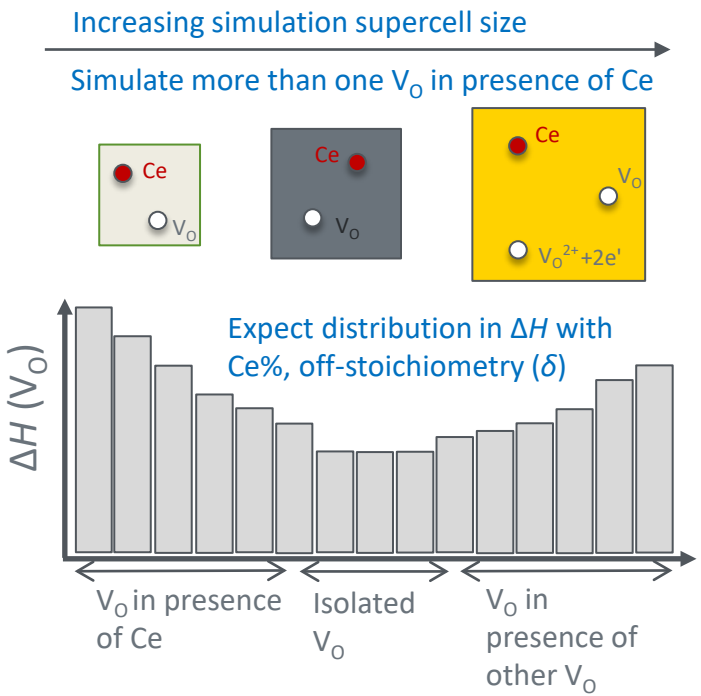


Defect diagram at $\Delta\mu_O$ = -1.61 eV, and $Sr_2Mn_2O_5$, Sr_2CeO_4 as competing phases

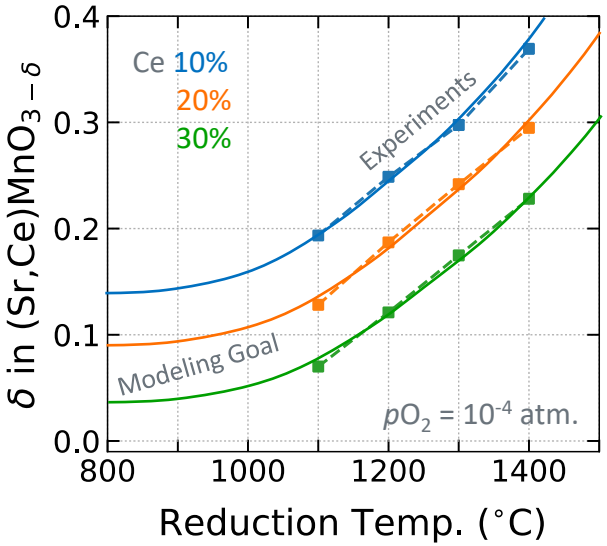
Develop a Defect Model to Complement Experiments

Next steps:

- O vacancy in presence of Ce and other O vacancies to model $\Delta H(V_O)$ dependence on Ce% and δ
- Incorporate localized polaron in order to understand O vacancy mechanism (neutral vs. charged)



Develop a defect model that can connect thermodynamic modeling with experiments

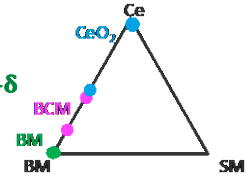


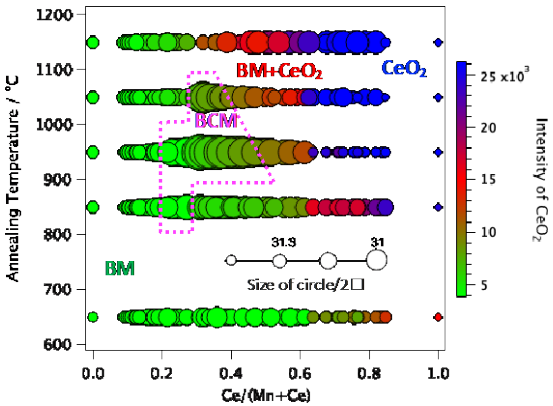
Accomplishments: Key Results

In Collaboration with Combi Node (NREL)

$Ba(Ce,Mn)O_{3-\delta}$

at 950°C

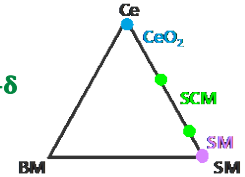


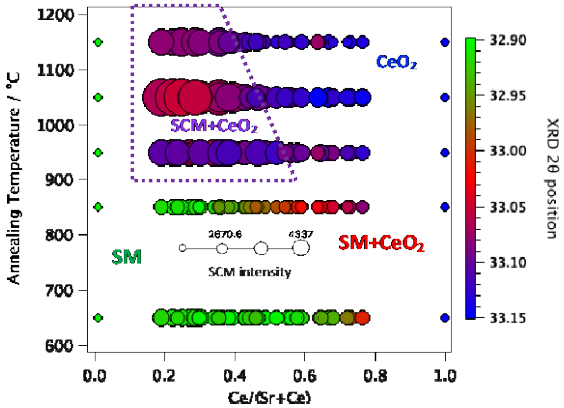


- BCM in the region of 0.2 – 0.5 Ce/(Mn+Ce)
- Increasing Ce in BCM leads to BM/CeO_2 segregation
- CeO_2 is dominant in higher temp

$(Sr,Ce)MnO_{3-\delta}$

at 950°C

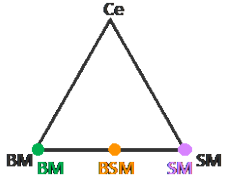


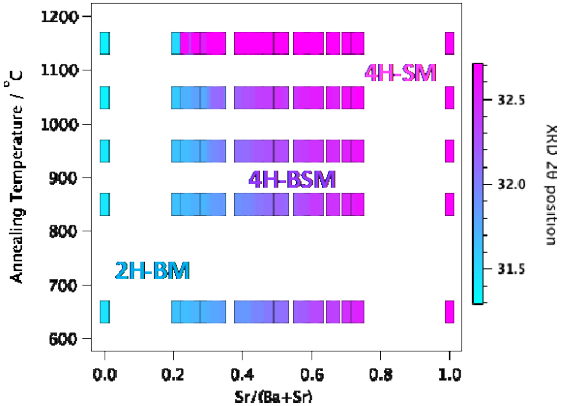


- SCM in the region of 0.15 – 0.55 Ce/(Sr+Ce)
- 4H-SM is dominate at lower Sr-fraction and temp
- CeO_2 is dominant at higher Sr-fraction and temp

$(Ba,Sr)MnO_{3-\delta}$

at 950°C





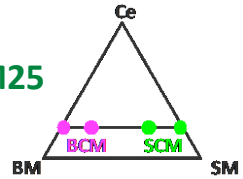
- 2H-BM is steadily shifted to higher angle to be a 4H-SM.
- 2H-BM is dominate at lower Sr-frac. and temp.
- 4H-SM is dominate at higher Sr-frac. and temp.

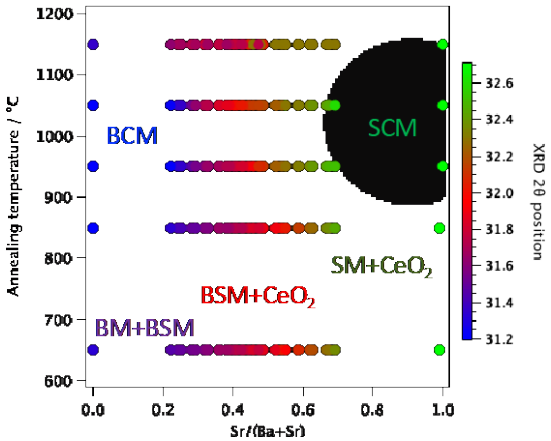
Accomplishments: Key Results

In Collaboration with Combi Node (NREL)

BCM25+SCM25

at 950°C

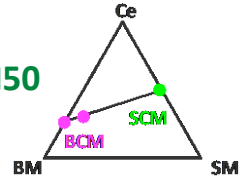


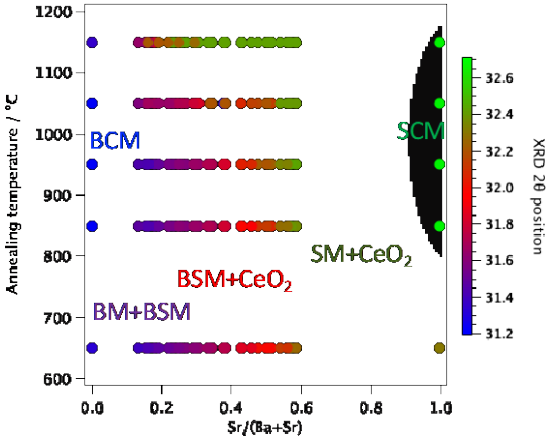


- BCM in the region of 0.0 – 0.25 Sr/(Ba+Sr) in BCM25+SCM25
- SCM in the region of 0.7 – 1.0 Sr/(Ba+Sr) in BCM25+SCM25
- CeO_2 is dominant in higher temp

BCM25+SCM50

at 950°C





- BCM in the region of 0.0 – 0.15 Sr/(Ba+Sr) in BCM25+SCM50
- SCM in the region of around 1.0 Sr/(Ba+Sr) in BCM25+SCM50
- CeO_2 is dominant in higher temp