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

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Colorado School of Mines
04/30/2019

P165

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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 – 02/28/2020
Year 1 Funding* Year 2 Funding*	$249,990 $265,324

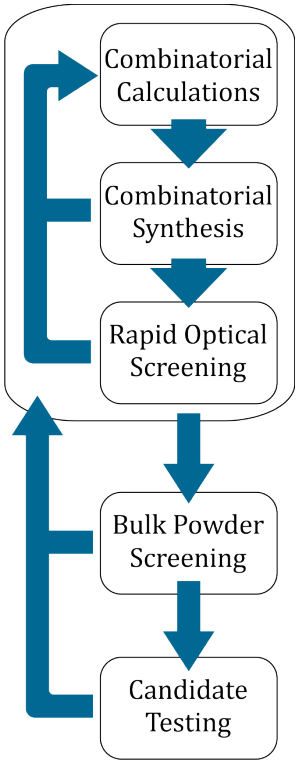
** this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

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:

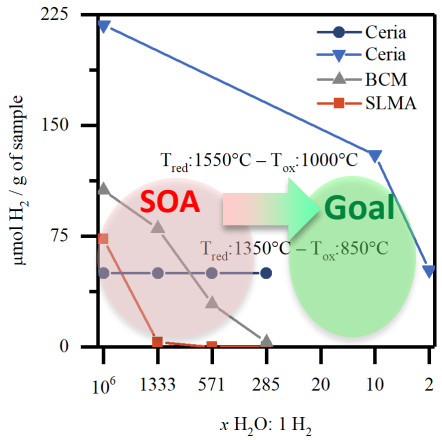
Today: 10's of compositions
Project Goal: 1000's of compositions

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

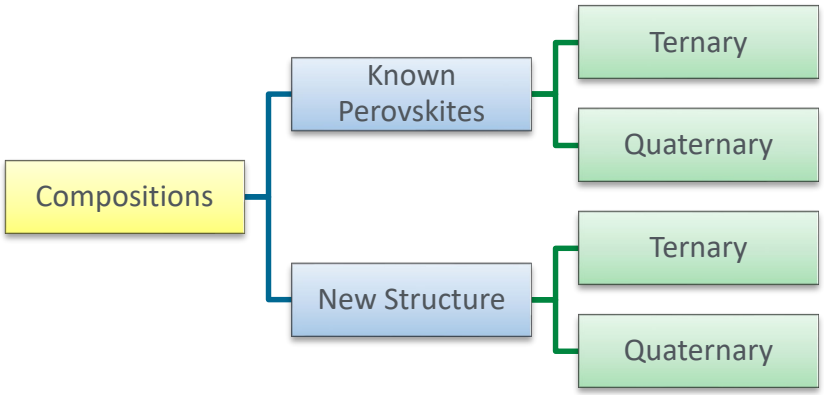
- Secondary defect calculations may be too time consuming to be useful
- Optical evaluation may be insufficient
- Screening of thin films may not fully correlate to bulk properties

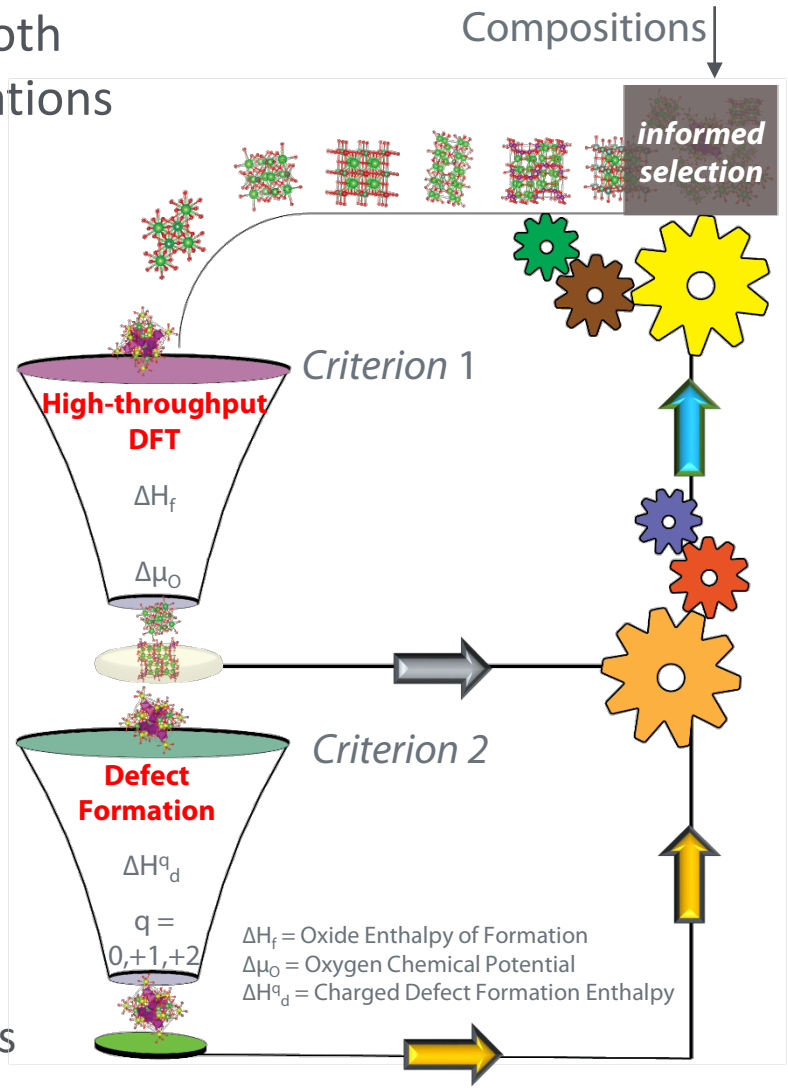
Partnerships

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

Approach- Innovation: DFT Screening

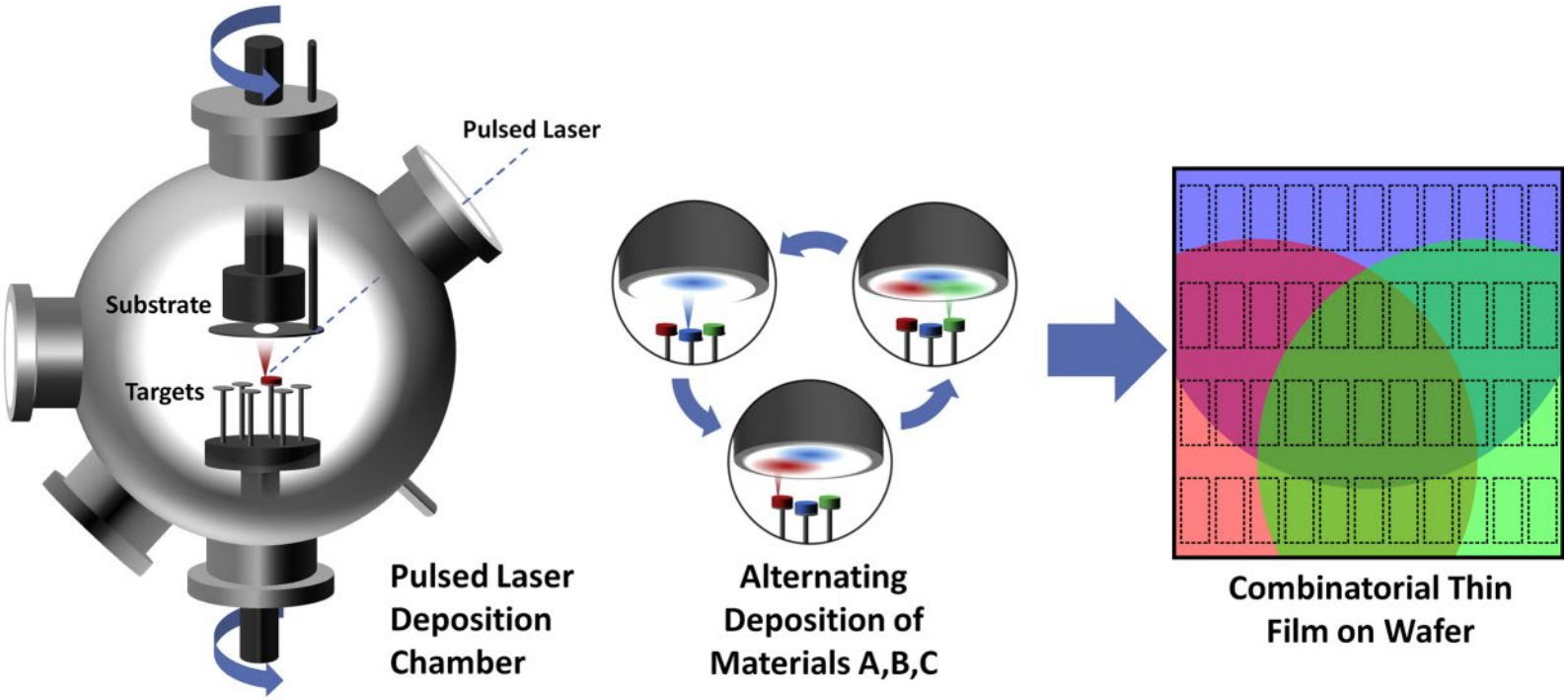
- A two-part screening method to leverage both high-throughput and detailed defect calculations focused on two types of composition





- 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



Adapted from
https://doi.org/10.1016/j.tsf.2015.08.054

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

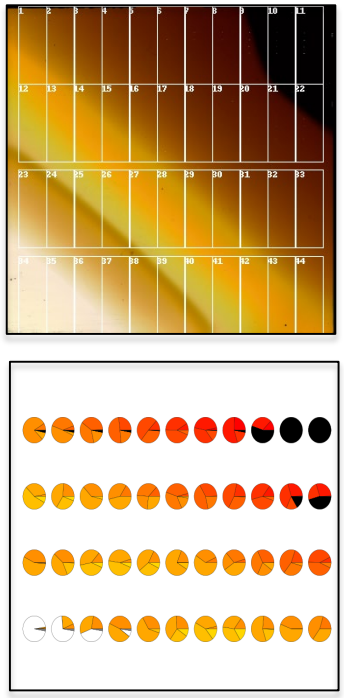
Approach- Innovation: Color Measurements

- Many transition metal containing oxides change color depending on oxygen content
- A single color measurement can evaluate tens of different compositions simultaneously

Professional Optical Scanner for image collection

3D-printed holder for 16 libraries and 5 references

44 measurements and analysis results (example)



Casey Haack, Dylan Hamilton, Michael Sanders, Ryan O'Hayre, Andriy Zakutayev, in preparation

- Each sample library is measured at 44 locations and analyzed in Hue-Saturation-Value space
- Each of the 44 pie charts represents a unique composition with HSV fraction/Hue

Approach- Innovation: Summary

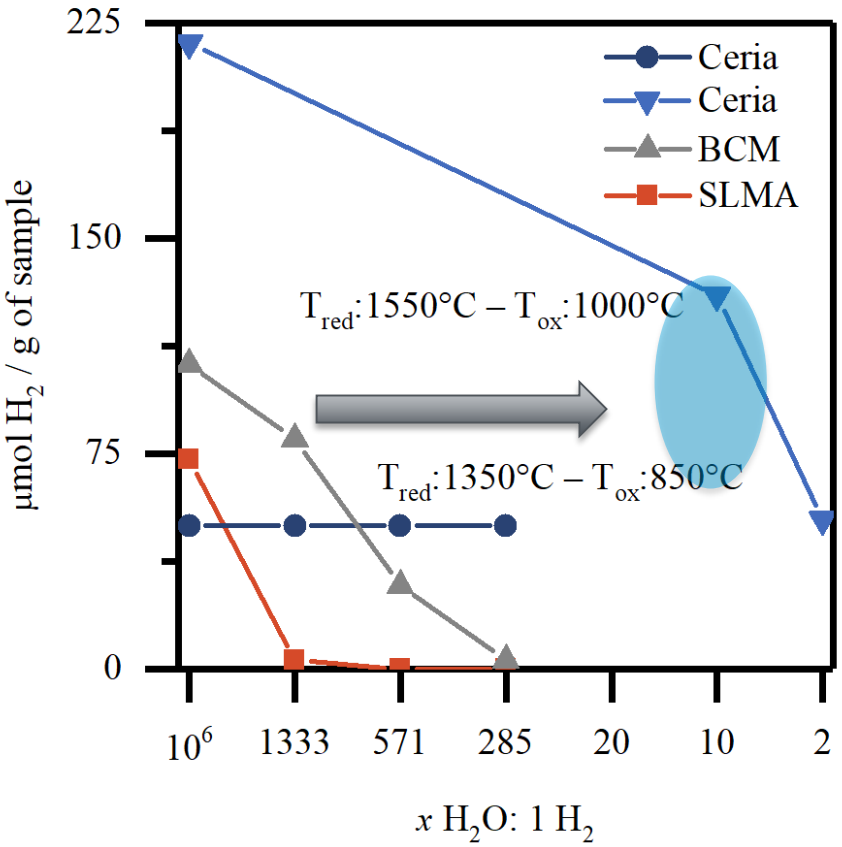
- Budget Period One acted as a proof-of-concept and development cycle to determine feasibility of combining high-throughput DFT screening with combinatorial and high-throughput STCH materials production and screening
  - Modifications to both the computational and combinatorial strategies have occurred as a consequence of the lessons-learned during Budget Period One

- Consortium resources and expertise have proven critical
  - Weekly interactions with node experts has accelerated progress with valuable modifications to our project plan

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 1 Go/No Go Milestones

Milestone Number	Milestone Type	Milestone Description	Milestone Verification Process
M1.3	Evaluation of results to inform next iteration	Experimentally validate method to qualitatively predict thermodynamic trends in oxide reduction (and hence potential STCH suitability) as a function of oxide composition by DFT across five different families and within at least one compositional family.	Extent of reduction measurements on five compositions from different oxide families and more than three across a single family
M3.2	Bulk materials testing	Bulk testing demonstrates that at least one material composition splits water with a hydrogen capacity at least equal to that of ceria under the reduction conditions of 1350°C and oxidation temperatures of 850°C-1000°C, under any steam-to-hydrogen ratio.	Production of at least 59 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.

Composition	Vo (DFT) [eV]	Extent of Reduction (Exp) [δ]
CSM1	1.8	0.175
CSM2	2.2	0.12
CSM3	2.7	0.075
BCM	3.0	0.175
BMO	2.5	0.45
BCO	10	0.02
CeO2	4	0.04
SLMA6464	1.5	0.20

Best of the CSM Family

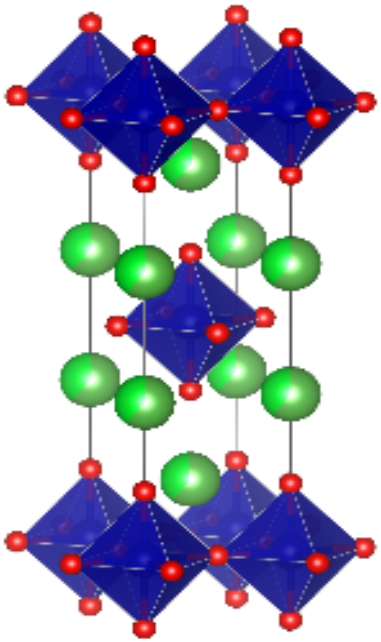
$Ce_{0.2}Sr_{1.8}MnO_4$ (CSM2) produced 247 µmol H2/g sample at slightly higher TR of 1400°C

Sample has been tested at the required 1350°C and also easily beat target (>150 µmol H2/g)

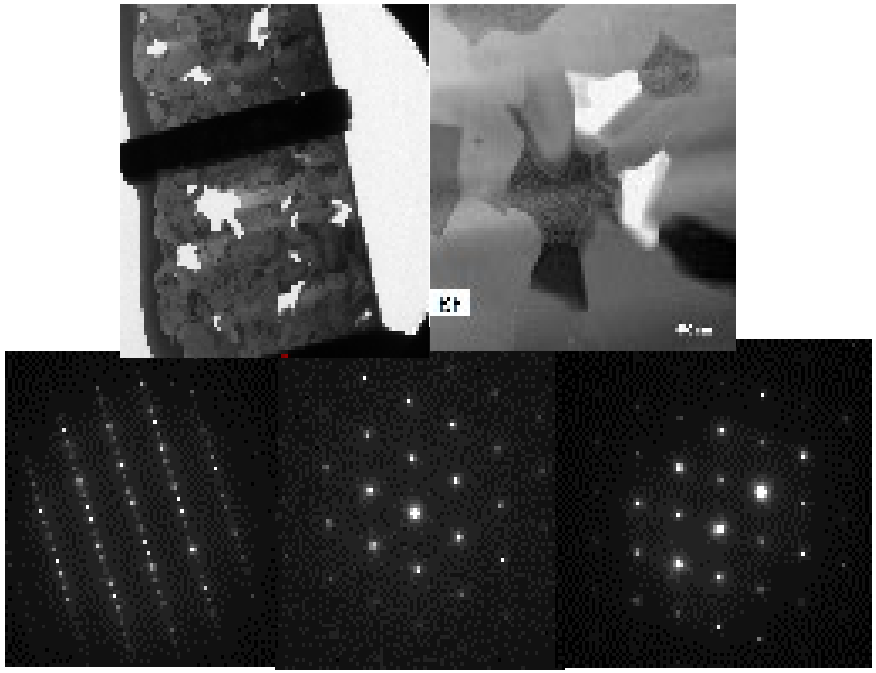
This sets the stage for the discovery of many more STCH compounds and a broader understanding of the property and behavior relationships for redox oxide-cycle water splitting

CSM is a Layered Perovskite (New compound!)

- Unique STCH-active $(SrCe)_2MnO_4$ structure discovered
- $Ce_xSr_{2-x}MnO_4$ layered perovskite, space group I4/mmm (139)
- Solid solution region for $0 < x < 0.4$ (0-20% Ce on A-site)
- Enables "tunable" E_v like SLMA



I4/mmm (Layered Perovskite)

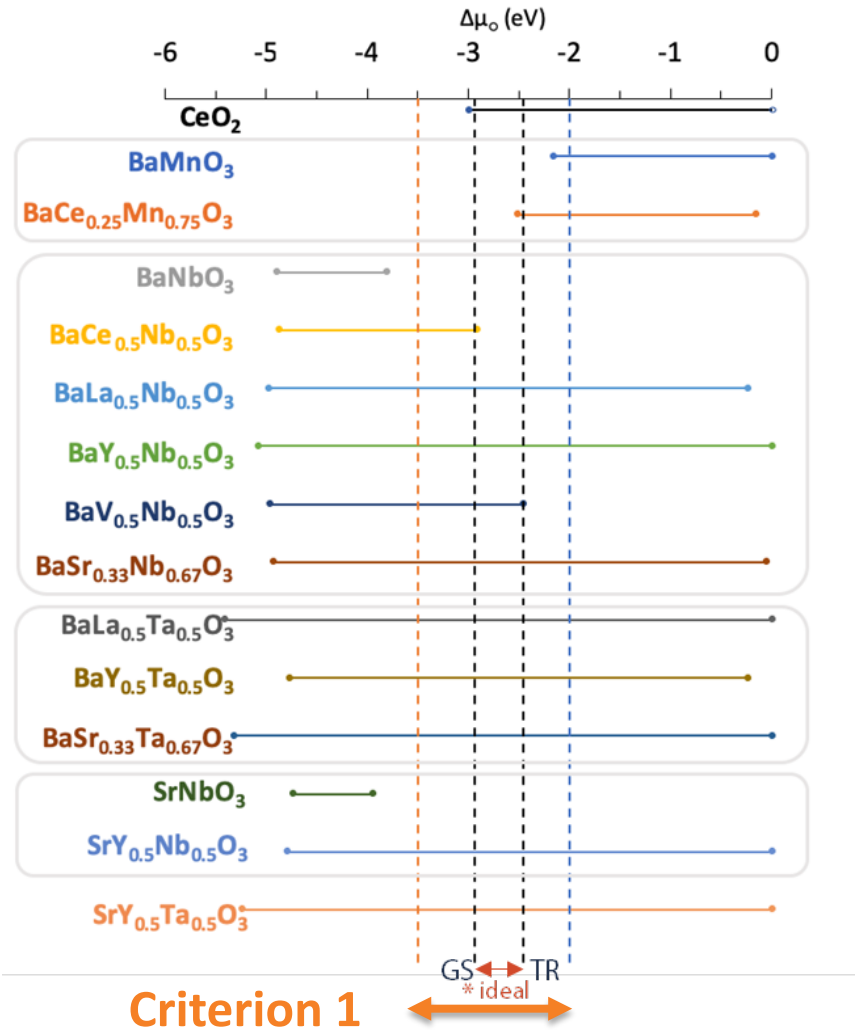


TEM images and diffraction

Accomplishments: Key Results

Task 1: Computational Stability Screening

In Collaboration w/First Principles Theory Node (NREL)



- Ideal oxygen chemical potential stability ($\Delta\mu_O$) range for STCH candidates *: [-2.94, -2.46]
- Compounds with longer tails are likely more stable towards oxidation or reduction
- $BaMnO_3$ decomposes at TR
- $BaCe_{0.25}Mn_{0.75}O_3$ stable at TR but weak at splitting
- $BaV_{0.5}Nb_{0.5}O_3$ looks promising but can be too stable to reduce

*: S. Lany, The Journal of Chemical Physics **148**, 071101 (2018)

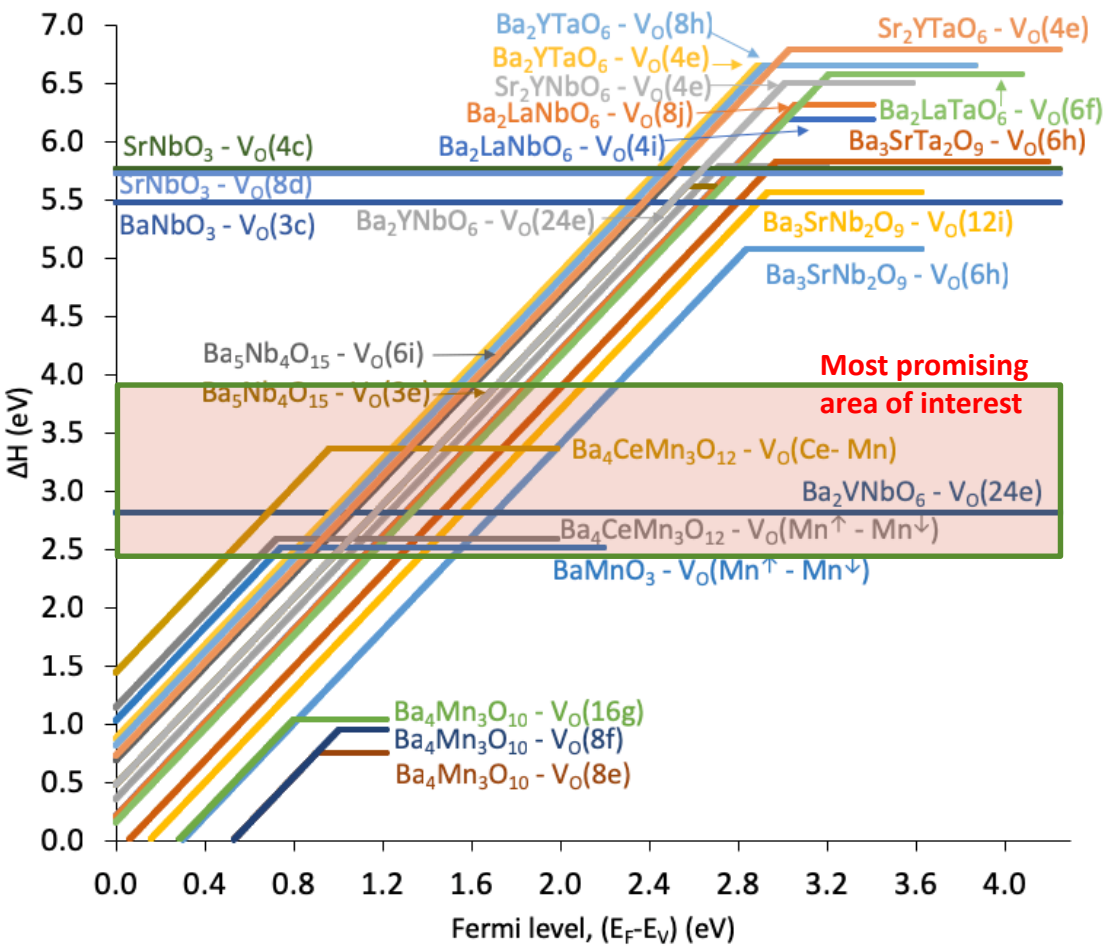
TR = Thermal reduction GS = Gas splitting

Accomplishments: Key Results

Task 1: Computational Defect-Formation Screening

In Collaboration w/First Principles Theory Node (NREL)

Charged Oxygen Vacancy (V_O^q) Formation Energy



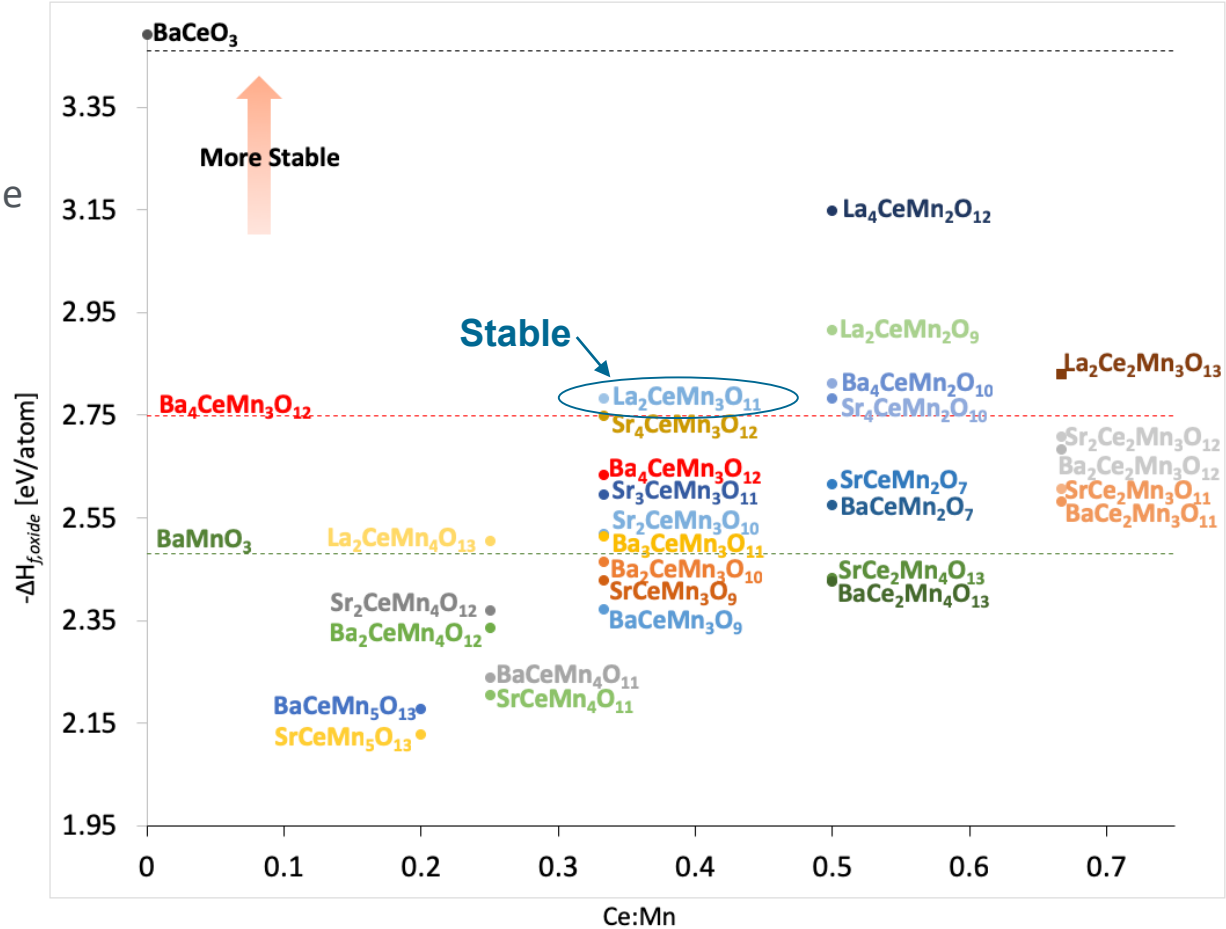
- Mn and Nb results in low and high V_O, respectively
- Y and Ta compounds have high V_O
- Sr replacing Ba [A-site] shifts up the V_O
- Sr replacing species at B-site shifts the V_O down
- V has strong influence on V_O
- Ce and V compounds' V_O are better positioned

Accomplishments: Key Results

Task 1: Computational Defect-Formation Screening

In Collaboration w/First Principles Theory Node (NREL)

- Results from stability and defect formation energy work lead to a structure-prototype search for additional potentially stable new (i.e., previously unknown) Ce and Mn containing materials
- Most were unstable compared to known compositions, but there were some new compositions of interest
- The most promising, $La_2CeMn_3O_{11}$, is in the process of being synthesized. Experimental work is still ongoing.



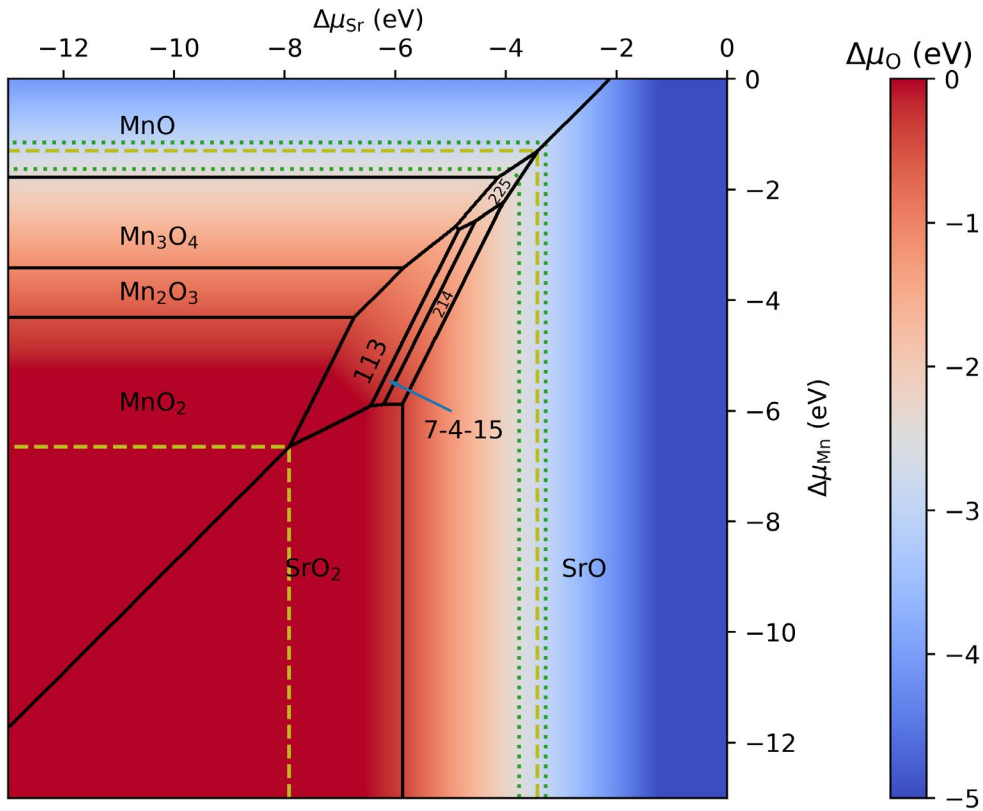
- Constraint: Ce: +4, Mn: +4
- Includes > 200 random and prototype searches for each composition
- Total number of calculation represented on this plot > 6000

Accomplishments: Key Results

Task 1: Computational Defect-Formation Screening

In Collaboration w/First Principles Theory Node (NREL)

"Deep Dive" into the role of Ce in the $Ce_xSr_{2-x}MnO_4/Sr_{1-x}Ce_xO_3$ system



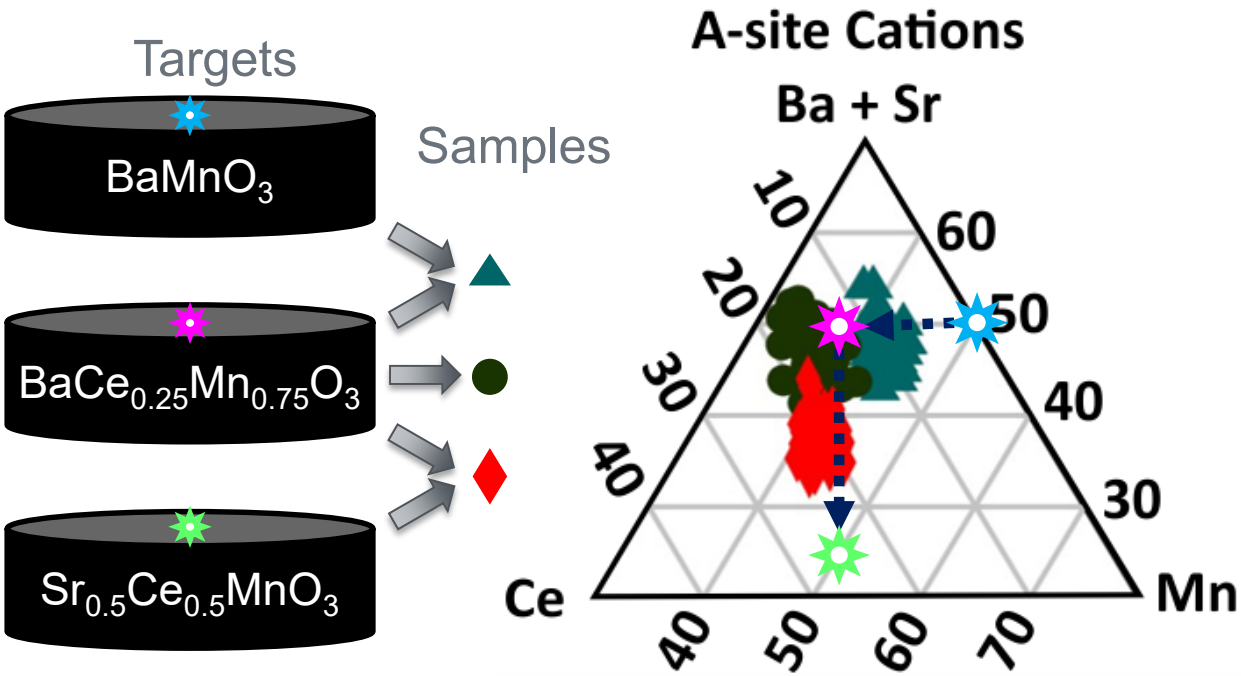
The stability regions for $SrMnO_3$ and Sr_2MnO_4 do not fall into the ideal $\Delta\mu_O$ limit for GS and TR (green lines).

- Can Ce-doping move the stability region?
- Are other phases more optimal? For example: $Sr_2Mn_2O_5$, a $SrMnO_3$-related ordered vacancy phase?

Accomplishments: Key Results

In Collaboration with Combi Node (NREL)

- Task 2: Combinatorial (synthesis)
  - The combinatorial PLD technique makes many chemical compositions at once
  - These "libraries" are screened for for structural and thermochemical behavior.

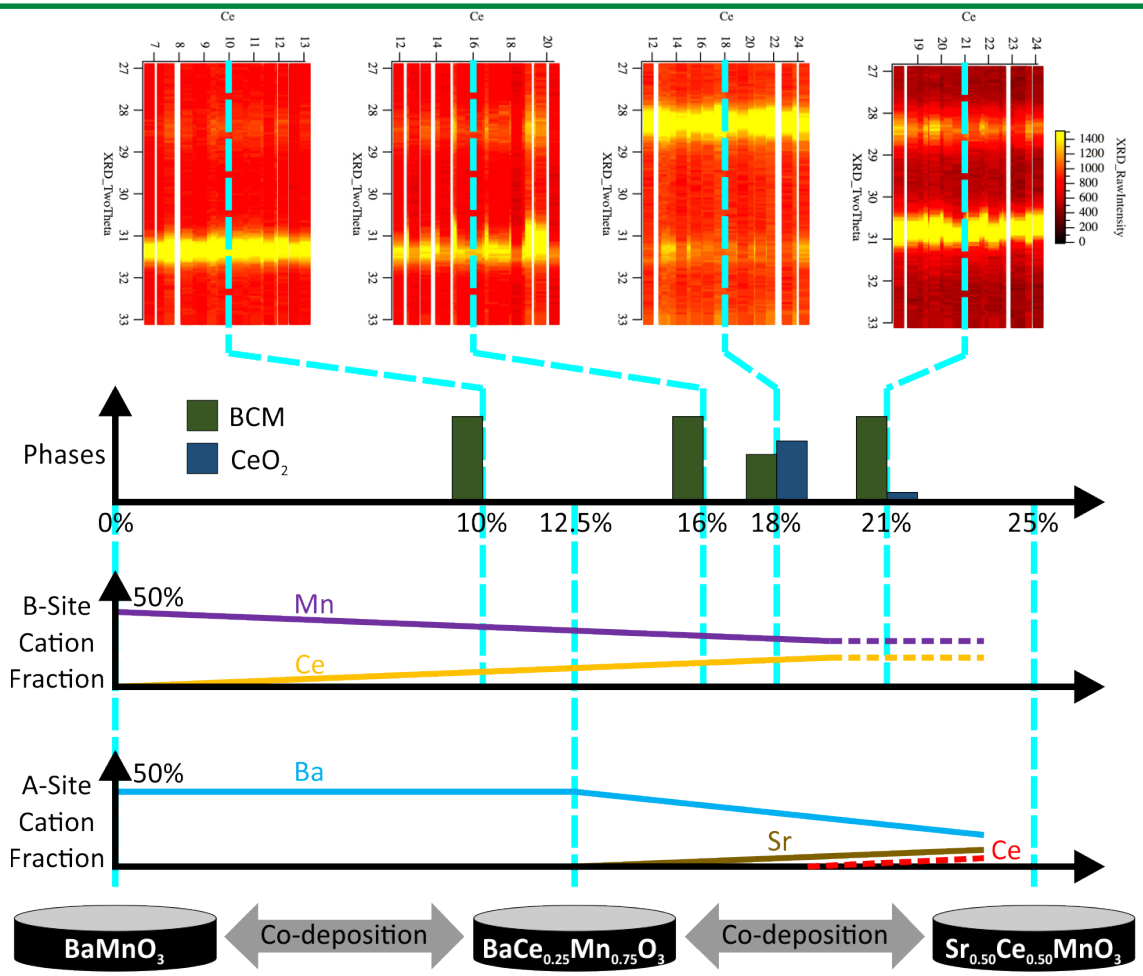


- Increasing Ce in BCM should make it better, but it is hard due to CeO_2 segregation
- We used combi PLD to investigate solubility limits of Ce in substituted BCM

BCM is thought to be a line compound, so changes in the Ce content could point to deviations in the stoichiometry, which suggests some ability to tune the reduction thermodynamics

Accomplishments: Key Results

In Collaboration with Combi Node (NREL)



- XRD results show that alloying BCM with Sr increases Ce solubility limit
- However, some Ce moves from B-cite to A-cite in perovskite structure
- It is not clear how A-site Ce influences the STCH stability and performance
- Redox annealing, color measurements, and quantification are in progress

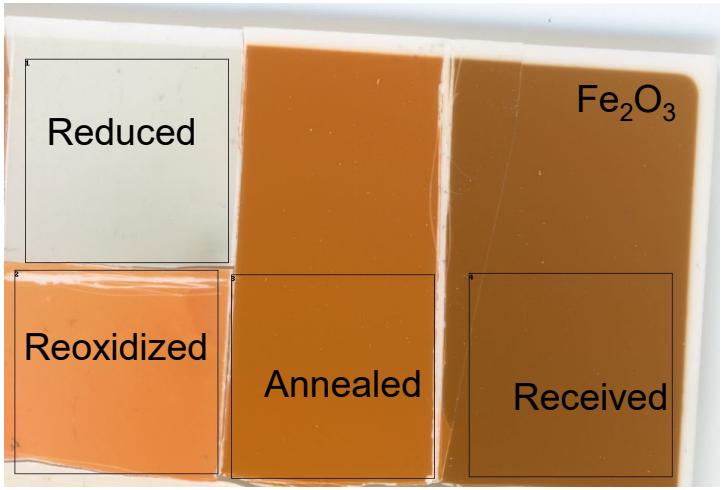
Yun Xu, Meagan Papac, Michael Sanders, Ryan O'Hayre, Andriy Zakutayev, in preparation

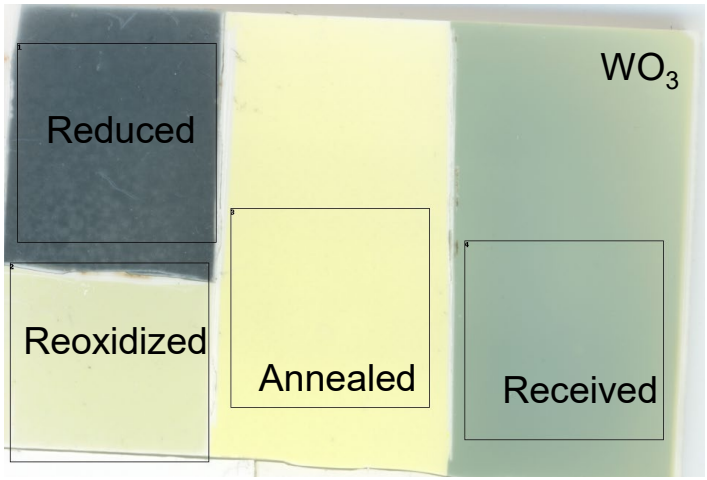
Concentration of Ce in BCM line compound can be increased by co-substituting it with Sr. This should improve the stability and performance of BCM (measurements in progress)

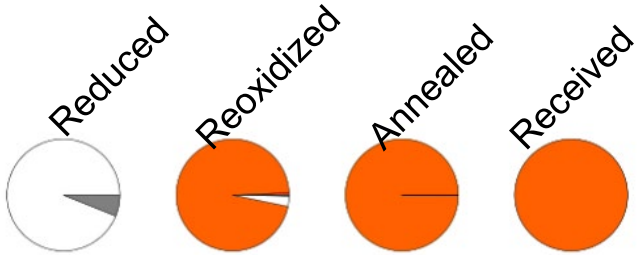
Accomplishments: Key Results

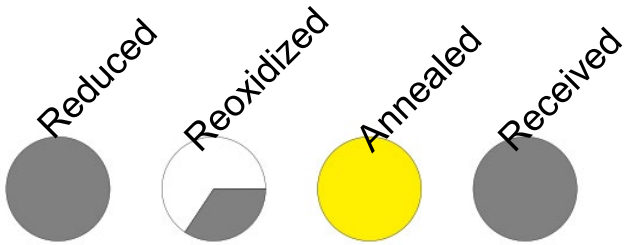
In Collaboration with Combi Node (NREL)

- Fe_2O_3 and WO_3 show reversible color changes upon redox annealing
- The color changes can be quantified by colored HSV pie-charts
- Similar quantitative analysis can be performed for BCM and new materials









The new sample measurement methods and color quantification algorithms have been developed and tested on the sample of prototypical Fe_2O_3 and WO_3 materials

Accomplishments: Key Results

In Collaboration with Combi Node (NREL)

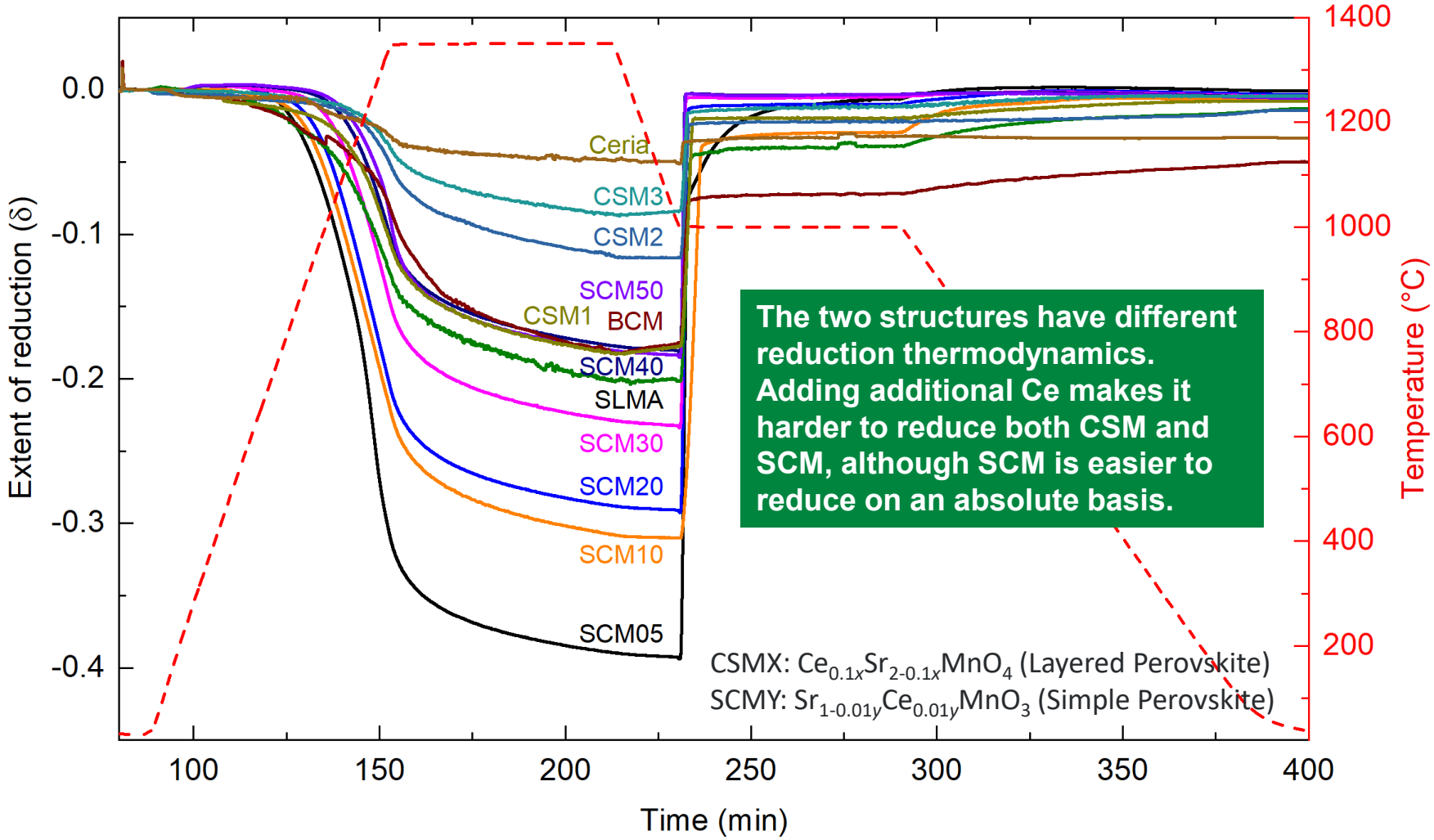
- Task 2: Combinatorial
  - Since 2018 AMR, progress was made on optical screening method
  - Color changes due to redox cycling have been observed for combinatorial films of known water-splitting compounds
  - Image analysis was added to identify areas with color changes
  - $BaCe_{0.25}Mn_{0.75}O_{3-\delta}$ (BCM) is thermochemically active, however the parent, $BaMnO_{3-\delta}$ (BMO), too easily reduces to split water

01539 — BCM-BMO Combi-library

Color changes have successfully differentiated thermochemically active compositions from merely thermal reducible compositions

Accomplishments: Key Results

- Task 3: Bulk Testing



The two structures have different reduction thermodynamics. Adding additional Ce makes it harder to reduce both CSM and SCM, although SCM is easier to reduce on an absolute basis.

Accomplishments: Outlook

- Meeting the Y2 Go/No Go criteria requires the discovery of a game-changing material
  - Y1 success has provided a broader understanding of the property and behavior relationships for redox oxide-cycle water splitting
  - Strategy adjustments have been made for Y2 to narrow the search, based on the Y1 results

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.

Accomplishments: Reviewer Responses

"The greatest project weakness is the experimental rapid screening. This needs to become quantitative rather than qualitative, and diffusional/thin film stability issues need to be resolved."

"It is not clear how the combinatorial thin film screening really fits in, as the samples shown have rather uniform color. It would have been more interesting to see whether the color shows gradations with changing stoichiometry."

- As discussed, the rapid screening has progressed, but is still unproven.
  - Substrate/film interactions will be reduced, if not eliminated, with a drop in process temperature (combined with chemical reduction)
  - Color uniformity will be improved with the addition of a dedicated gas-tight substrate heating chamber for redox testing
  - The improvement of the above factors will allow for better pre- and post-testing characterization and quantitative analysis

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 • 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 • 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

- Both Y1 Go/No-Go Milestones were met
- Introduction of new STCH compound (second in testing)
- Greater understanding of thermodynamic requirements
- Development of potential screening process

	Theory	Combinatorial	Bulk	Total
Compounds Investigated (overlap)	400 (30)	400 (30)	10 (10)	750

- Successful collaboration with three EMN nodes
- Two publications
- Positive reviews from HPTT & AMR

Success during Budget Period One created a strong starting point for Budget Period Two, but the Go/No-Go is challenging

Publications and Presentations

- $BaCe_{0.25}Mn_{0.75}O_{3-\delta}$ — a promising perovskite-type oxide for solar thermochemical hydrogen production, Energy Environ. Sci., 2018, **11**: 3256-3265

- Phase identification of the layered perovskite $Ce_xSr_{2-x}MnO_4$ for solar thermochemical water splitting, Inorganic Chemistry, In Revision

- The Effect of Structure on Oxygen Vacancy Formation Energy in Ce-Substituted Sr-Mn Oxides (Presentation), *MRS Spring Conference 2019, Phoenix AZ,* April 2019

- The "Perovskite Playground": Engineering Defect Chemistry in Doped Perovskite and Perovskite-Related Oxides for High Temperature Redox (Invited Presentation), *MRS Spring Conference 2019, Phoenix AZ,* April 2019

Technical Back-Up Slides

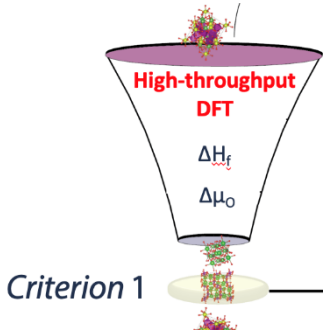
DFT Criteria

Criterion 1: **Stability** under STCH conditions

- Enthalpy of formation (ΔH_f) is estimated by referencing FERE* energies of constituent elements:

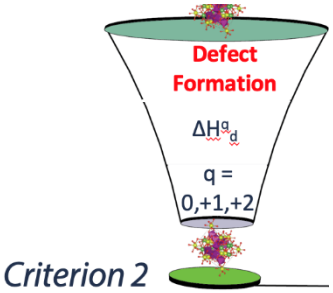
$$\Delta H_f^{\mathrm{FERE}}(\mathrm{A}_{n_1}\mathrm{B}_{n_2}\ldots) = \Delta H_f^{\mathrm{GGA}+U}(\mathrm{A}_{n_1}\mathrm{B}_{n_2}\ldots) - \sum_i n_i\,\delta\mu_i^{\mathrm{FERE}}.$$

- The oxygen chemical potential ($\Delta\mu_O$) can be estimated by evaluating ΔH_f of all competing phases.
  - competing phases are obtained from existing NREL MatDB database[Φ] or evaluated individually
- The ideal condition for STCH[⊥] places a constraint on oxygen chemical potential: $\Delta\mu_0 \in [-2.94, -2.46]$



Criterion 2: Defect thermodynamic favorability

- Large electronic entropy[⊥] contribution for charged defect (V_O) level lies above about $E_{cbm}(0)$-0.4 eV.



*: V. Stevanović et al., Phys. Rev. B 85, 115104 (2012) ; S. Lany, Phys. Rev. B 78, 245207 (2008)
Φ : https://materials.nrel.gov/
⊥: S. Lany, The Journal of Chemical Physics **148**, 071101 (2018)

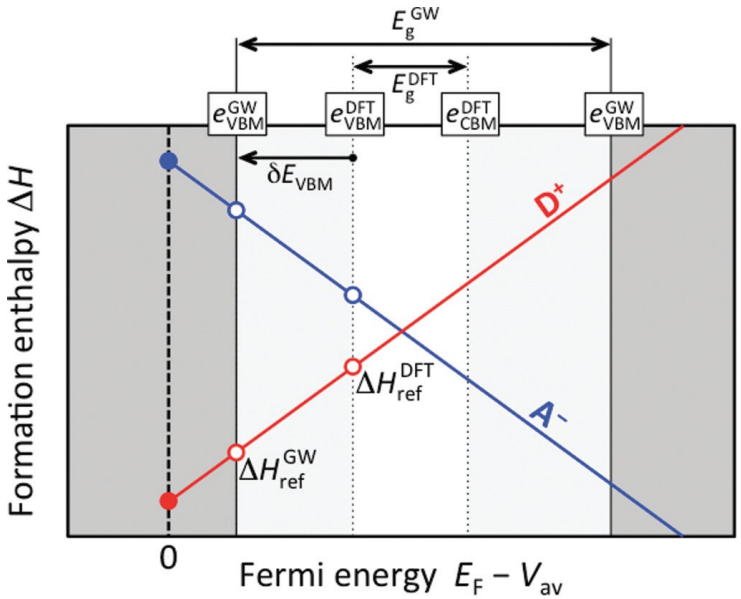
Defect Calculations Approach

$$\Delta H_{D,q}(\mu, E_F) = [E_{D,q} - E_{host}] + [\mu_{host} - \mu_D] + q \cdot E_F$$

Phys. Rev. B, 2013. ***88****(11),115201*

Method: GGA+U
FERE elemental reference energy was used.

Orbital	U values
Mn-*d* shell	3.0 eV
Ce-*d* shell	1.5 eV
Ce-*f* shell	2.0 eV



- **Defect configuration**: different oxygen Wyckoff positions are considered
- **Magnetic configuration**: different defect magnetic configurations are sampled