Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

HydroGEN: Solar Thermochemical Hydrogen (STCH) and STCH Supernode

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Project ID # p148D

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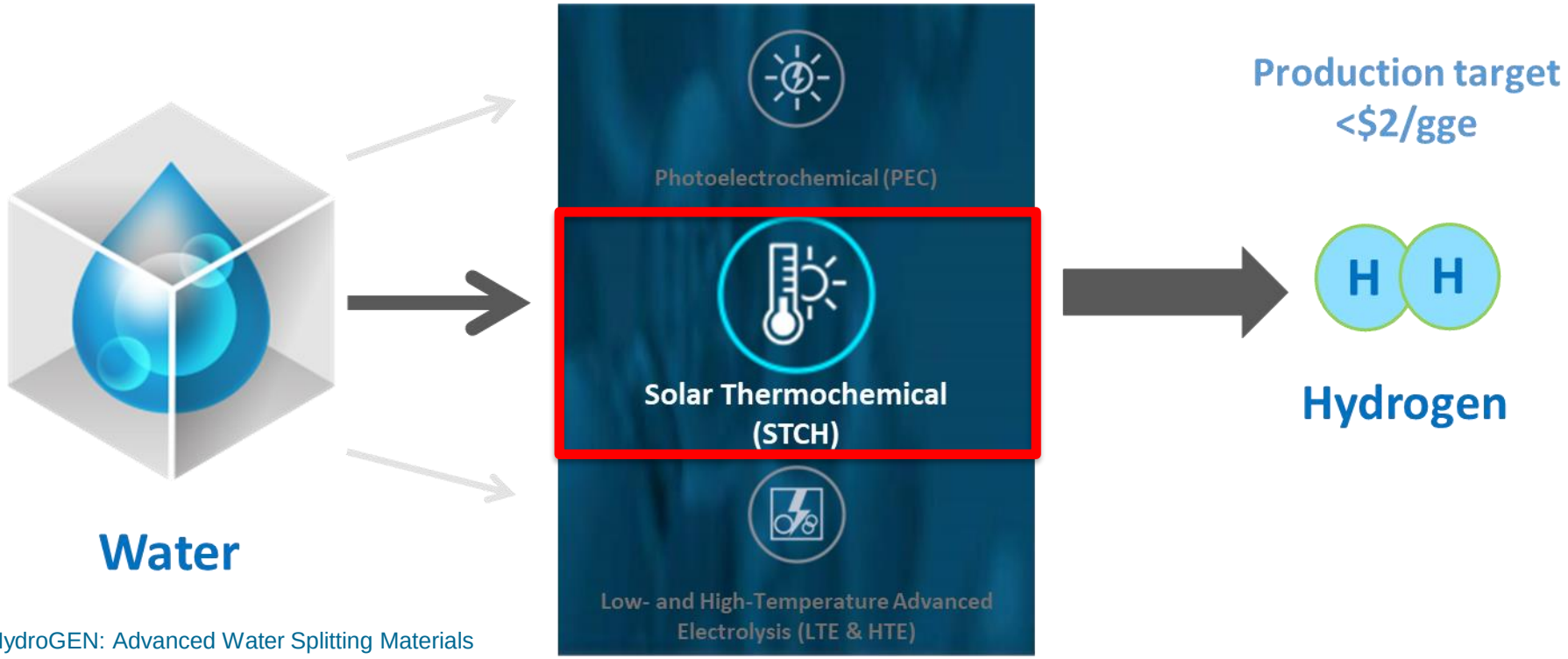
NREL | BERKELEY LAB | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory | SRNL

Advanced Water-Splitting Materials (AWSM) Relevance, Overall Objective, and Impact

AWSM Consortium 6 Core Labs:

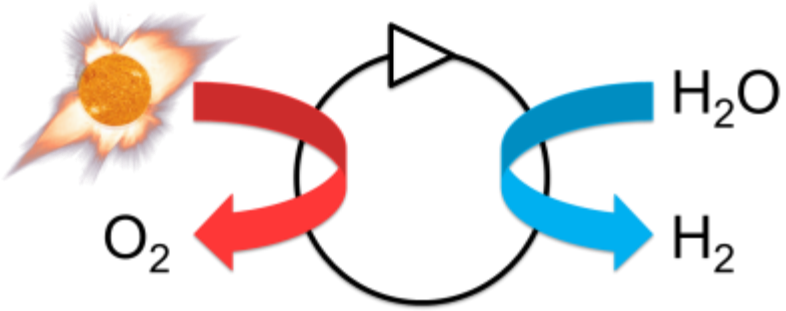
NREL National Renewable Energy Laboratory; Berkeley Lab; Sandia National Laboratories; Idaho National Laboratory; Lawrence Livermore National Laboratory; SRNL

Accelerating R&D of innovative materials critical to advanced water splitting technologies for clean, sustainable & low cost H_2 production, including:



Overview – STCH and Hybrid STCH Technologies

Thermochemical Cycle



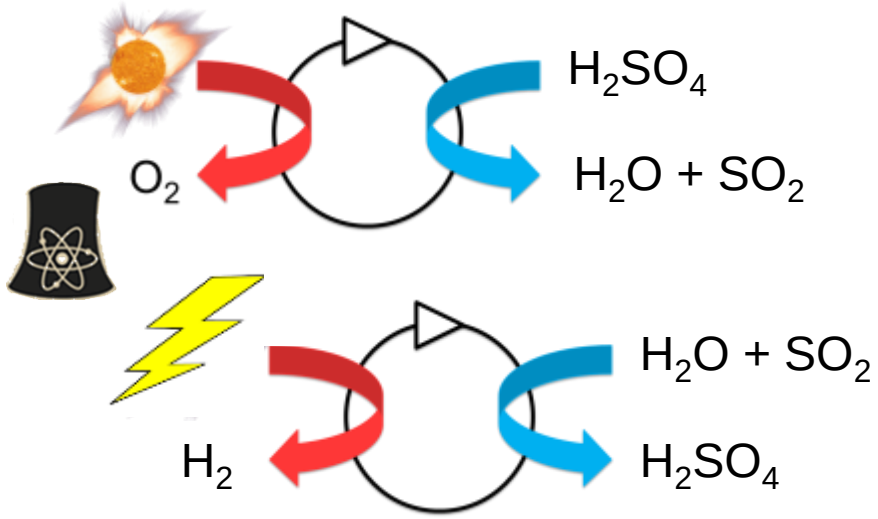
$$MO_x \rightarrow MO_{x-\delta} + \frac{\delta}{2} O_2 \qquad \text{(1) Reduction}$$

$$MO_{x-\delta} + \delta \cdot H_2O \rightarrow MO_x + \delta \cdot H_2 \qquad \text{(2) Oxidation}$$

$$\delta \cdot H_2O \rightarrow \frac{\delta}{2} O_2 + \delta \cdot H_2 \qquad \text{(3) Thermolysis}$$

- Metal cation is redox active element in two-step cycle.
- R&D effort focused on MO_x materials discovery.

Hybrid Cycle

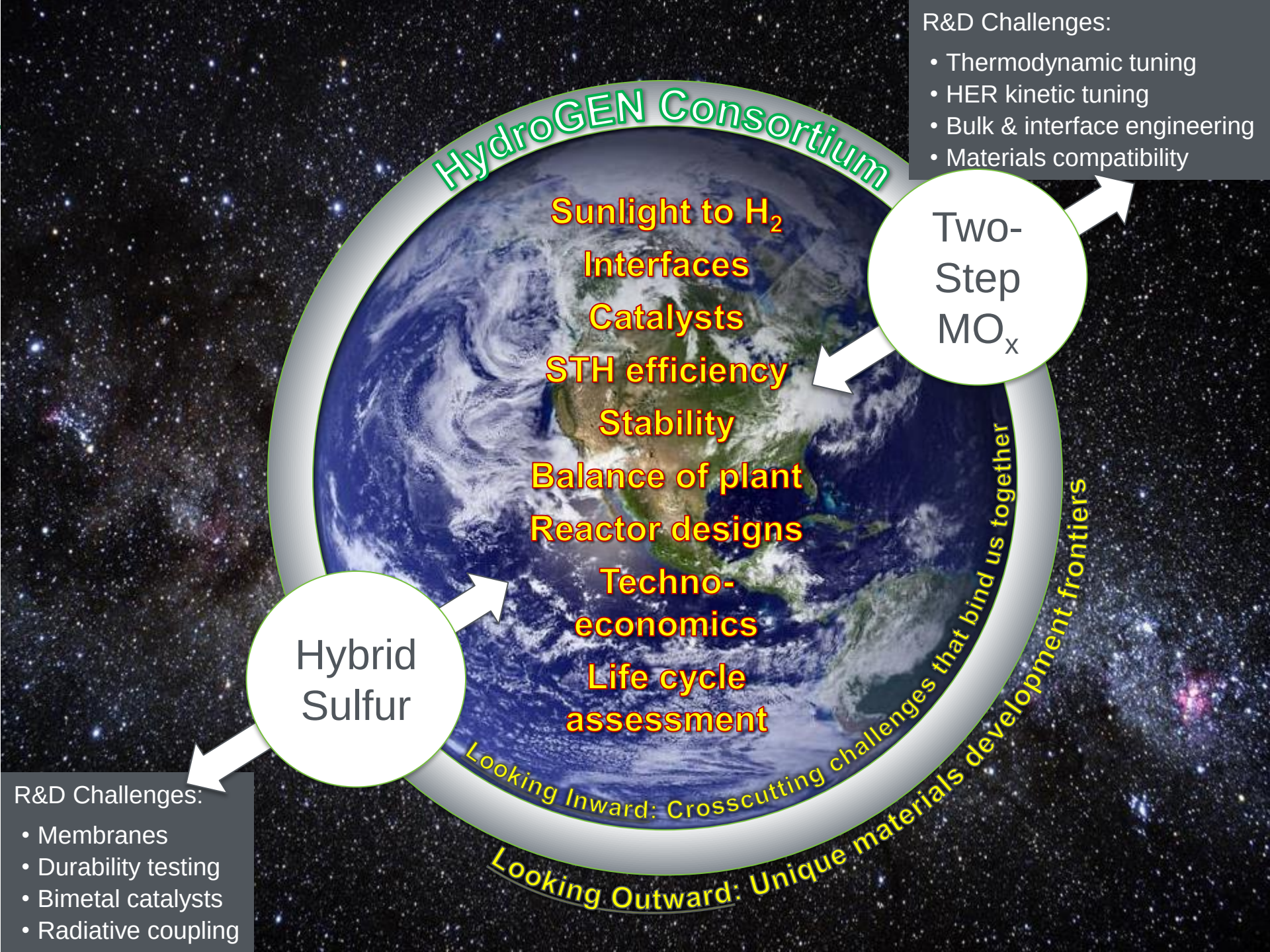


$H_2SO_4 \leftrightarrow H_2O + SO_2 + ½\ O_2$
(thermochemical; 800-900 °C)

$SO_2 + 2\ H_2O \rightarrow H_2SO_4 + H_2$
(electrochemical; 80-120 °C)

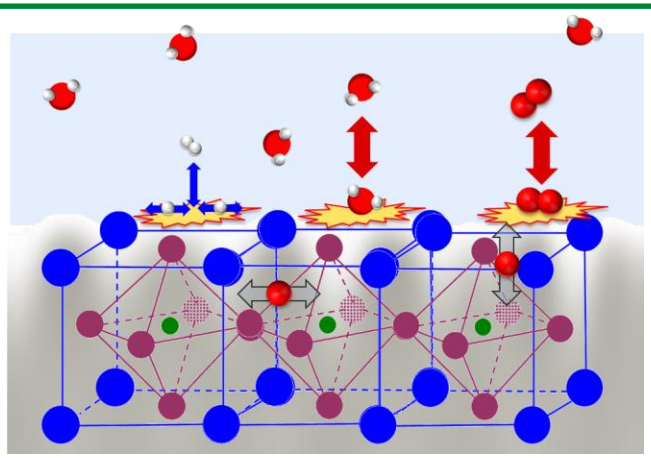
Net Reaction: $H_2O \rightarrow H_2 + ½\ O_2$

- Sulfur is redox active element in two-step cycle.

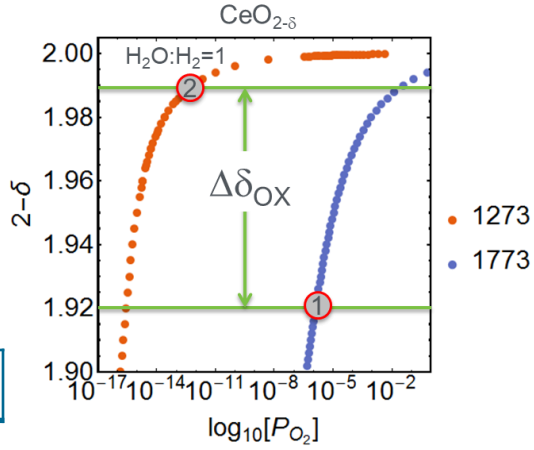

HydroGEN Consortium
Sunlight to H_2
Interfaces
Catalysts
STH efficiency
Stability
Balance of plant
Reactor designs
Techno-economics
Life cycle assessment
Looking Inward: Crosscutting challenges that bind us together
Looking Outward: Unique materials development frontiers
Two-Step MO_x
Hybrid Sulfur
R&D Challenges:
• Thermodynamic tuning
• HER kinetic tuning
• Bulk & interface engineering
• Materials compatibility
R&D Challenges:
• Membranes
• Durability testing
• Bimetal catalysts
• Radiative coupling

Principal Material Challenges for Non-Stoichiometric Oxides:
Reduction Temperature (T_R) & Solid State O-atom Activity ($\mu_{O,solid}$)

challenge: decrease T_R and increase $\Delta\delta_{OX}$

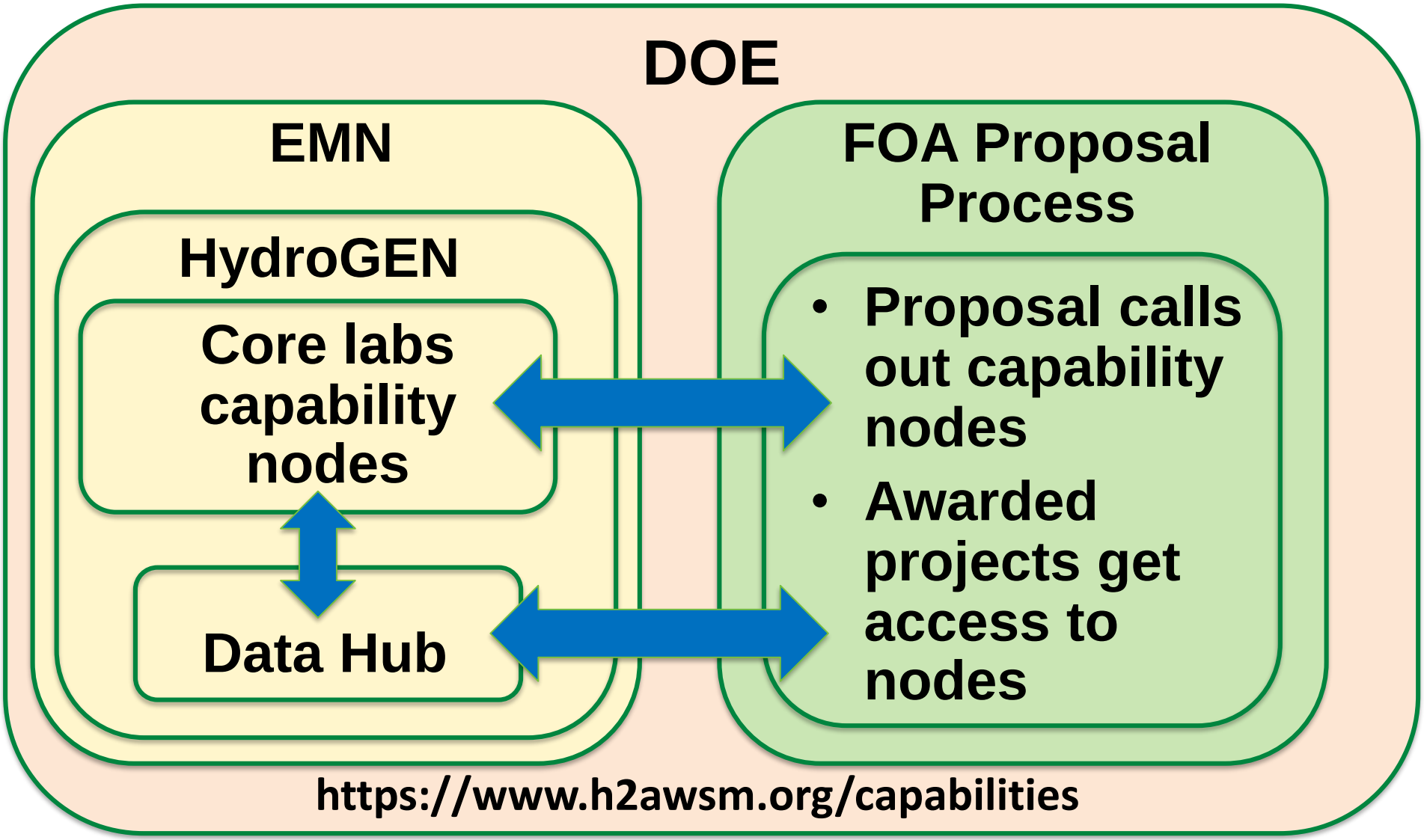


- Oxygen storage materials with a twist.
  - O-atom "harvested" from H_2O not Air
  - Bulk phenomena largely govern O-atom exchange with environment
- Material subject to extreme environments.
  - Redox cycling on the order of seconds
  - Large thermal stress per cycle
    - 800 $^oC < T < 1450\ ^oC$; ΔT_{RATE} ~100 ^oC/sec
  - Large chemical stress per cycle
    - 10^{-14} atm< p_{O2} <10^{-1} atm
- Water splitting at extremely low p_{O2}.
  - Strongly reducing "oxidizing" atmosphere



"O" activity in $H_2O:H_2$	$\mu_{gas} > \mu_{solid}$	μ_{gas} ~10^{-13}atm

Approach – HydroGEN EMN



Approach – HydroGEN EMN

Barriers
- Cost
- Efficiency
- Durability

STCH Node Labs

Sandia National Laboratories

Idaho National Laboratory

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

Lawrence Livermore National Laboratory

Support through:

Personnel
Equipment
Expertise
Capability
Materials
Data

STCH FOA Projects

Arizona State University

Colorado School of Mines

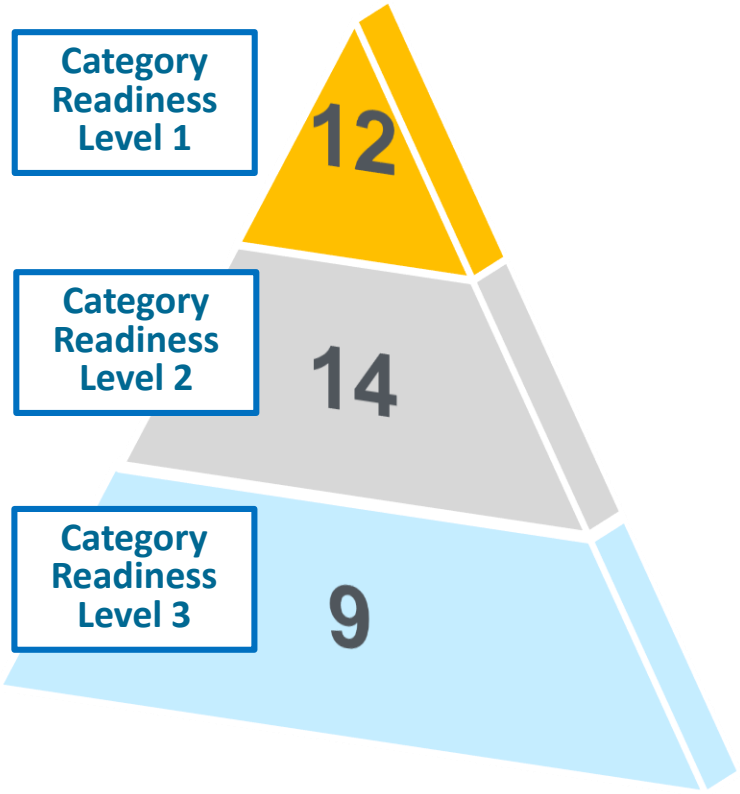
Northwestern University

UCSD

UF University of Florida

Greenway Energy LLC
Engineering consultant in Aiken County, South Carolina

Collaboration: 35 STCH Nodes, 1 Supernode



Analysis: 2 **Characterization: 6**
Computation: 3 **Synthesis: 1**

Node is **fully developed** and has been used for AWSM research projects

Analysis: 3 **Characterization: 5**
Computation: 6 **Synthesis: 2**

Node requires some development for AWSM

Analysis: 2 **Characterization: 5**
Computation: 4 **Synthesis: 1**

Node requires significant development for AWSM

- Nodes comprise equipment and expertise including uniqueness.
- Category refers to availability and readiness.
- Many nodes span classification areas.

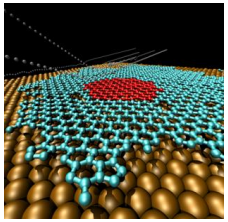
14 Nodes utilized by current STCH projects

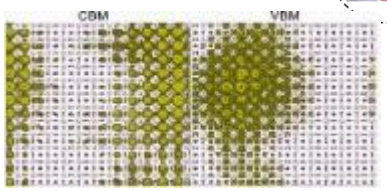
Collaboration: HydroGEN STCH Node Utilization

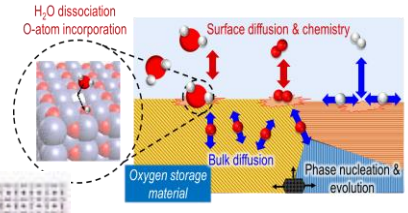
FY'20 Projects

Lab	Node	ASU	CSM	CUB	NWU	GWE	UF	UCSD	Super	NSF
LLNL	Mesoscale Modeling				✓					
LLNL	Ab Initio Modeling								✓	
NREL	Defect Modeling		✓	✓			✓	✓	✓	✓
SNL	Uncertainty Quant.	✓								
NREL	Defect Engineering	✓			✓				✓	✓
NREL	Thin Film Combinatorial		✓		✓					

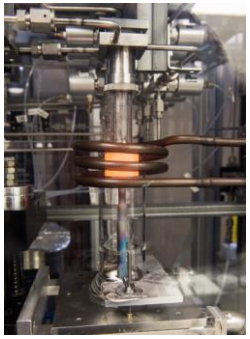
Computation

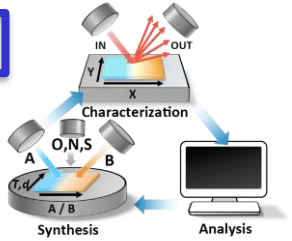


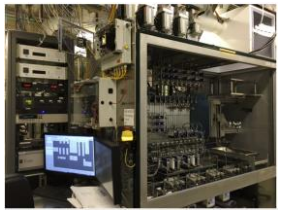




Material Synthesis







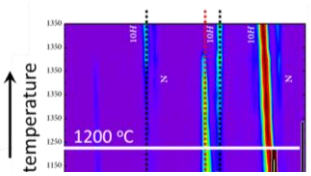
Collaboration: HydroGEN STCH Node Utilization

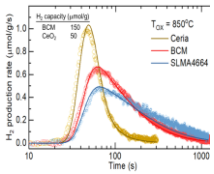
FY'20 Projects

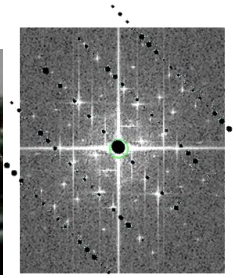
Lab	Node	ASU	CSM	CUB	NWU	GWE	UF	UCSD	Super	NSF
INL	Catal. Harsh Environment					✓				
SNL	HT-XRD & Therm. Analysis	✓		✓	✓			✓	✓	
SNL	Adv. Electron Microscopy							✓	✓	
SNL	Laser Heated SFR	✓	✓	✓			✓		✓	
SNL	AP-XPS						✓			
NREL	Engineering BOP					✓				
NREL	TEA Hydrogen Production			✓						
SRNL	AWSM Requirements Flow Sheet TEA					✓				

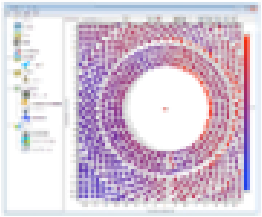
Characterization

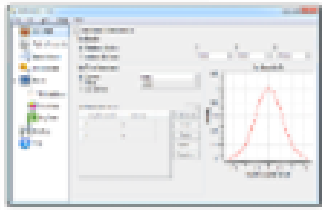
Analysis











Project Accomplishment
STCH Supernode

15 Team Members from 6 HydroGEN Nodes and 3 Labs

NREL:

- First Principles Materials Theory for Advanced Water Splitting Pathways. (S.Lany)
  - Role of charged defects in generating configurational entropy
  - Comp. screen material thermodynamics
- Controlled Materials Synthesis and Defect Engineering. (D.Ginley)
  - Controlled material defect engineering for DFT validation and descriptor testing
  - High resolution *operando* X-ray metrology at SLAC
- Additional personnel
  - Bob Bell, Anuj Goyal, Phil Parilla, Dan Plattenberger, Sarah Shulda, Nick Strange

LLNL:

- Ab Initio Modeling of Electrochemical Interfaces. (T.Ogitsu)
  - Large-scale ab initio simulations of material properties
- Additional personnel
  - Brandon Wood

SNL:

- High-Temperature X-Ray Diffraction (HT-XRD) and Complementary Thermal Analysis. (E.Coker)
  - *operando* XRD, validate structure models
  - Thermal analysis, validate thermo models
- Virtually Accessible Laser Heated Stagnation Flow Reactor for Characterizing Redox Chemistry of Materials Under Extreme Conditions. (A.McDaniel)
  - Characterize and quantify redox performance
  - Assess material's efficacy for water splitting
- Advanced Electron Microscopy. (J.Sugar)
  - Characterize material morphology, composition, and structure with advanced electron microscopies and spectroscopies.
- Additional personnel
  - Andrea Ambrosini, James Park

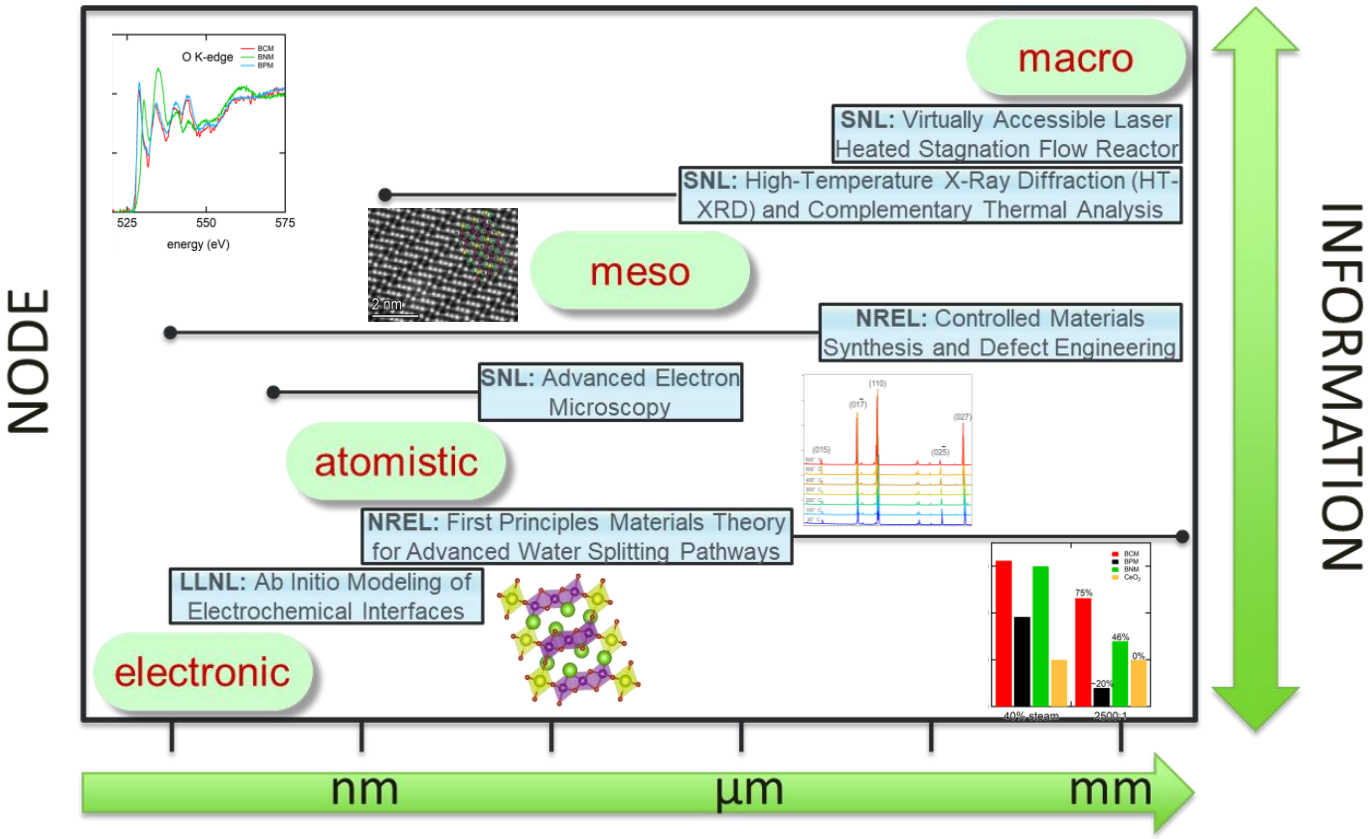
Supernode Goal:

principal research outside scope of seedling projects

Atomistic Understanding of MnO_6 Arrangements that Influence WS Activity

Important Interrelationships:

- electronics
- defects
- structure
- performance

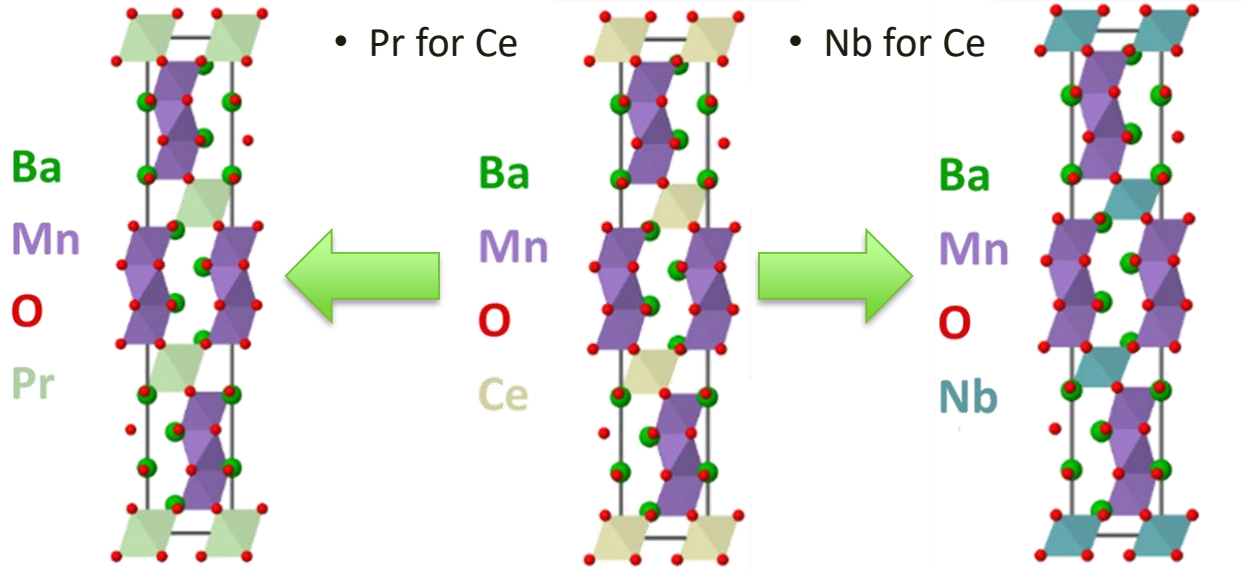


- Objectives.
  - Discover and synthesize model perovskite system
  - Develop and exercise multi-length-scale observation platforms and methods
  - Apply first principles theory to derive atomistic understanding of WS activity

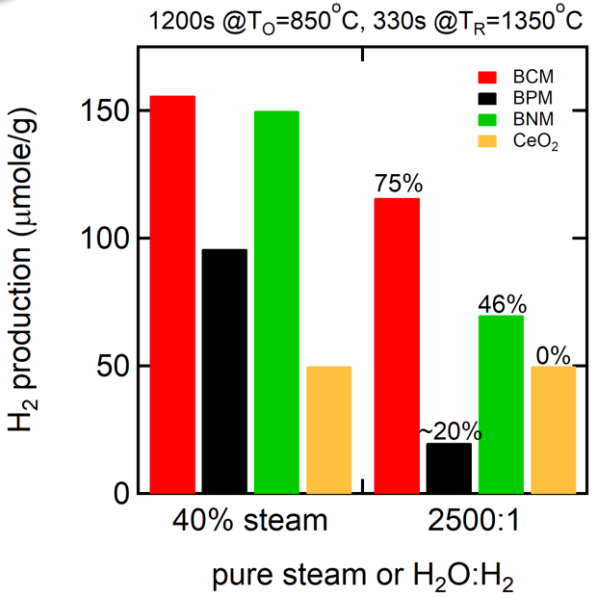
Accomplishment: Discovered Two New Water Splitting Compounds Structurally Identical Variants to BCM

Significant variations in $\Delta\delta_{OX}$

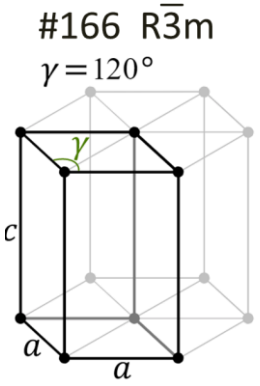
$Ba_4PrMn_3O_{12}$ (BPM) — $Ba_4CeMn_3O_{12}$ (BCM) — $Ba_4NbMn_3O_{12}$ (BNM)



LSFR result

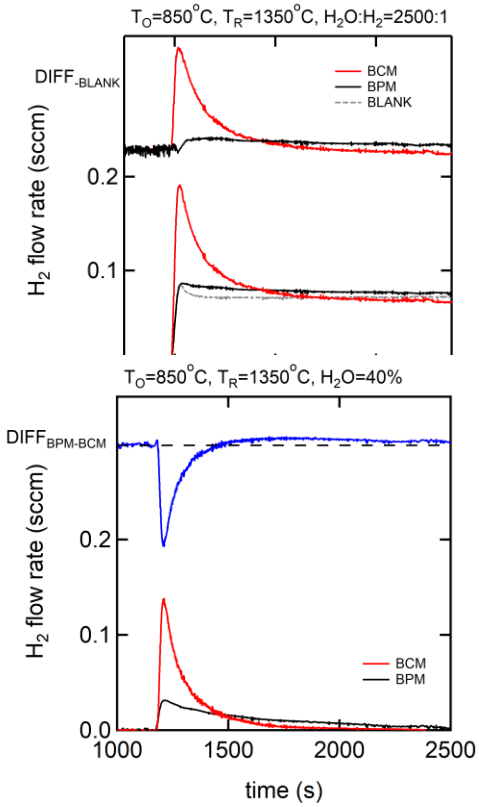


- BXM (X = Ce, Pr, Mn) identical space group symmetry.
  - Perfectly ordered 12R-phase @ full stoichiometry
- Oxidation state $Pr^{+4} = Ce^{+4}$; Δ_{radii} ~ -2%; Mn^{+4}.
- Oxidation state $Nb^{+5} \neq Ce^{+4}$; Δ_{radii} ~ -25%; $Mn^{+3/+4}$.

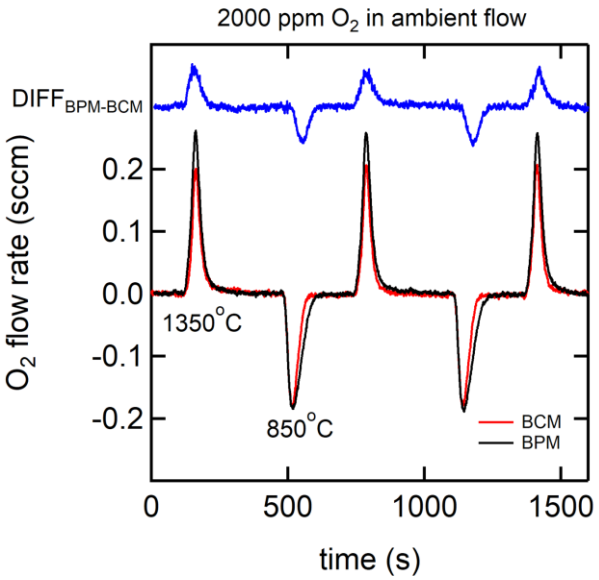


H_2 production exceeds CeO_2 cycled at T_R = 1350 °C

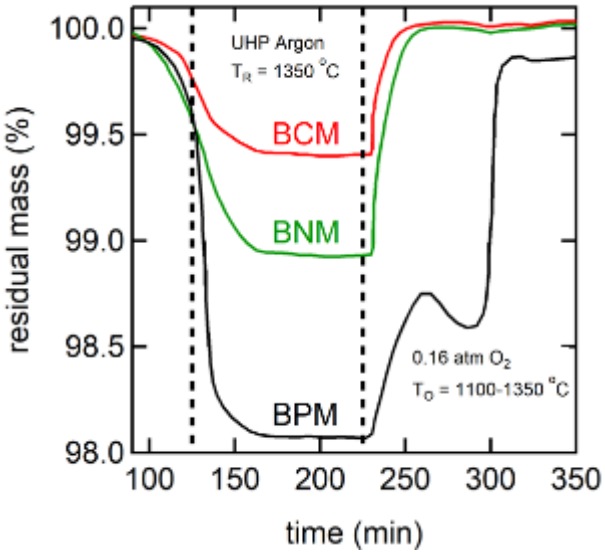
Accomplishment: TGA and LSFR Experiments Reveal Different Redox Behaviors within BXM Family



LSFR result



TGA result

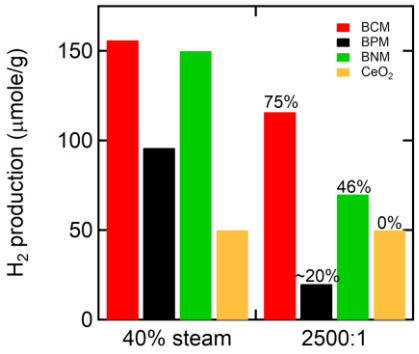


Pr variant has TWO additional 4f electrons and empty d-states

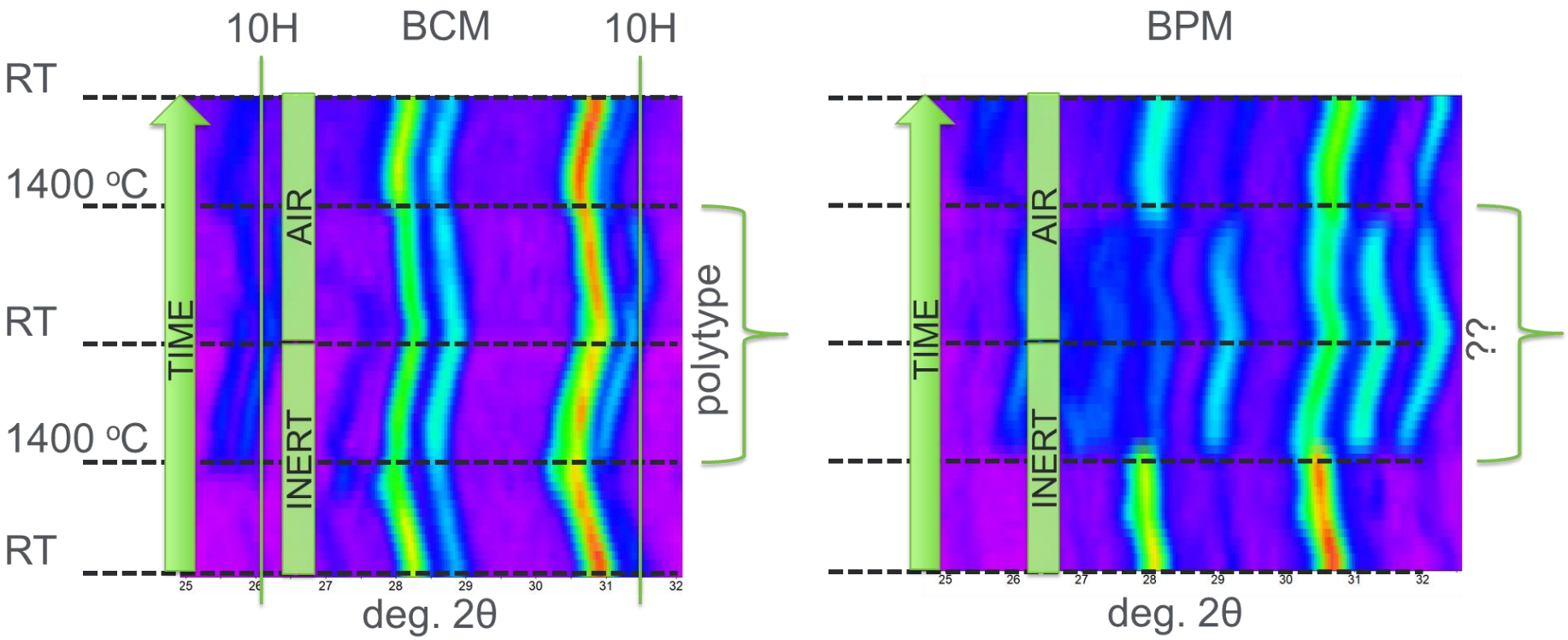
Ce:[Xe] $4f^1\ 5d^1\ 6s^2$

Pr:[Xe] $4f^3\ 6s^2$

- O_2 redox capacity of BXM follows: BCM < BNM < BPM.
  - Consistent with flow reactor O_2 cycling data
- $\Delta\delta_{OX}$ for BPM < BCM in 40% H_2O and 2500:1 H_2O:H_2.
  - Identical crystallography, different electronic structure



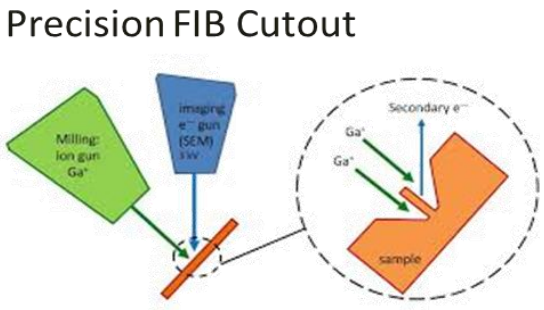
Accomplishment: HT-XRD Experiments Reveal Different Redox Crystallography within BXM Family

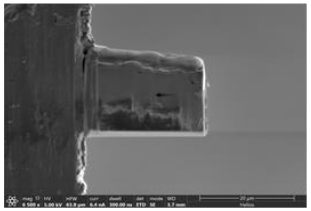


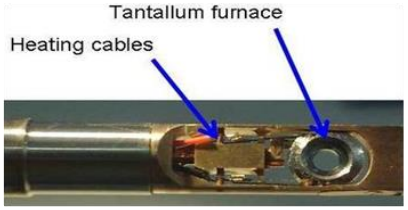
- 12R polytype transition in BCM is reversible and known.
- BPM clearly exhibits more complicated redox phase behavior.

unclear if non-stoichiometry or phase transition more important to WS

Accomplishment: Developed Experimental Method for In Situ Vacuum Reduction in HR/STEM

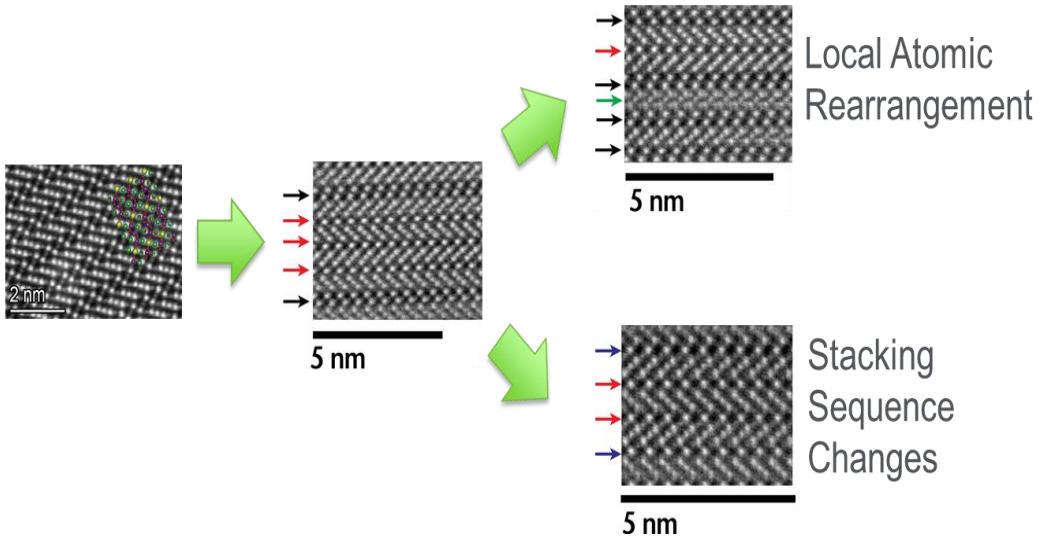






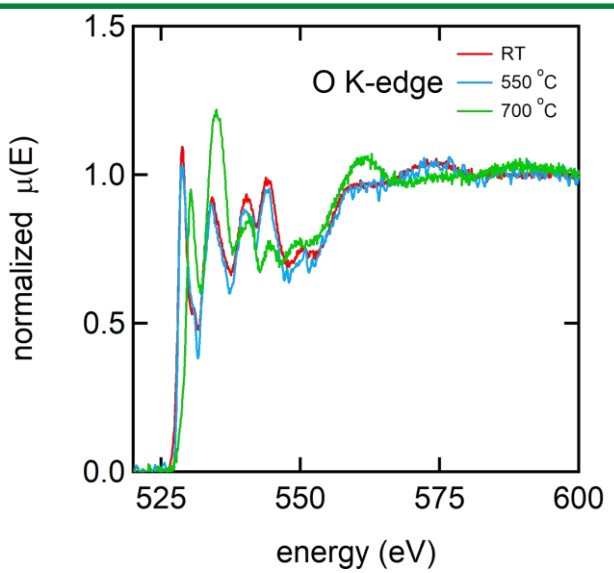
THERMAL REDUCTION

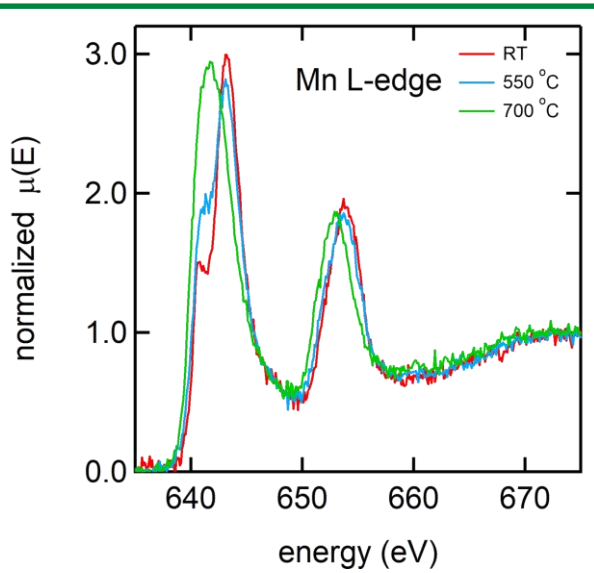
- FIB for precision prep of powders, pellets, and films.
  - Orient FIB cutout along low index crystal planes
- Heating rates >> 100 °C per second.
  - In situ thermal reduction

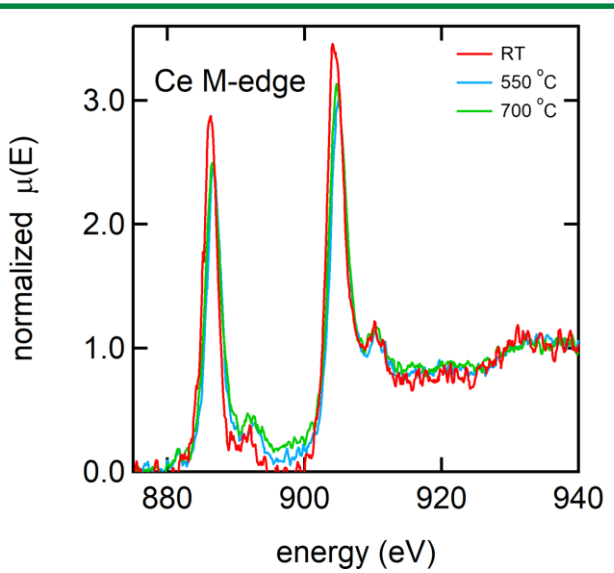


real space atomic-scale imaging may resolve mechanistic details of polymorph transformation

Accomplishment: Electron Energy Loss Spectroscopy (EELS) Measured In Situ During Vacuum Reduction





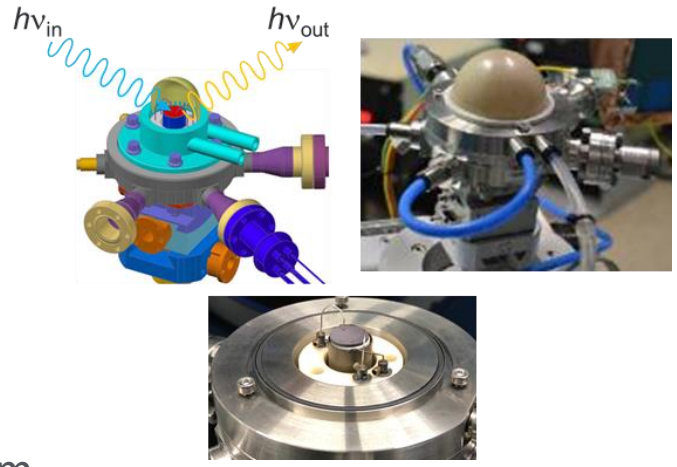


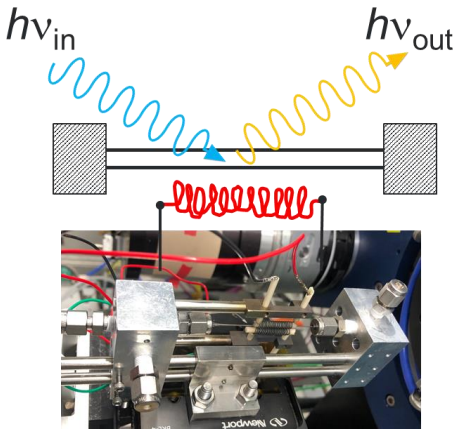
- EELS information equivalent to soft X-ray XAS.
- Clear and obvious changes to electronic structure local to MnO_6 manifold (coordination chemistry and oxidation state).
  - Features in O K-edge and Mn L-edge change shape and intensity
- Ce electronic states may not participate in reduction process (questions Seedling project's suppositions).

theory needed to resolve interrelationships between structure and performance

Accomplishment: Developed Operando Synchrotron X-Ray Scattering Techniques

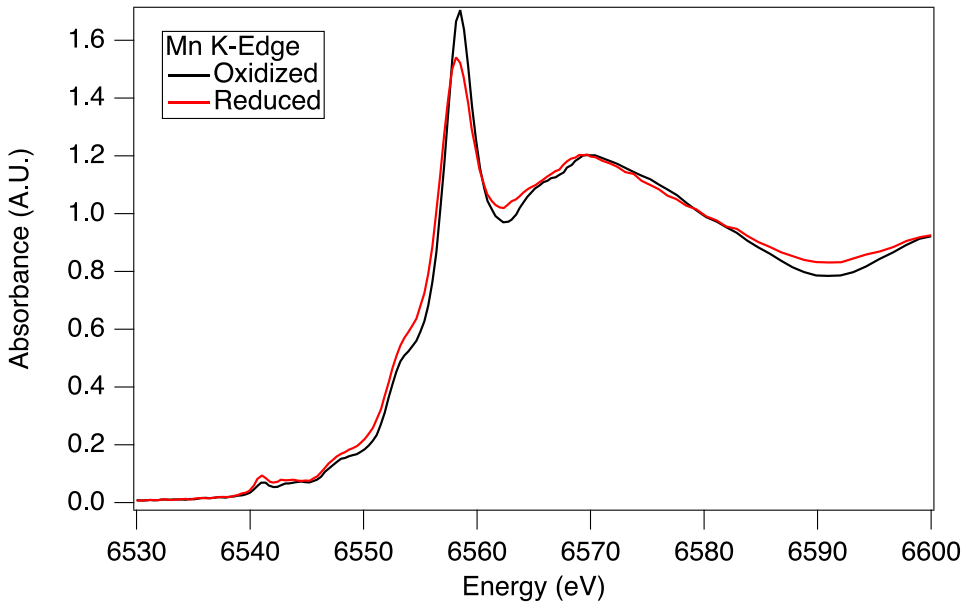
- "Phoenix" high-temp operando flow cell.
  - Designed by SNL for use at SLAC
  - Accommodate powder and rigid forms
  - Flexible environmental controls (P, T, atm)
- In situ capillary cell.
  - Accommodate powder forms
  - Heating under limited control of ambient atm
  - High quality XRD for refinement of high temperature unit cell parameters
    - self-centering in situ XRD (no correction factors)
- Spinning capillary cell.
  - Accommodate powder forms
  - High-precision XRD for refinement of crystal parameters
  - Eliminate XAS self-absorption by diluting sample with diamond powder



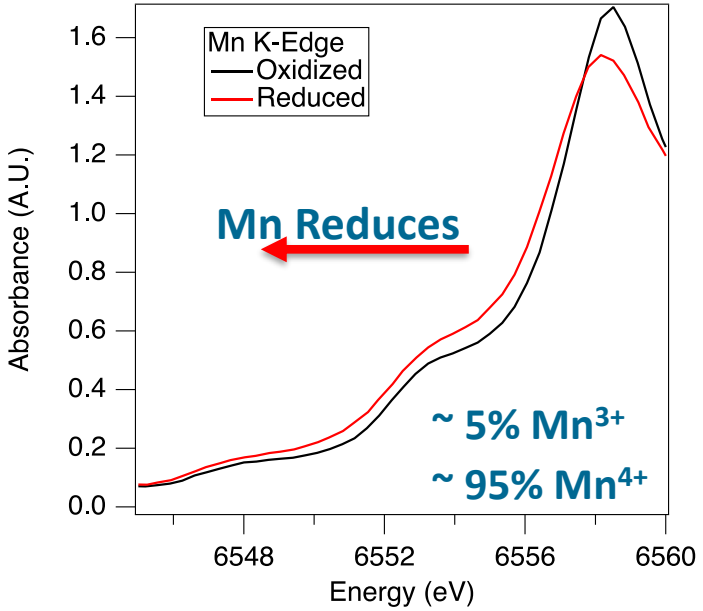


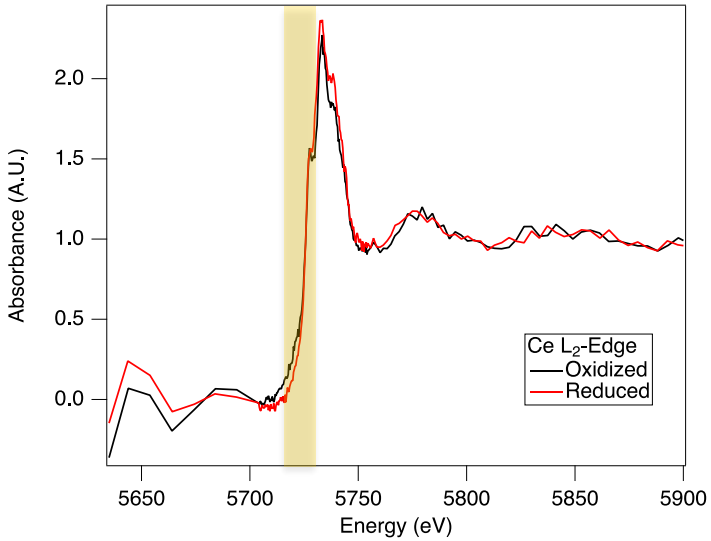
synchrotron X-ray experiments compliment HR/STEM diffraction and EELS

Accomplishment: Measured XAS on Lower Electronic Shells of Heavier Elements Inaccessible to EELS using Hard X-ray



In-operando hard-XAS identifies Mn as the active redox element





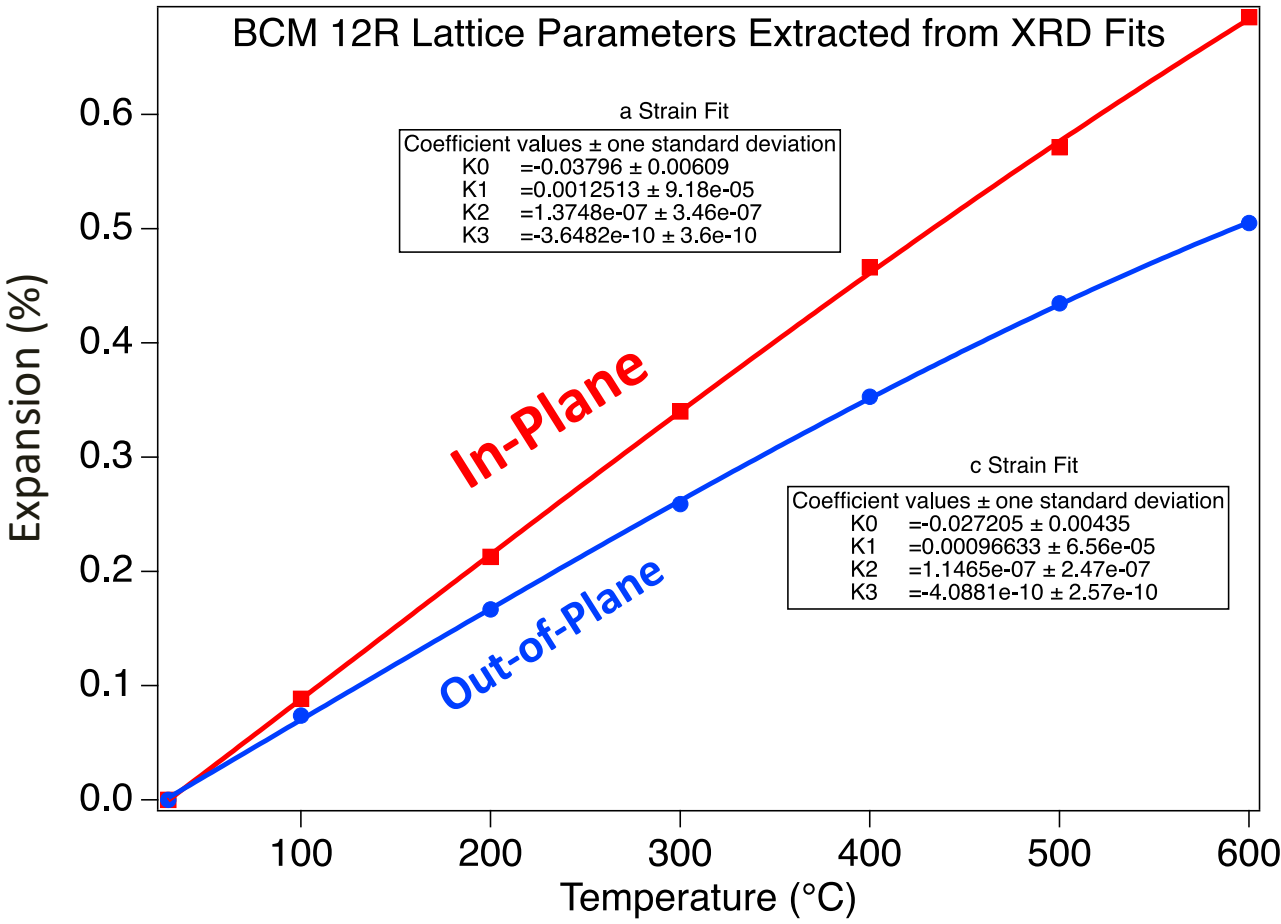
build a more complete electronic structure picture with information from different edges:

- Mn K (XAS) and L (EELS)
- Ce L (XAS) and M (EELS)

Accomplishment: Synchrotron XRD Identifies Anisotropic Thermal Expansion in BCM

- Anisotropic thermal expansion coefficients extracted from indexed diffraction peak shifts.
  - 35% difference in expansion coefficient by 600°C
- Anisotropic expansion modifies structure.
  - Cation-oxygen bonding angles change.
  - Electronic band structure is altered.

Anisotropic Thermal Expansion with Greater In-Plane (a) vs Out-of-Plane (c) Strain for BCM



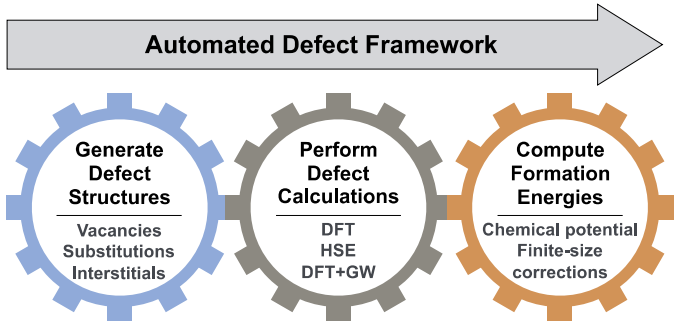
temperature dependent structure changes observable only via synchrotron XRD

Accomplishment: Defect Modeling, XAS Analyses, Databases, Tools and Collaborative Efforts

- **NRELMatDB**: Database of computed materials properties
  - DFT relaxed structures
  - Thermochemical properties
  - GW electronic structure

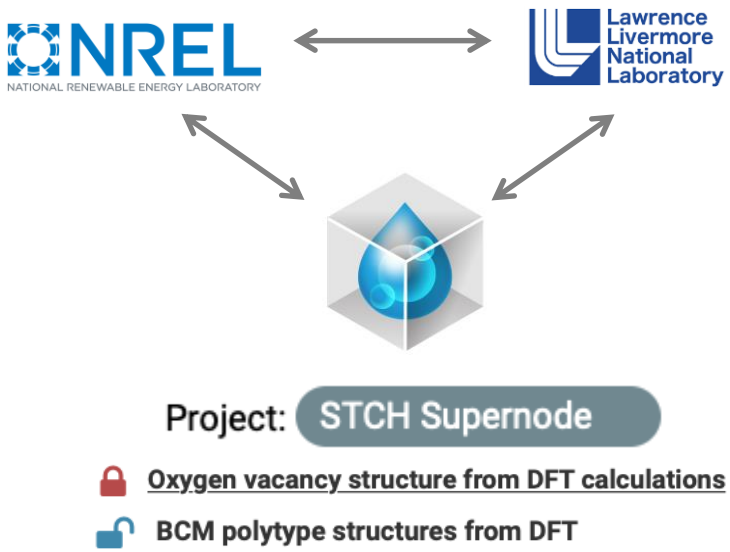
V. Stevanović et al, PRB 85 115104 (2012)
S. Lany, J. Phys. Cond. Mater. 27, 283203 (2015)

Tools: github.com/pylada/pylada-defects



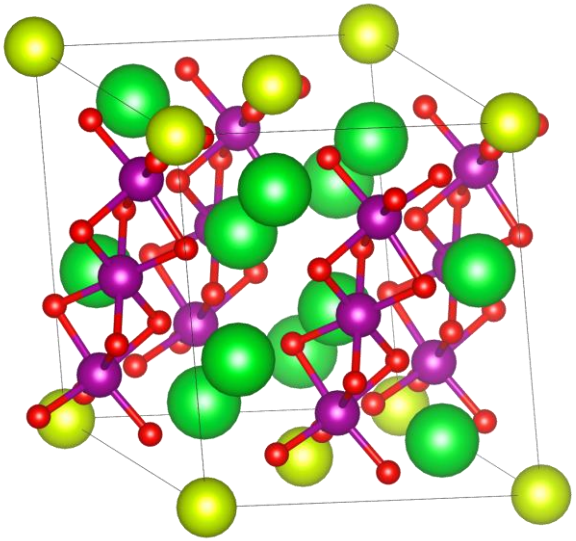
A. Goyal, S. Lany et al. Comp. Mater. Sci. 130 (2017)

- **Collaborative** efforts between NREL and LLNL
  - Defect modeling and analysis in BCM
  - Update Hydrogen Data Hub with defect structures and defect formation energies

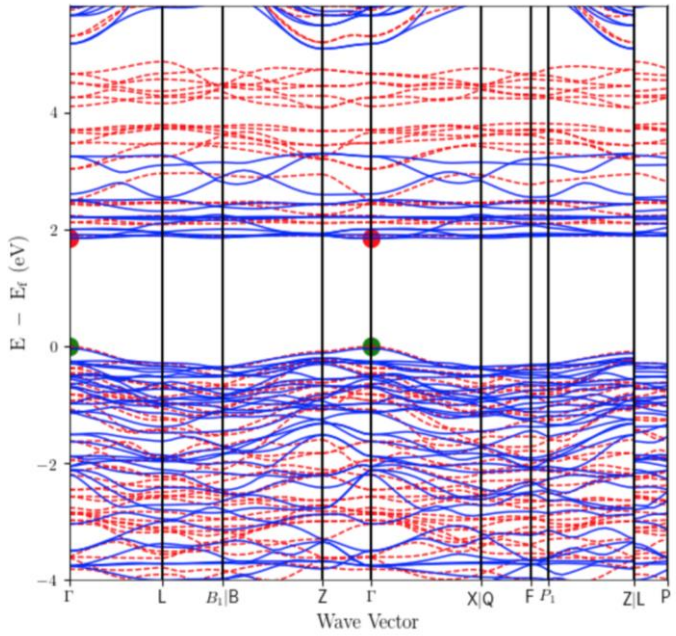


Accomplishment: Developing DFT Method for Analysis of EELS and XAS

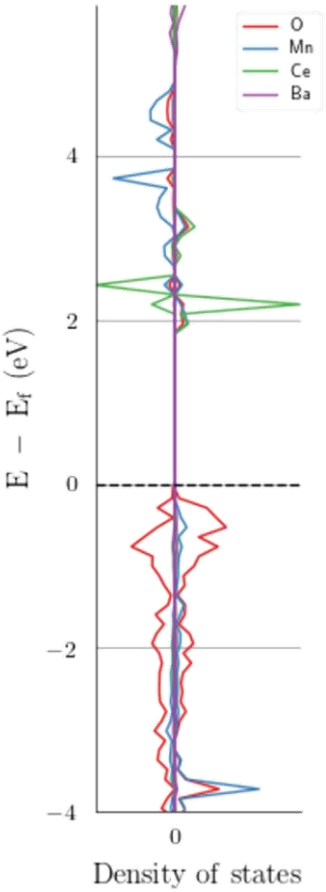
BCM/BPM/BNM:



Band Structure



PDOS



- Pre- & near-edge XAS probes PDOS.
- Mn_3O_{12} trimers form triangular lattice in a-b plane.
  - Anti-ferromagnetic frustrated spin system (↑↓↑/↓↑↓)
- Origin of AF: Mn-O hybridization (super exchange).

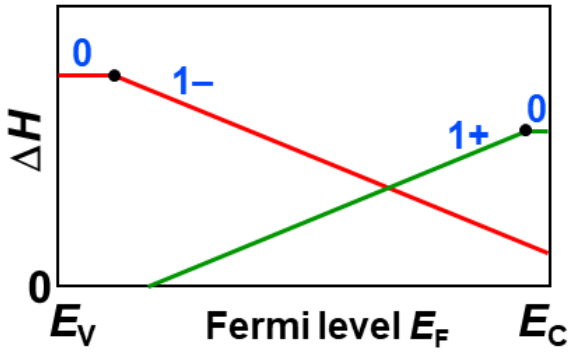
sign indicates spin ↑

Accomplishment: Applied First Principles Materials Theory to Defect Equilibria in BCM

Defect equilibria from first principles

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

- Supercell total energies
- Atomic chemical potentials
- Electron chem. potential



Defect formation energy	$\Delta H = \Delta H_{D,q}(\mu, E_F)$
Defect concentration	$c_D \approx N_{site} \times \exp(-\Delta H/kT)$
Electron/hole density	$c_e = \int f_{FD}(E-E_F)\, g(E)\, dE$
Charge neutrality	$-c_e + c_h + \Sigma\,[q \cdot c(D^q)] = 0$
Self-consistent solution	$\Delta H(E_F) \longrightarrow c_D(\Delta H) \longrightarrow E_F$
pO_2 dependence of μ_O (ideal gas)	$\Delta\mu_O(T,P_0) = \frac{1}{2}[H_0+\Delta H(T)] - \frac{1}{2}T\cdot[S_0+\Delta S(T)]$ $\Delta\mu_O(T,P) = \Delta\mu_O(T,P_0) + \frac{1}{2}kT\ln(P/P_0)$

$$M_xO \rightarrow M_xO_{1-\delta} + \frac{\delta}{2} \cdot O_2 \quad \textbf{red}$$

$$M_xO_{1-\delta} + \delta \cdot H_2O \rightarrow M_xO + \delta \cdot H_2 \quad \textbf{ox}$$

$$H_2 + \tfrac{1}{2}\, O_2 \leftrightarrow H_2O$$

- Ideal gas chemical potential $\Delta\mu$ O_2, H_2, H_2O
- T-dependence of E_g, m^*_e
- Configurational entropy of defects, dopants, and pairs

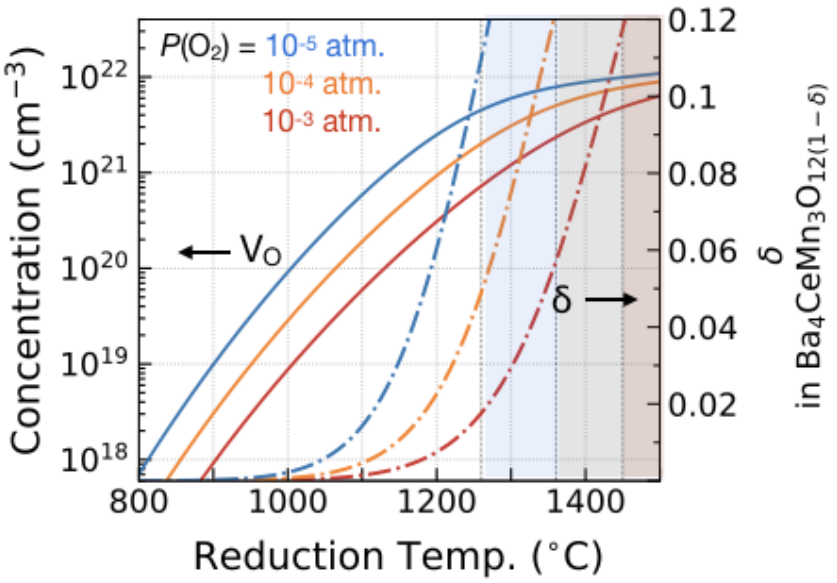
Accomplishment: Thermodynamic Modeling of BCM Reduction

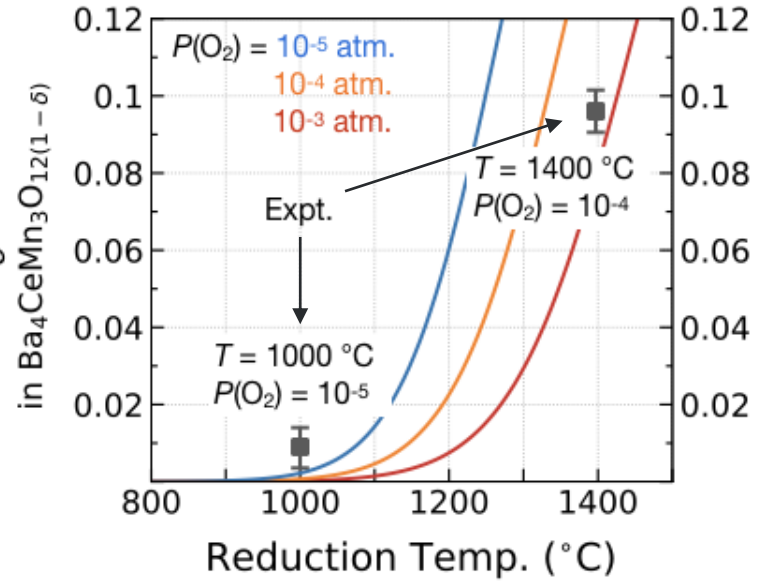
$$Ba_4CeMn_3O_{12} \longrightarrow Ba_4CeMn_3O_{12(1-\delta)} + 6\delta O_2$$

- Maximum *T* limited by decomposition into $BaMnO_2$ and $BaCeO_3$
- Reduction: $0.08 \leq \delta \leq 0.12$

theory agrees with experimental data within 0.1 eV in $\Delta\mu_O$

experimental data courtesy: Eric Coker, Sandia





Accomplishment: Thermodynamic Modeling of BCM Oxidation

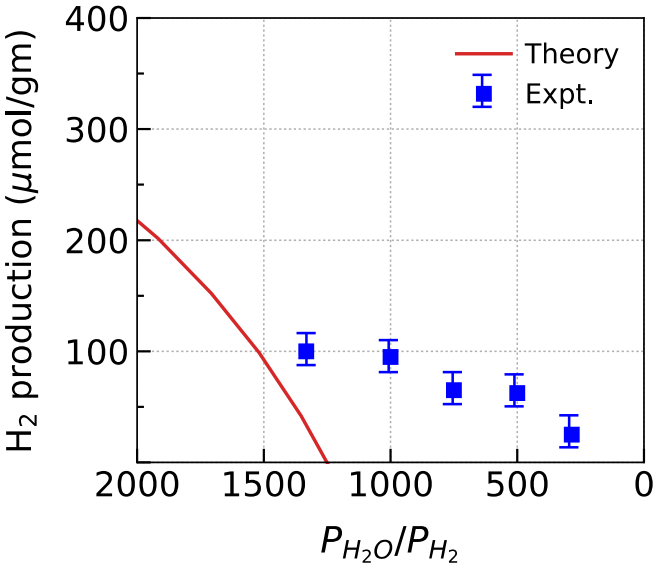
$$Ba_4CeMn_3O_{12(1-\delta)} + 12\Delta\delta H_2O \longrightarrow Ba_4CeMn_3O_{12(1-\delta+\Delta\delta)} + 12\Delta\delta H_2$$

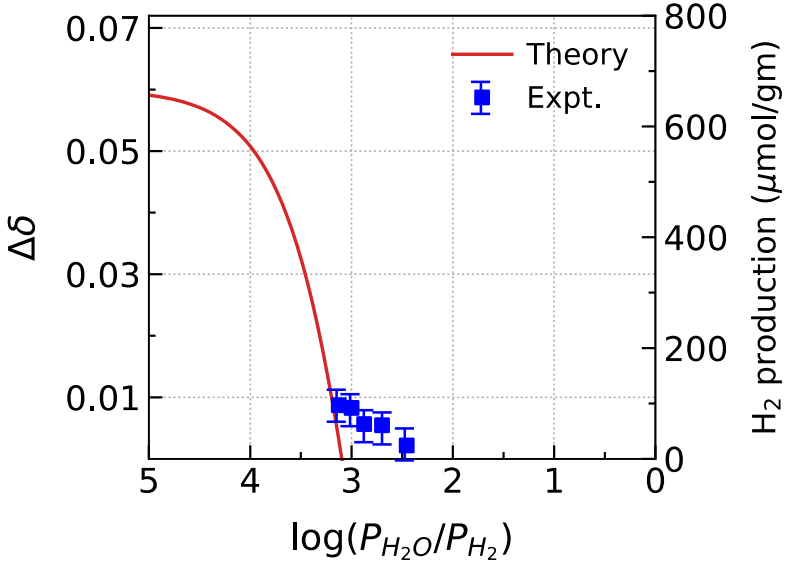
$$H_2 + 1/2O_2 \leftrightarrow H_2O$$

- Ideal gas: Higher pH_2 → lower pO_2 → less oxidation → lower Δδ

  Experimental data: D. R. Barcellos, R. O'Hayre et al, EES 11 3256 (2018)

δ = 0.06
T_{ox} = 850 ° C
pH_2O = 1 atm





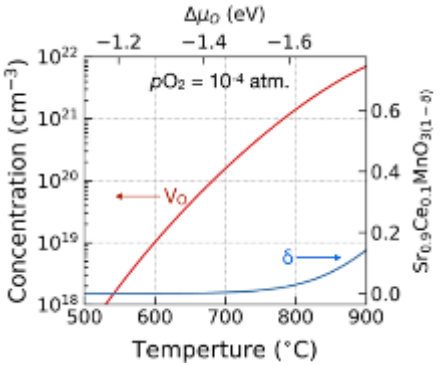
Project Accomplishment Summary Slides

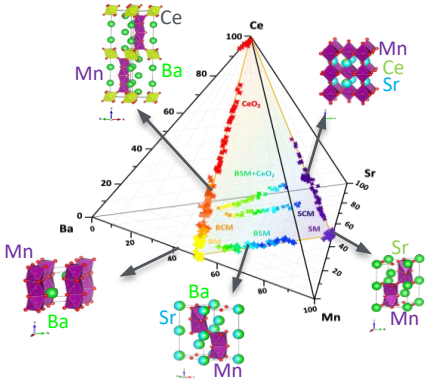
Successful High-Throughput Approach

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

Ryan O'Hayre and Michael Sanders, Colorado School of Mines

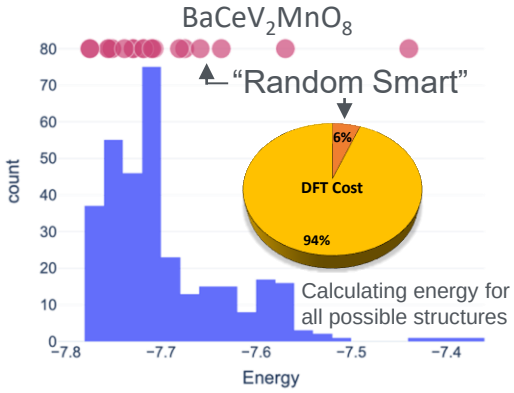
- Translating DFT defect calculations into predictions of Reduction vs Temp
- Validating against actual exp. data for known compositions

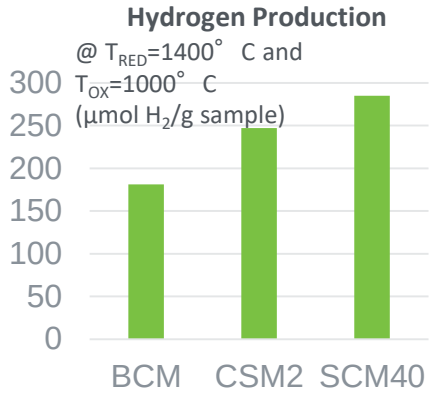




- Exploring structure changes between $BaMnO_3$, $SrMnO_3$, and CeO_2 additions

- New "Random Smart" structure prediction process
  - Uses unsupervised ML algorithm
- Significant speedup
  - ~16X for a complex quinary oxide composition



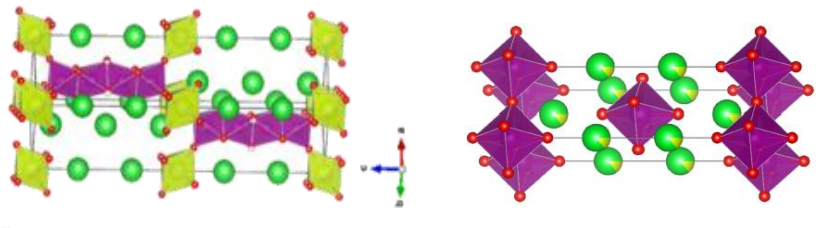


- Steady increases in hydrogen yield from BCM ($BaCe_{0.25}Mn_{0.75}O_3$) & CSM2 ($Ce_{0.2}Sr_{1.8}MnO_4$) to SCM40 ($Sr_{0.6}Ce_{0.4}MnO_3$)

- Successfully integrating high-throughput computation and experiment to discover, down-select, screen, and validate new STCH-active oxides

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

PI: Ryan O'Hayre and Michael Sanders, Colorado School of Mines



Abstract: *We have developed two novel perovskite-related manganates containing cerium, one with Ce on the B-site, BCM ($BaCe_{0.25}Mn_{0.75}O_3$), and the other on the A-site, CSMx ($Ce_xSr_{2-x}MnO_4$). Both have improved H_2 production when compared to ceria. BCM is the first perovskite to show significant water-splitting under simulated high steam utilizations.*

Goals & Approach:

- Demonstrate significant progress towards relevant 2020 targets.
- Reduce sufficiently at < 1400° C.
- Oxidize under <10:1 H_2O:H_2 ratio.
- First study to incorporate water-splitting results under simulated high steam utilization conditions.

Significance of Result:

- Validates DFT predictive power in STCH material development.
- Narrows the target window for oxygen vacancy formation energy.
- Increased H_2 yield under both low and high steam utilization regimes.

Keywords: *Perovskite, STCH, DFT*

Publications:

	Imp. Fact
1. R. Barcellos, D., et al., *$BaCe_{0.25}Mn_{0.75}O_{3-\delta}$—a promising perovskite-type oxide for solar thermochemical hydrogen production*. Energy & Environmental Science, 2018. 11(11): p. 3256-3265.DOI: 10.1039/C8EE01989D	33
2. 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	4.9

Screening Perovskite Oxides for STCH

PROJECT ID: P166

Accomplishment

Computationally Accelerated Discovery and Experimental Demonstration of High-Performance Materials for Advanced Solar Thermochemical Hydrogen Production

Charles Musgrave, University of Colorado Boulder

Thermodynamic Screening

Perovskite Oxide Database Generation

> 4.4 Million Compositions

τ

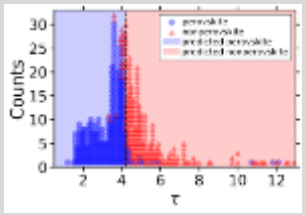
120,145 Compositions Stable as Perovskites

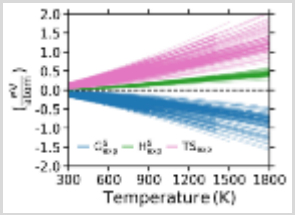
BVM

836,217 Predicted Perovskite Structures

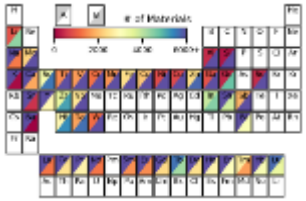
DFT

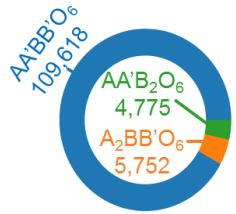
> 50,000 DFT Analyzed Perovskites



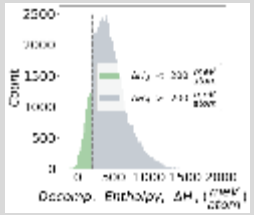


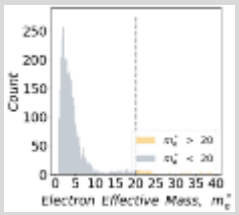
Machine Learning Perovskite Stability





Bond Valence Method Structure Generation





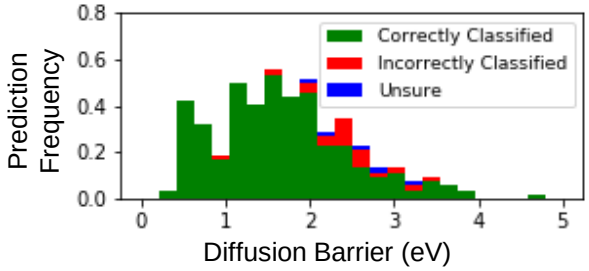
DFT *Property Calculations*

The Materials Project

DFT Properties Available Soon in the MP Database

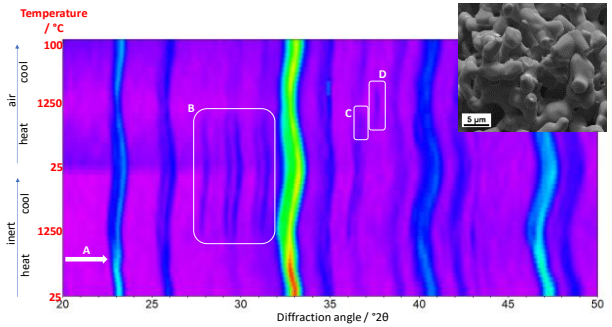
Kinetic Screening

Machine-Learned Model Developed for Diffusion Kinetics



Experimental Testing

New Materials Successfully Cycled in Air (SNL Collaboration)



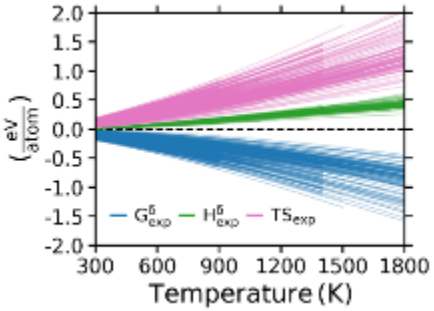
- Utilizing *ab-initio* calculations with machine learned models and experiments to screen thermodynamic and kinetics of > 830,000 structures

Computationally Accelerated Discovery and Experimental Demonstration of High-Performance Materials for Advanced Solar Thermochemical Hydrogen Production

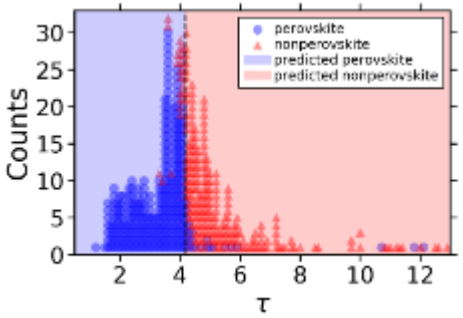
PI: Charles Musgrave, University of Colorado Boulder

Machine-learned Models of Materials Stability for Rapid STCH Screening

Gibbs Energy



Perovskite Stability



Abstract: Here, we used the SISSO approach to identify a simple and accurate descriptor to predict the Gibbs energy for stoichiometric inorganic compounds with ~50 meV/atom resolution for 300 K < T < 1800 K. We also developed an accurate and physically interpretable machine-learned tolerance factor, τ, that correctly identifies 92% of compounds as perovskite or not.

Goals & Approach:

- Project goal is to utilize machine learned models, *ab-initio* calculations and experiments to develop new STCH materials
- Determining the stability of compounds, particularly under relevant reaction conditions, has been a long-standing challenge in the discovery of new materials
- Utilizing the SISSO machine learning approach enables the rapid screening of stability of relevant compounds (perovskites) at high temperatures

Significance of Result:

- τ reduces the number of required DFT calculations for perovskites by > 40 x
- Gibbs energy model depends only on composition and 0 K structure, enabling rapid screening of material stability at STCH conditions

Keywords: *machine-learning, SISSO, stability, STCH, oxidation kinetics, O vacancy diffusion*

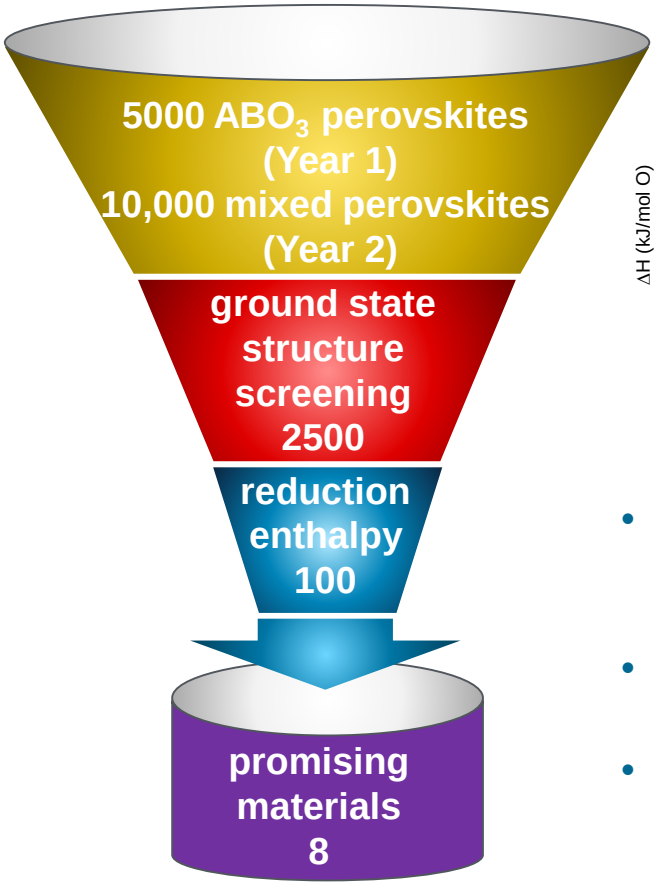
Publications:

		Imp. Fact
1.	C. Bartel et al. (DOI: 10.1038/s41467-018-06682-4)	11.9
2.	C. Bartel et al. (DOI: 10.1126/sciadv.aav0693)	12.8
3.	R. Trottier et al. (DOI: 10.1021/acsami.0c02819)	8.5

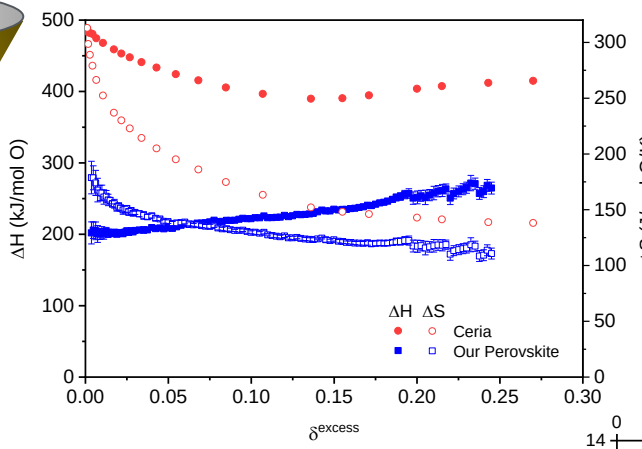
Computational/Experimental Strategy Leads to Improved STCH Compound

Transformative Materials for High-Efficiency Thermochemical Production of Solar Fuels

Chris Wolverton and Sossina Haile, Northwestern University

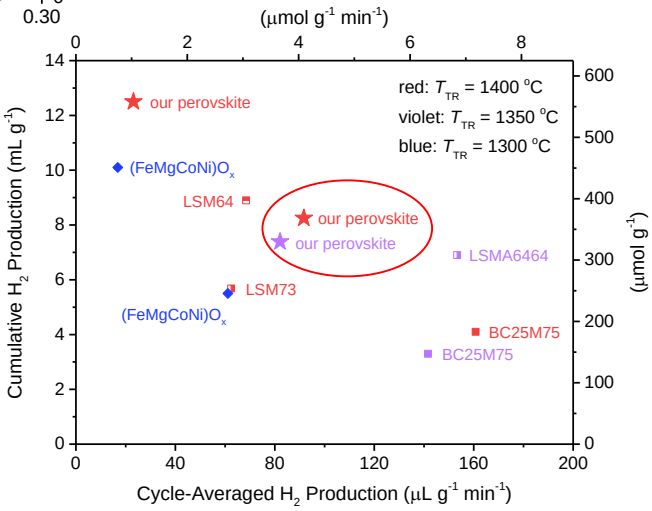


DFT screening identified high-performance STCH perovskites

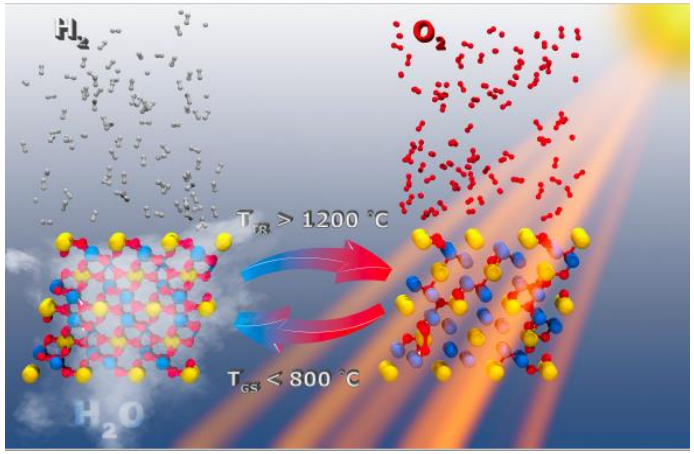


- Achieved 12.5 mL/g H_2 from 1400 - 1000 °C, pH_2O = 0.4 atm
- Elucidated the gas-phase limit on the fuel production
- Our perovskite supersedes other materials considering both cumulative and cycle-averaged H2 productivity

- Exceptional stability at 1500 °C under $pO_2 = 10^{-5}$ atm
- Intermediate enthalpy within 200 – 300 kJ/mol-O
- High entropy, higher than typical perovskite materials



$CeTi_2O_6$ - A Promising Oxide for Solar Thermochemical Hydrogen Production



Abstract: A large entropy of reduction is crucial in achieving high-efficiency solar thermochemical Hydrogen (STCH). We perform a systematic screening to search for Ce^{4+}-based oxides which possess large onsite electronic entropy associating with Ce^{4+} reduction. We find $CeTi_2O_6$ with the brannerite structure is the most promising candidate for STCH since it processes a smaller reduction enthalpy than ceria yet large enough to split water and a large entropy of reduction.

- An efficient DFT search strategy developed for new STCH materials with high entropy of reduction and moderate enthalpy of reduction. Search for high-entropy Ce^{4+} compounds combined with DFT calculation of enthalpy of reduction.

Significance of Result:

- $CeTi_2O_6$ has a comparable reduction of entropy with CeO_2 but small reduction enthalpy than CeO_2.
- A new route of designing STCH materials
- This material may help to reach the DOE goal of hydrogen production

Keywords: STCH, oxides, on-site electron entropy

Publications:
S. S. Naghavi et al., ACS Appl. Mater. Interfaces (under review. 2020)

Imp. Fact
8.4

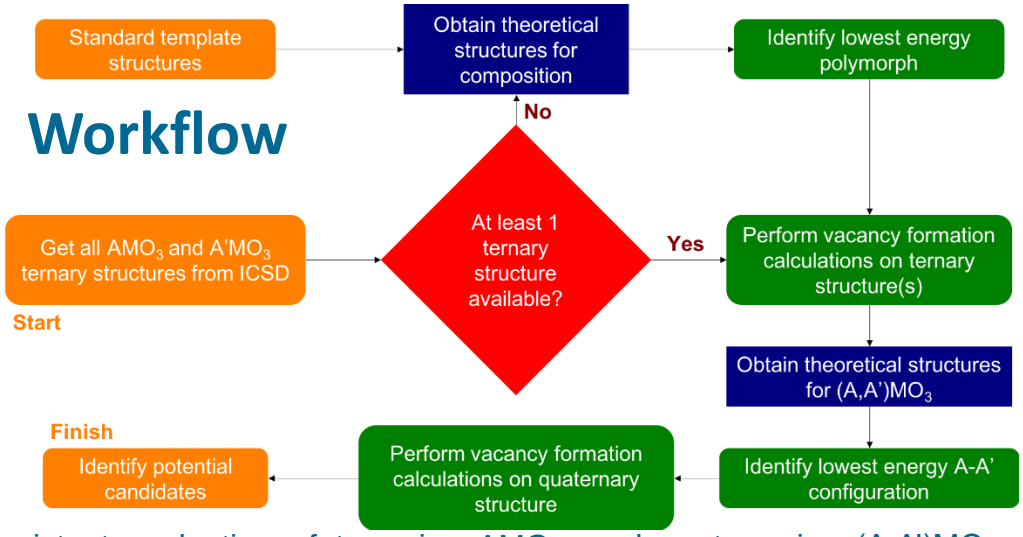
Identifying optimal candidates via efficient theoretical screening of $(A,A')MO_3$ perovskites (M = 3*d* metal)

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

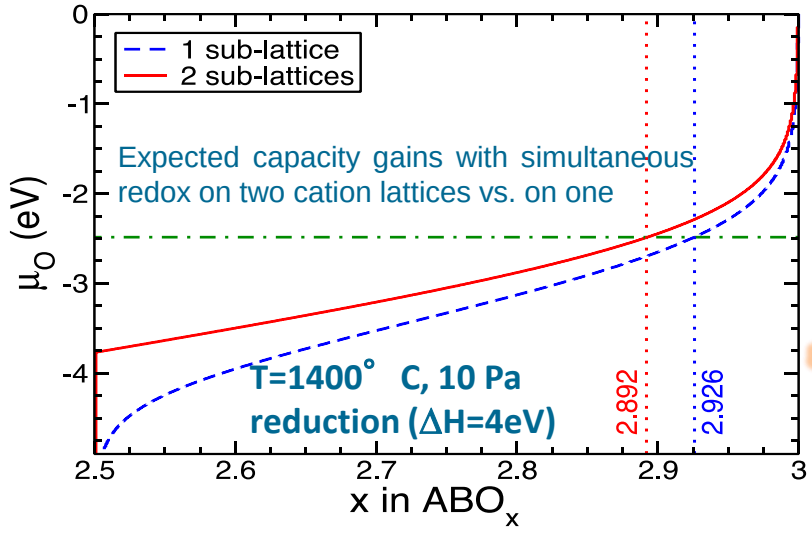
PI: Ellen B. Stechel, Arizona State University; Co-PI: Emily A. Carter, Princeton University

Developed a theoretical workflow that systematically calculates the oxygen vacancy formation energy in ternary and quaternary perovskites, which enabled the successfully identification of candidate(s) with simultaneous cation redox in our target window for reduction enthalpy.

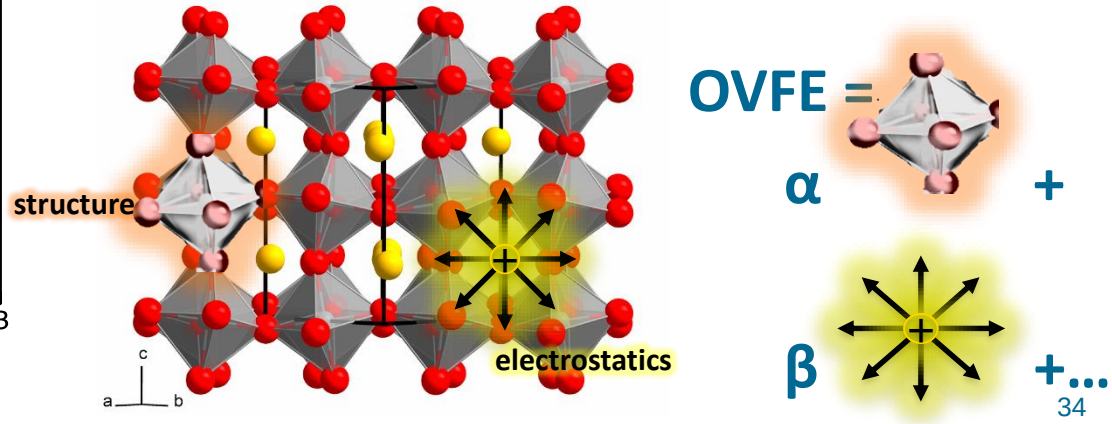
On-going collaboration with NREL colleagues for synthesis and validation, followed by validation of the predicted thermodynamics at Sandia.



Consistent evaluation of ternaries AMO_3, and quaternaries $(A,A')MO_3$ perovskites to identify optimal oxygen vacancy formation energy

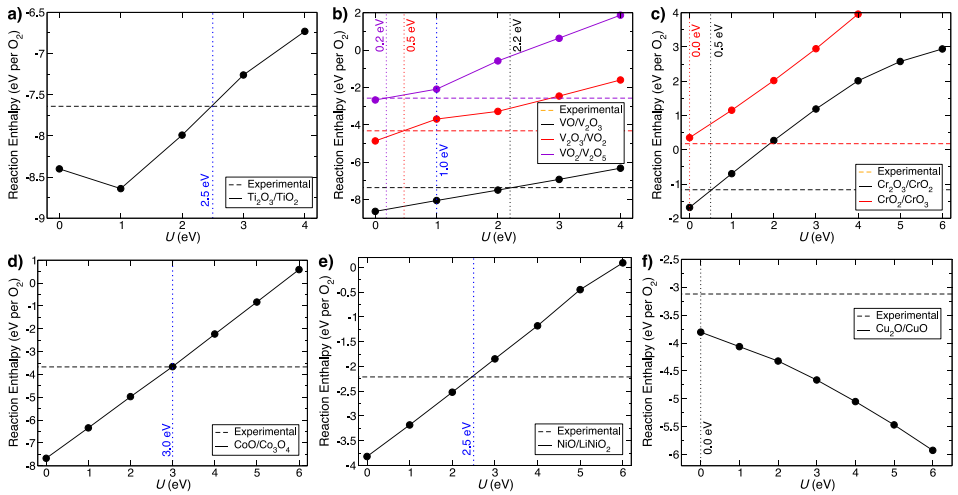


Materials design principles from Machine Learning (ML)



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

PI: Ellen B. Stechel, Arizona State University; Co-PI: Emily A. Carter, Princeton University



Abstract: *Evaluating optimal U corrections for 3d transition metal oxide systems, specifically Ti, V, Cr, Co, Ni, and Cu, within the strongly constrained and appropriately normed (SCAN)+U exchange-correlation (XC) framework. The optimal U values were calculated based on experimental oxidation enthalpies.*

Goals & Approach:

- Develop a theoretical framework to screen for novel solar thermochemical water splitting candidates
- Constructing a theoretical SCAN+*U* framework provides a better fundamental underpinning for materials screening

Significance of Result:

- We found that the SCAN+*U* framework provides a better description of the thermodynamic, structural, electronic, and magnetic properties of several transition metal oxide systems
- SCAN+*U* framework developed here will be useful in materials screening for several applications
- This work is a critical component that helps us to evaluate candidate metal oxide perovskites, including A-A'-M-O (M = 3*d* metal) systems for thermochemical water splitting

Keywords: *DFT, SCAN, SCAN+U, property prediction*

Publications:

O.Y. Long, G.S. Gautam, and E.A. Carter, Phys. Rev. Mater. in press, 2020 (DOI: N/A; Journal link: https://journals.aps.org/prmaterials/accepted/6a078Z45A1a1cb04708d634115850ae25654f991b)

Engagement with 2B Team and Data Hub

- Collaboration with 2B Team Benchmarking Project.
  - 2B working groups and annual meeting
  - Node feedback on questionnaire & draft test framework
  - Defining: baseline materials sets, testing protocols
- STCH data metadata definitions in development.
- Large number of STCH datasets uploaded to hub.
  - Designing custom APIs to facilitate error-free, auto-uploading

Summary

- HydroGEN supports 7 STCH FOA projects with 14 nodes.
- Developing and validating tools for accelerated materials discovery are major seedling project themes.
  - Computational material science proving effective
- Working closely with the project participants to advance knowledge and utilize capabilities and the data hub.
- Applying atomistic theory and advanced experimentation in STCH Supernode to understand behavior of Mn-O based water splitting materials.
  - Discovered 2 new water splitting compounds (BPM, BNM) structurally identical to BCM
  - Experiments reveal different redox behaviors within BXM family
  - Hot stage TEM/EELS reveal electronic structure changes in BCM under reduction
  - Operando synchrotron X-ray scattering shows structural changes in BCM under reduction
  - Developing DFT methods to model core-hole spectroscopies
  - Applied first principles materials theory to model defect equilibria in BCM

Future Work

- Leverage HydroGEN Nodes at the labs to enable successful budget periods 1 (new), 2 (continuing), and 3 (continuing) seedling R&D activities.

- Integrated research conducted within STCH Supernode.
  - Further investigate stoichiometric and defect structures in BXM
  - Derive atomistic insights into water splitting performance, structure, and charge compensation mechanisms in BXM induced by redox chemistry

- Work with the 2B team and STCH working group to further establish testing protocols and benchmarks.

- Utilize data hub for increased communication, collaboration, generalized learnings, and making digital data public.

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HydroGEN
Advanced Water Splitting Materials

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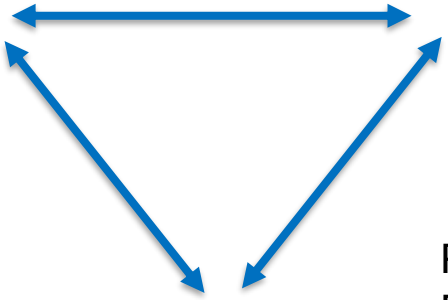

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