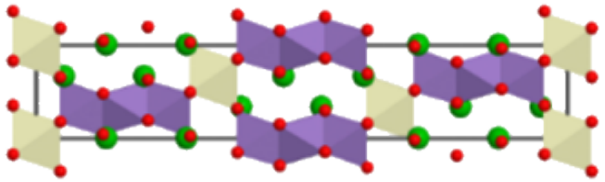
SAND2022-10031C

Sandia National Laboratories

Prospecting for Green Hydrogen Using Complex Perovskites and Concentrated Sunlight



PRESENTED BY

Anthony McDaniel

SSI*23, July 19, 2022
Boston, MA

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SAND2022-XXXX

Acknowledgements

HydroGEN Advanced Water Splitting Materials Consortium National Laboratory Solar Thermochemical Water Splitting Research Team:

Sandia National Laboratories

- Andrea Ambrosini, Sean Bishop, Eric Coker, James Park, Andrew Smith, Joshua Sugar, Jamie Trindell, Mathew Witman

National Renewable Energy Laboratory

- Robert Bell, David Ginley, Anuj Goyal, Stephan Lanny, Dan Plattenberger, Philip Parilla, Sarah Shulda

Lawrence Livermore National Laboratory

- Tadashi Ogitsu

SLAC National Accelerator Laboratory

- Nicolas Strange

Funding provided by [illegible] **ogies Office**

Office of
ENERGY EFFICIENCY & RENEWABLE ENERGY

Outline

Introduction.

An interesting story about complex perovskites.

- $Ba_4CeMn_3O_{12}$ and $Ba_4PrMn_3O_{12}$

Searching for a commercially viable metal oxide.

- Navigating a highly constrained requirement space
- Application of first principles theory and machine learning to material discovery

Summary.

Global Efforts To Advance “Green” Hydrogen

H2@Scale℠
U.S. Department of Energy

Australian Government
Department of Industry, Science, Energy and Resources

Policies and initiatives | Regulations and standards | Funding and incentives | About us | Publications | News

Australia’s National Hydrogen Strategy

U.S.News

2021 Best Countries » See the Worst Countries for Racial Equality

Home / News / Business News

German Government Agrees on National Hydrogen Strategy

ENERGY earthshots
U.S. DEPARTMENT OF ENERGY
Hydrogen

China prepares multi-pronged hydrogen strategy

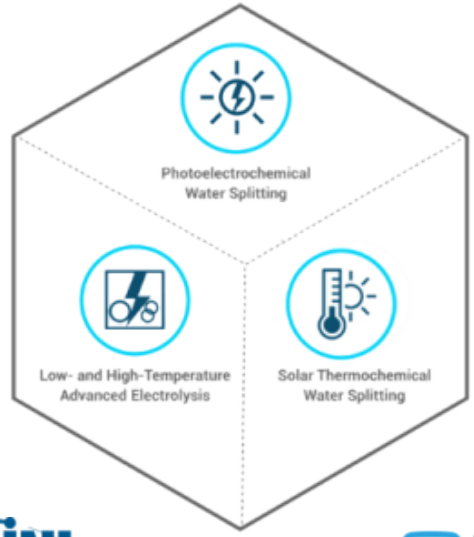
Address KEY technology challenges to advance the readiness level of large scale, low cost renewable H_2 production.

~~$1 per 1 kilogram in 1 decade ("1 1 1")~~

Hydrogen As Far As The Eye Can See

HydroGEN
Advanced Water Splitting Materials

+



= H_2

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

DOE's HydroGEN Advanced Water Splitting Materials consortium (H_2AWSM):

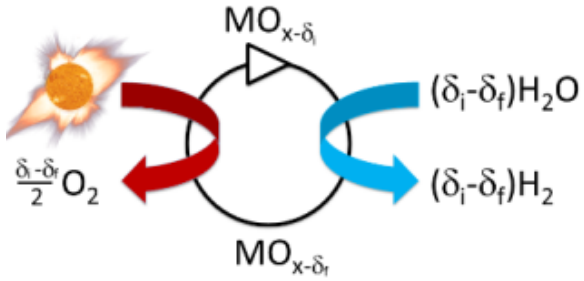
- Enables access to 5 core National Laboratories through collaborations with awarded projects
- Experimental facilities, computational resources, subject matter experts

US DOE heavily invested in developing advanced water splitting technology pathways.

- Electrolysis, photoelectrochemical, thermochemical, microbial

Solar Thermochemical Water Splitting Is A Simple Concept: Heat + H_2O In, H_2 + O_2 Out

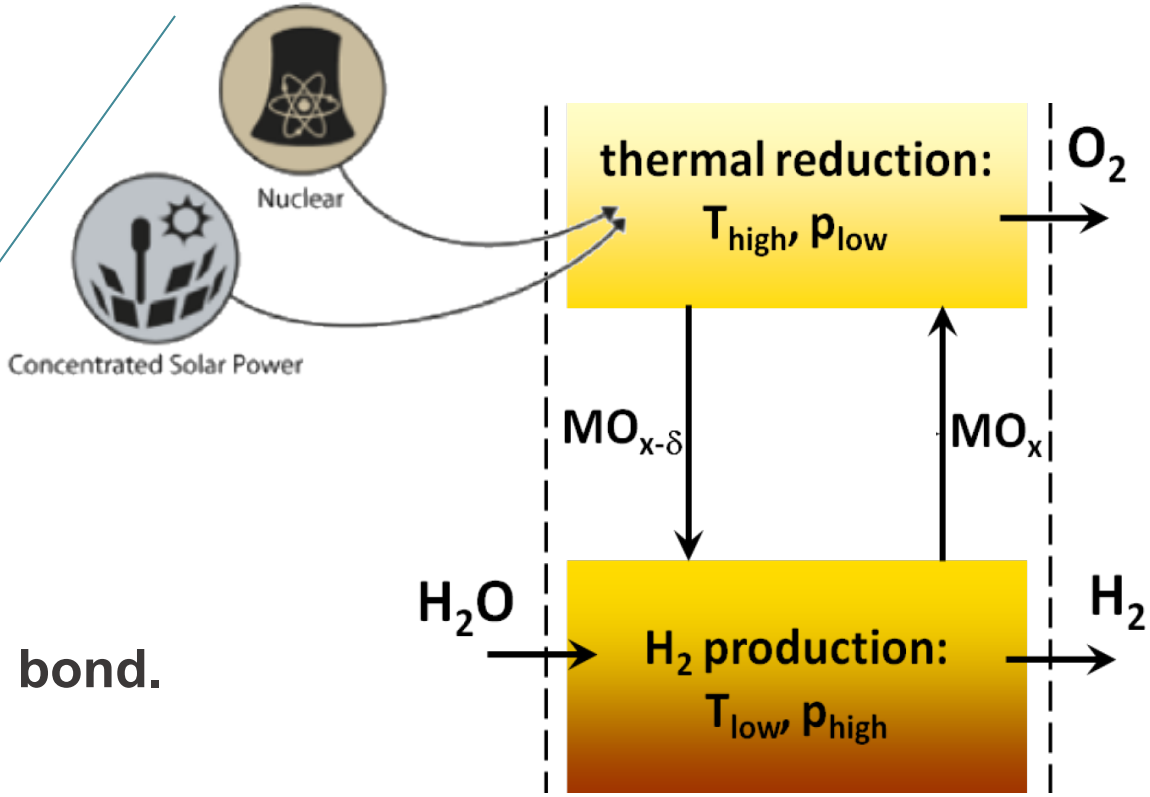
Chueh et al., *Science*, 10.1126/science.1197834 (2010).
Abanades et al., *Energy*. **31**, 2805–2822 (2006).



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

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

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



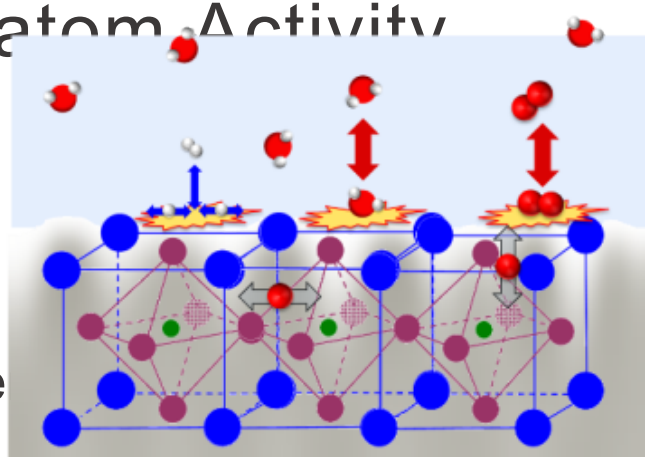
Direct storage of solar energy in a chemical bond.

DOE's HydroGEN Advanced Water Splitting Materials (H_2AWSM) consortium is focused on two-step, non-volatile MO_x.

- h2awsm.org

Principal Material Challenges For Non-Stoichiometric Oxides: Reduction Temperature (T_R) & Solid State O-atom Activity (μ_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 environme

Material subject to extreme environments.

- Redox cycling on the order of seconds
- Large thermal stress per cycle
  - 800 °C< T <1450 °C; ΔT_{RATE} ~100 °C/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	$\mu_{O,gas} > \mu_{O,solid}$	$\mu_{O,gas} \sim 10^{-13} atm$

Pilot and Near Commercial Scale Reactors Exist

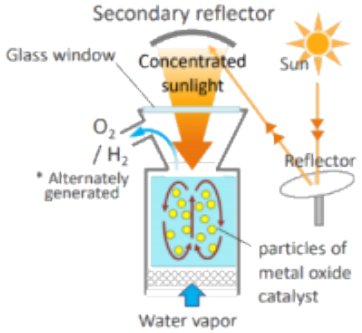
REACTOR

CONCENTRATOR

https://www.solarpaces.org/worlds-largest-solar-reactor-will-split-h2o-hydrogen/

Hydrosol Plant project is the largest solar thermochemical H_2 plant in the world.

- DLR (Germany), CIEMET (Spain), HYGEAR BV (Netherlands), and ELLINIKA PETRELAIA AE (Greece)
- Two-step metal oxide cycle @ 750 kW_{th}



CSIRO's 500kW class solar concentrating system to be used in the project.

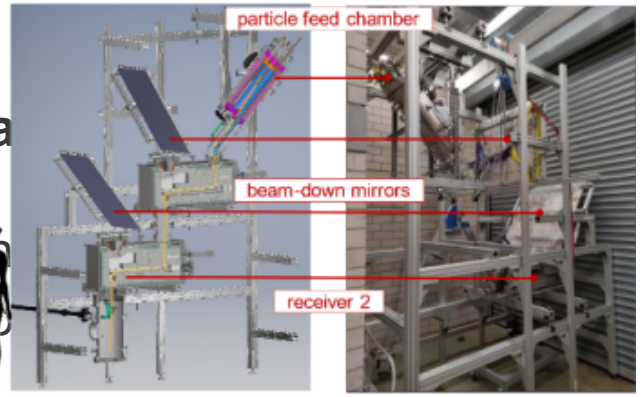
https://arena.gov.au/projects/solar-thermochemical-hydrogen-research-and-development/

Joint solar thermochemical hydrogen R&D.

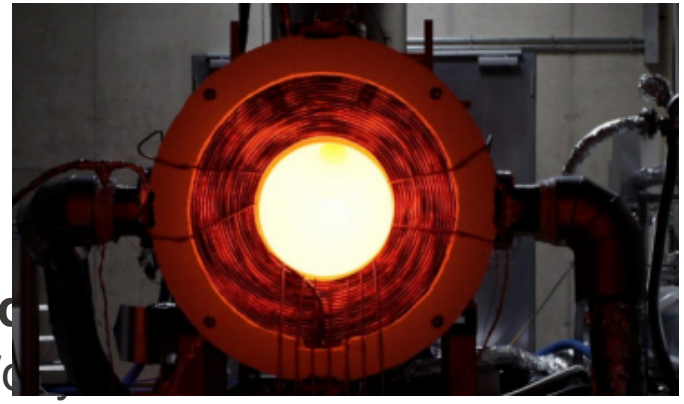
- ARENA (Australia) and Niigata University (Japan)
- Two-step metal oxide cycle @ 500 kW_{th}

Advancing particle receiver design of sola thermochemical fuels.

- Sandia National Labs (USA) and DLR (Germa
- Two-step metal oxide cycle @ 50 kW_{th} on mir



Synhelion



Large scale production plants that offer advantages in efficiency and

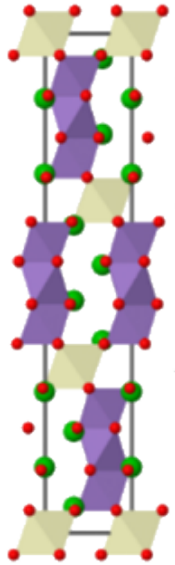
- Can thermochemical H_2 challenge largest SMR facility in the world @ 345t H_2/d

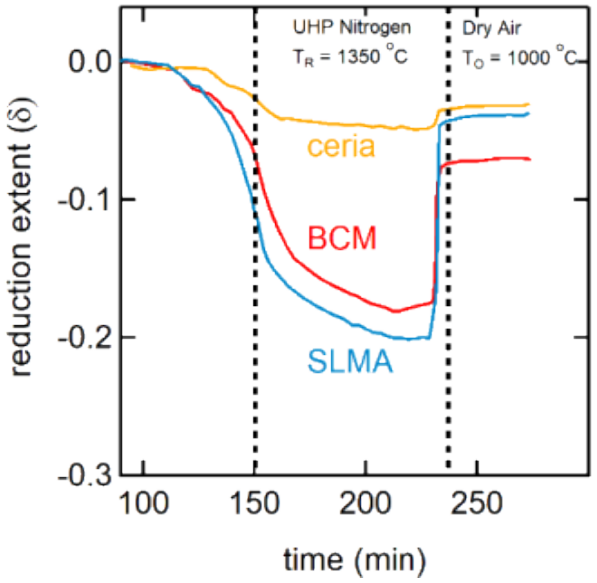
An Interesting Story About Layered Perovskites

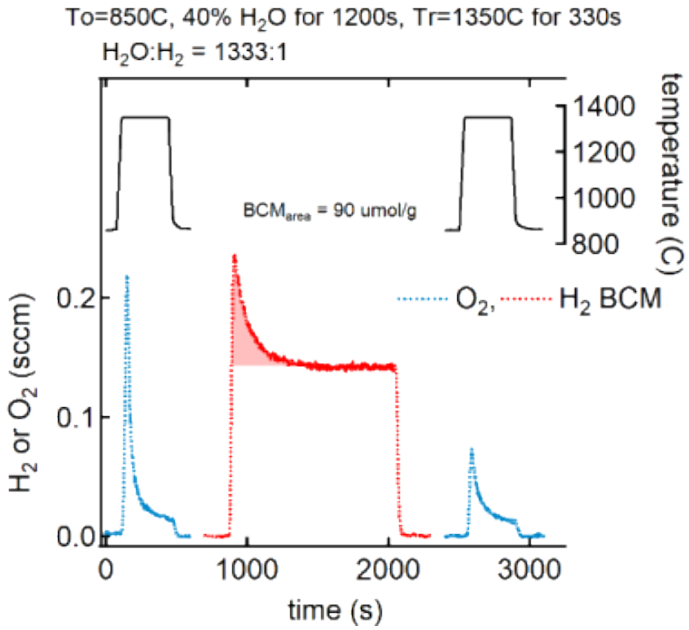
$Ba_4CeMn_3O_{12}$ – A Promising STCH Perovskite Oxide

Barcellos et al., *Energy & Environmental Science*, 10.1039/C8EE01989D (2018).

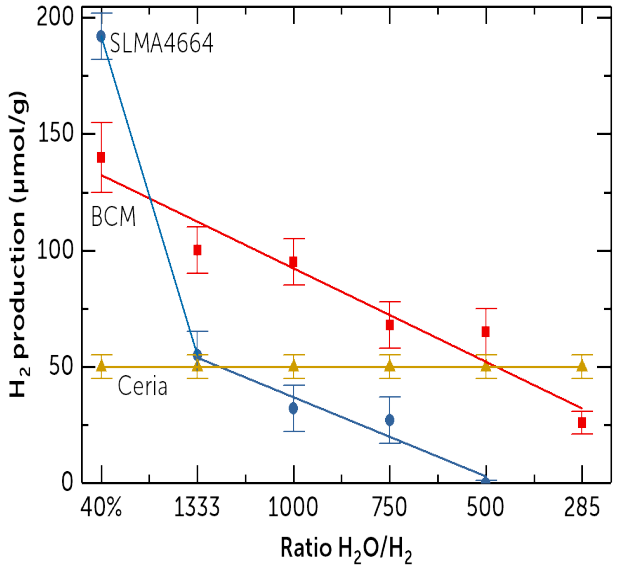
$Ba_4CeMn_3O_{12}$ (BCM)







flow reactor result

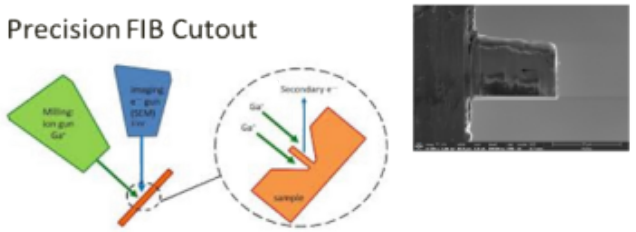


BCM is a perfectly ordered 12R-phase line compound at full stoichiometry.

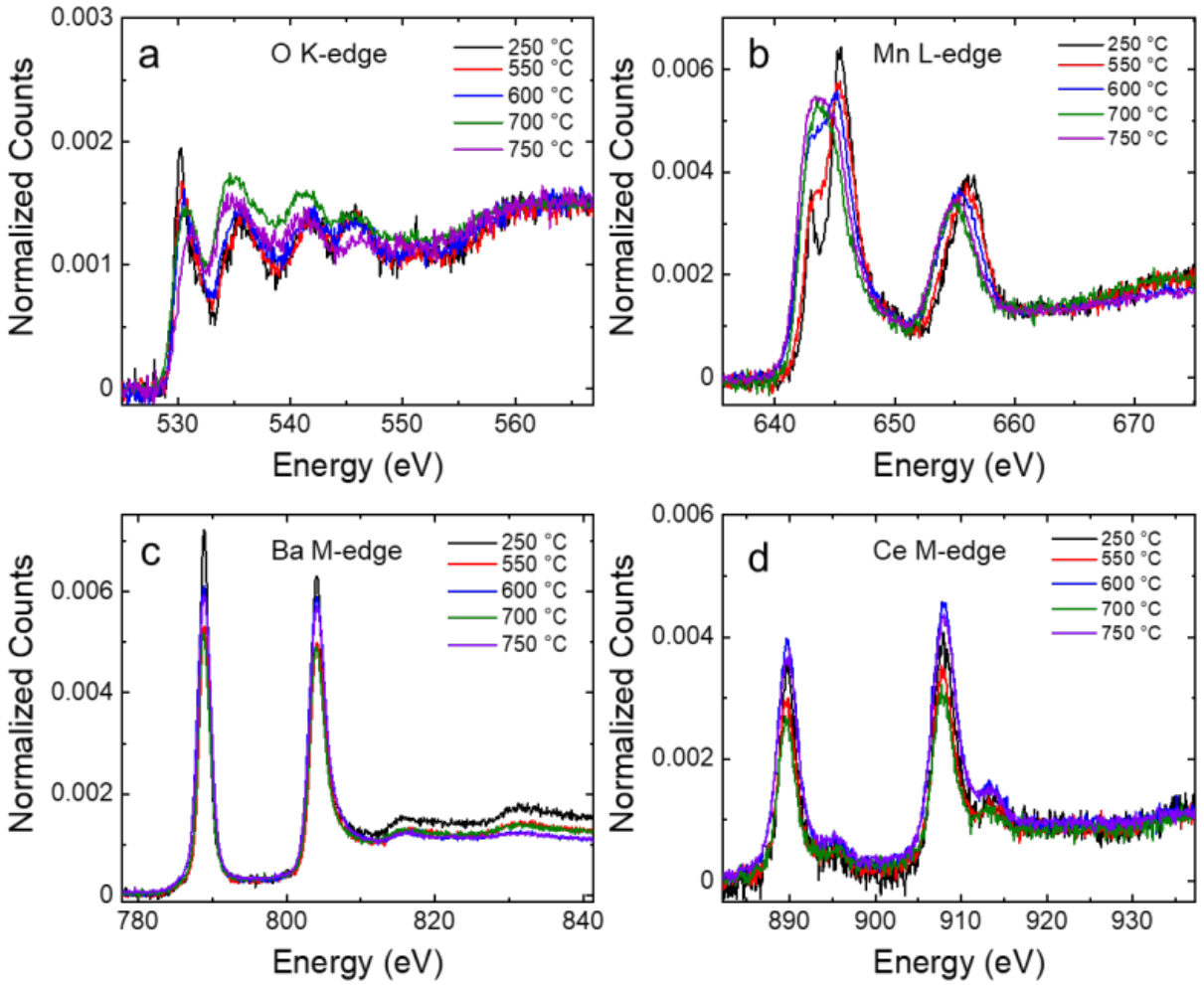
- Disconnected network of face-sharing MnO_6 octahedron trimers
- Two unique O-atom sites, no B-site mixing

BCM – first perovskite material demonstrated to lower T_{RED} and maintain $\Delta\delta_{OX}$ in $H_2O:H_2$ mixtures.

Hot Stage In Situ Vacuum Reduction Of BCM: Electron Energy Loss Spectroscopy (EELS) Probes Local Electronic States



theory needed to resolve interrelationships between structure and performance



FIB precision sample prep.

- Orient FIB cutout along low index crystal planes

Heating rates >> 100 ºC per second.

Clear and obvious changes to electronic structure local to MnO_6 manifold in BCM.

- Features in O K-edge and Mn L-edge change shape and intensity
- Coordination chemistry and Mn oxidation state change

Trend-wise loss of intensity in Ce electronic states.

- Unclear to what extent O 2p – Ce 4f manifold

DFT Probes Electronic Structure Of Reduced 12R-BCM

12R-BCM	O1	O2
$\Delta H(V_O^0)$ eV	2.66	3.29

Two unique O-atom sites exist in 12R-BCM:

- Internal to Mn trimer (O1-face sharing), ends of Mn trimer (O2-corner sharing)
- ΔH_d(O2) > ΔH_d(O1)

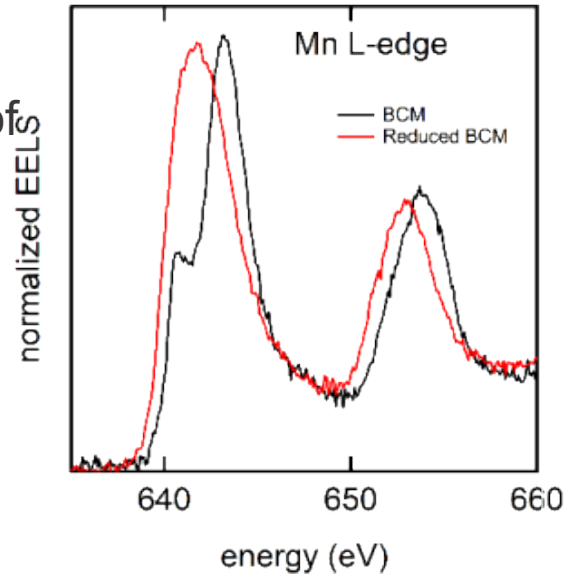
O K-edge EELS:

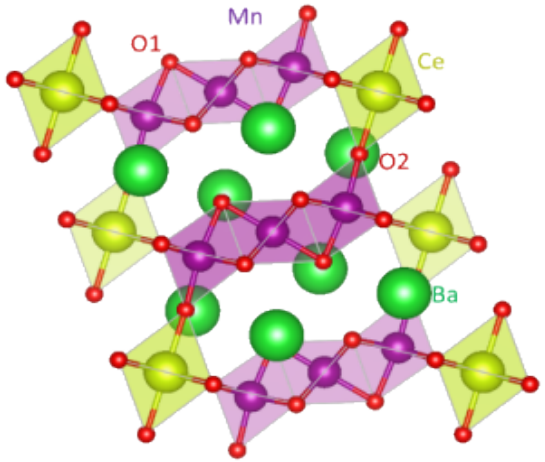
- Near edge → O2 p hybridized with Mn 3d spin states and Ce 4f
- Mid edge → O 2p interacting with Ba d states

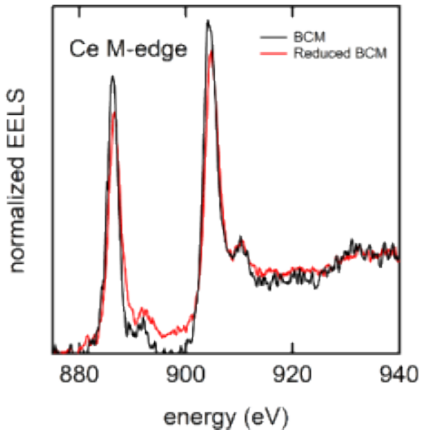
Reduction of BCM by forming V_O:

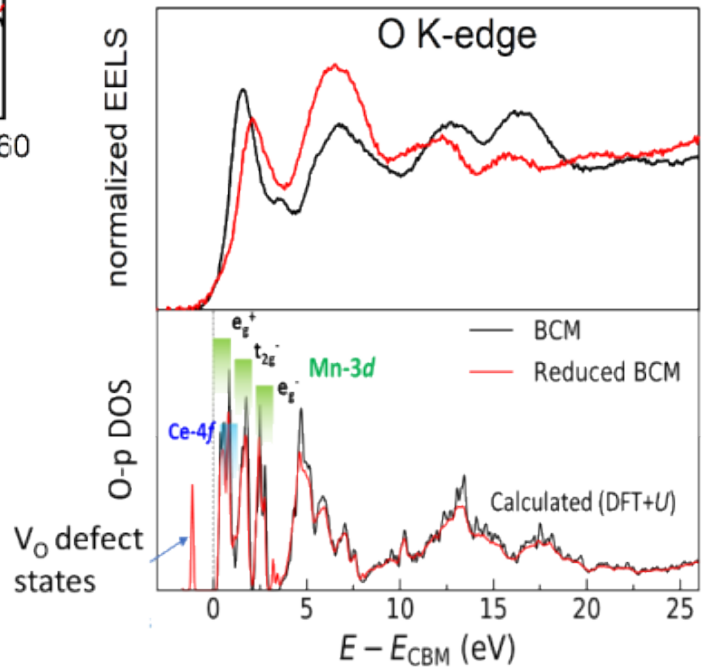
- V_O attenuates O-p DOS as nearest cations reduce ($Mn^{4+} \rightarrow Mn^{3+}$) and defect states in band gap appear
- Mn-O coordination changes (6-fold → 5-fold)
- Altered geometry of neighboring Mn changes crystal field splitting

Ce oxidation state does not change







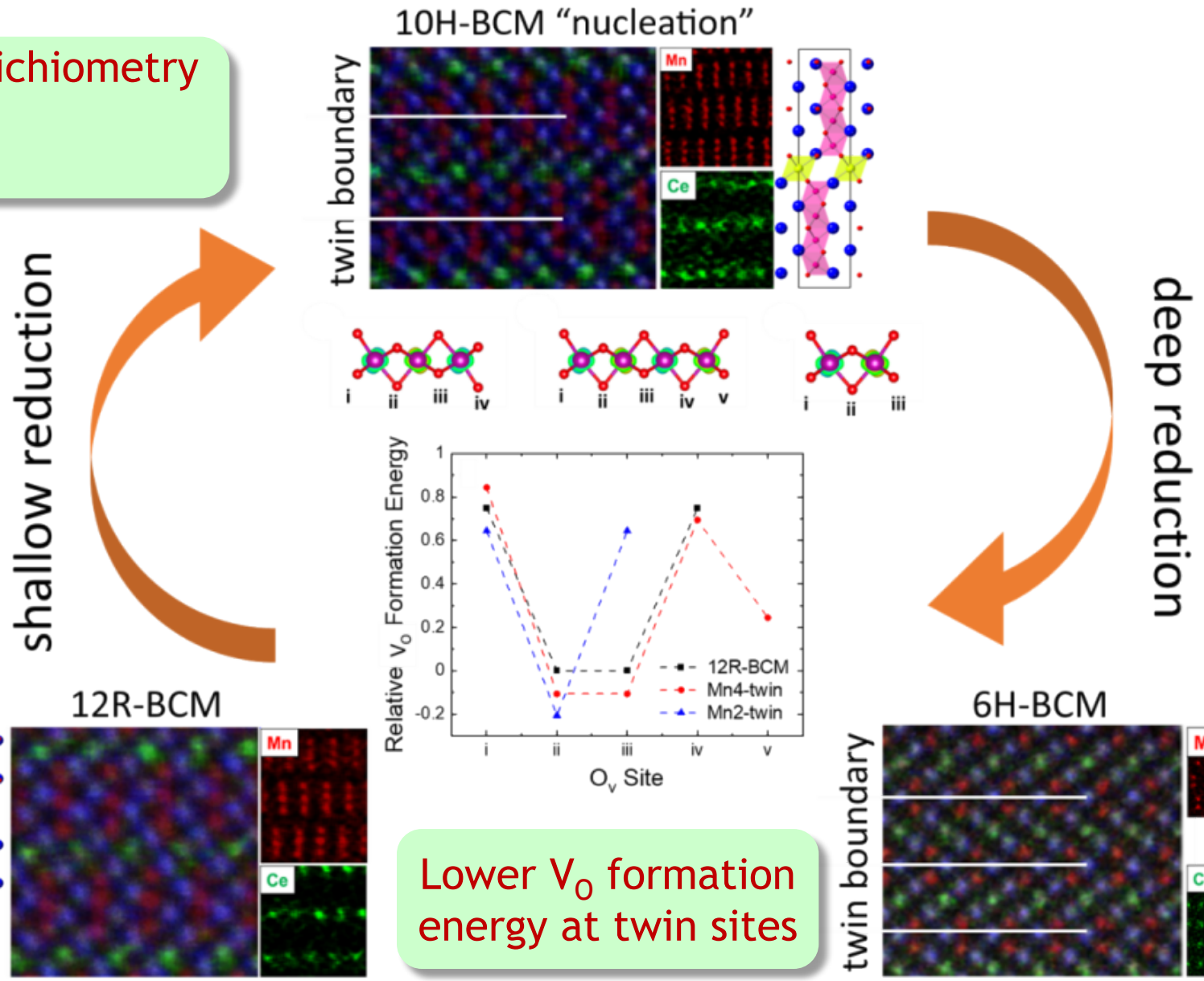


BCM's Polymorph Merry-Go-Round

Strange et al., *Inorg. Chem.*, 61, 6128−6137 (2022)
Trindell et al., in review *Chem.Mat.* (2022)

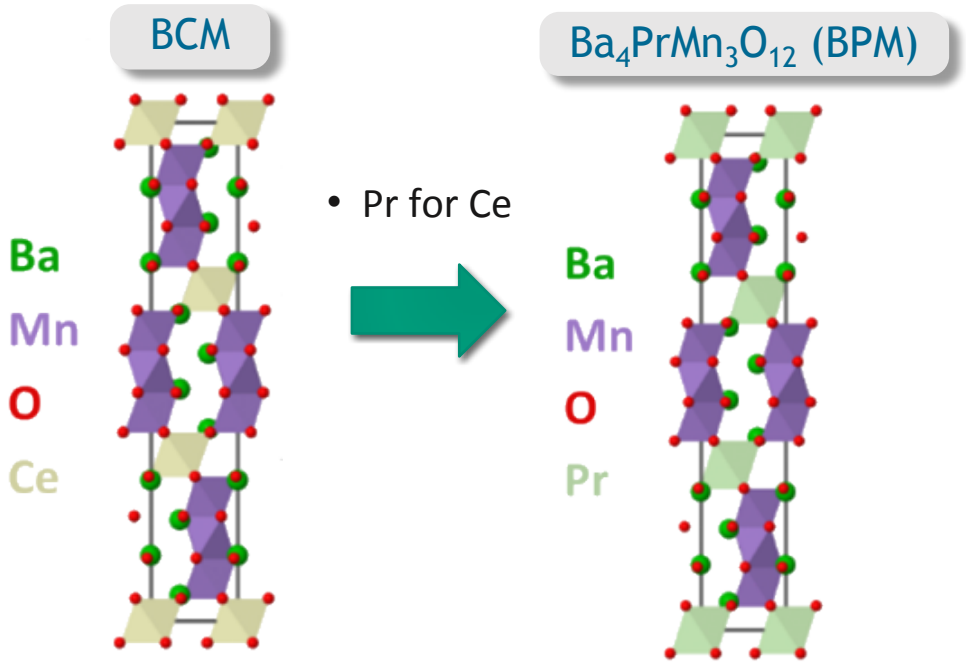
- Maintain 1:3 Ce:Mn stoichiometry
- Reversible
- Reasonable kinetics

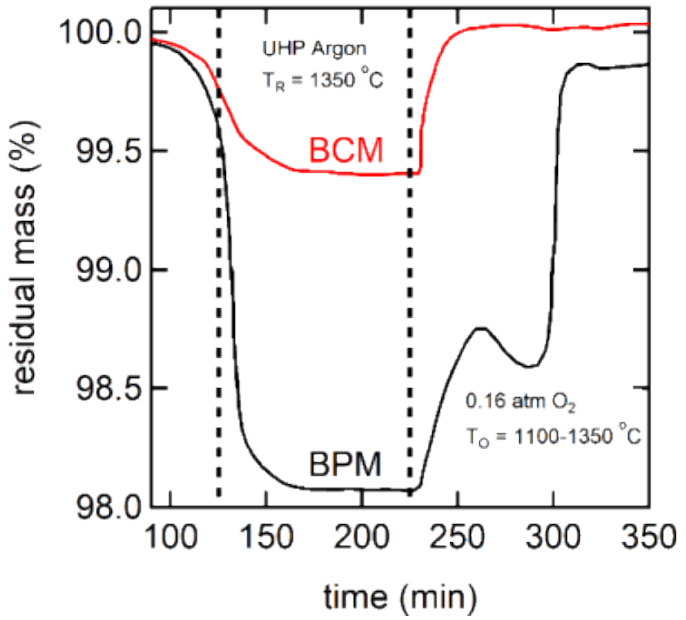
Nucleation of water-splitting phases and/or non-stoichiometry within polymorphs?



Lower V_O formation energy at twin sites

A New Water Splitting Compound: Pr-Based Compositional Variant To BCM





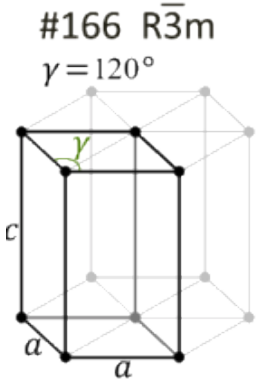
	12R-BPM	12R-BCM
Bandgap (eV)	1.401	1.956
$\Delta H(V_{O1})$ (eV)	2.64	2.66
$\Delta H(V_{O2})$ (eV)	2.92	3.29

Significant variations in $\Delta\delta_{OX}$ may be due to difference in ΔH_d

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

Ce^{4+}:[Xe] $4f^0\ 5d^0\ 6s^0$

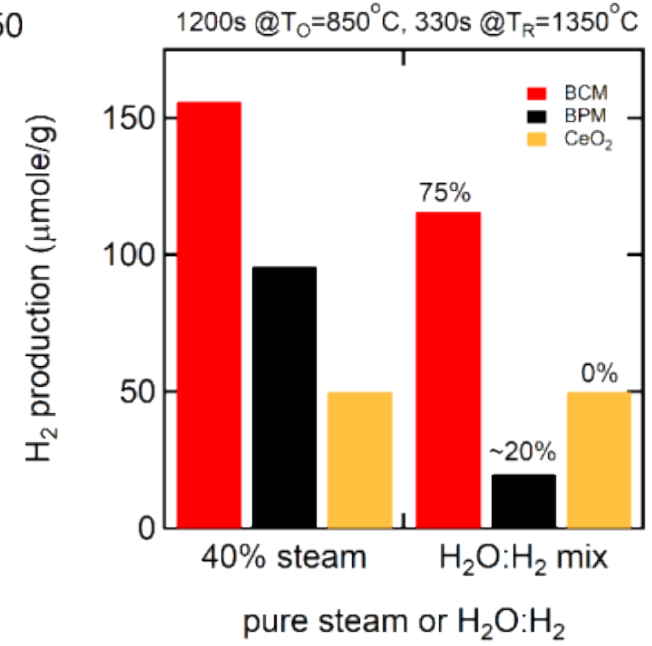
Pr^{4+}:[Xe] $4f^1\ 6s^0$



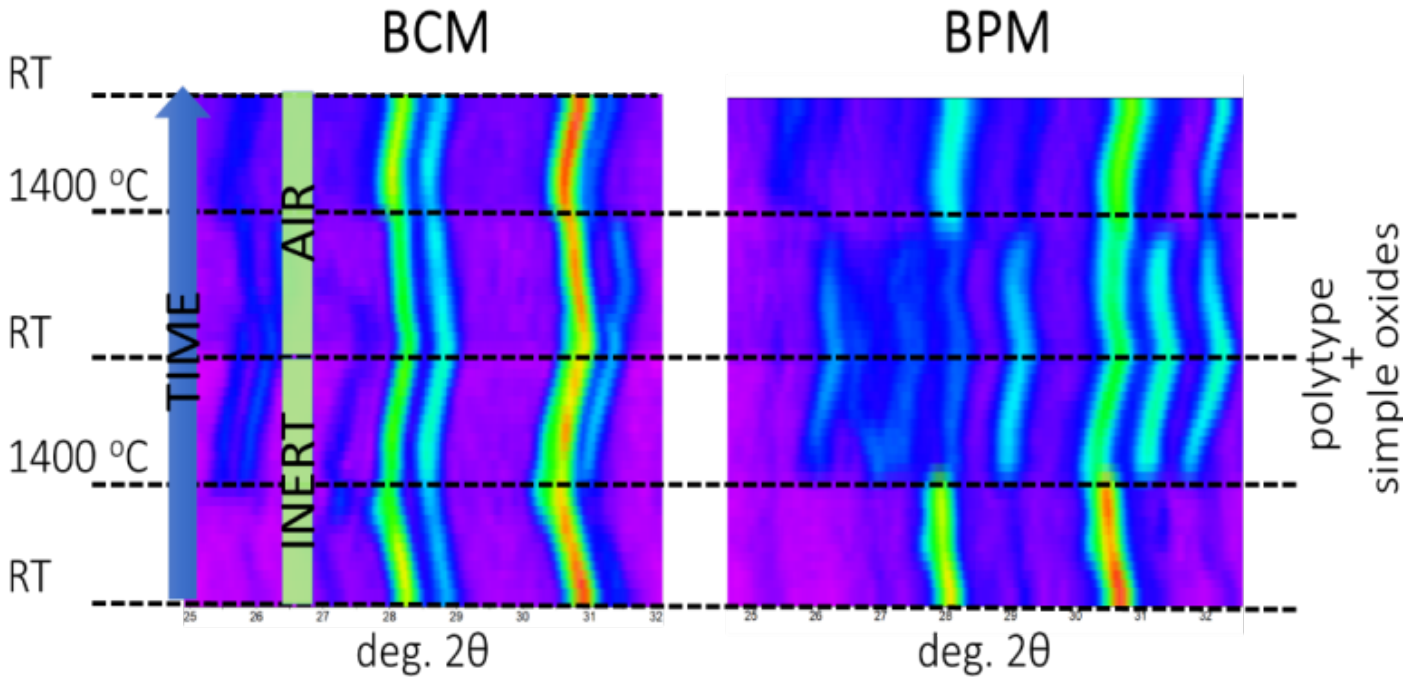
BCM and BPM identical space group symmetry.

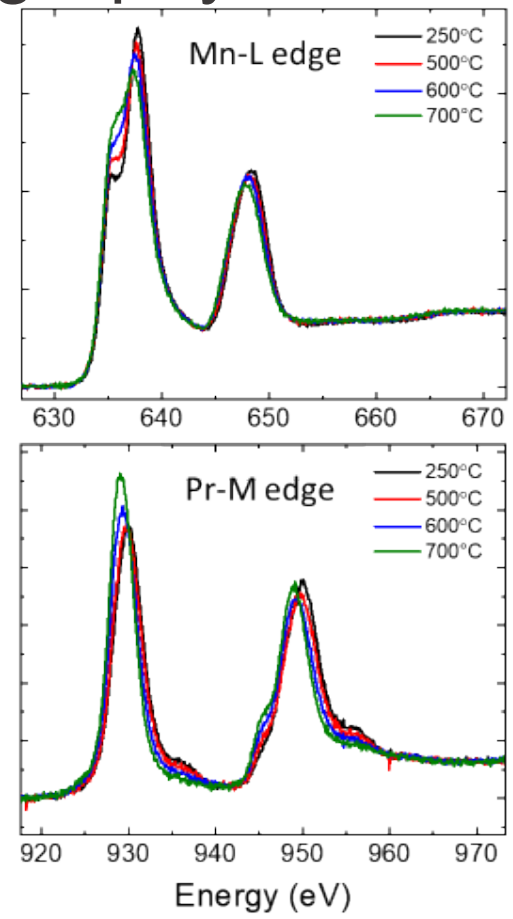
- Perfectly ordered 12R-phase @ full stoichiometry

Oxidation state Pr^{+4} = Ce^{+4}; ∆radii ~ -2%.



Experiments Reveal Different Redox Crystallography And Redox Functionality Within BXM Family





12R to 6H polytype transition in BCM is reversible.

- MnO_6 timer reduced to a dimer, partial occupancy of Mn on Ce site increases configurational entropy

BPM clearly exhibits more complicated redox phase behavior.

- Both Mn and Pr cations are redox active
- Crystallographic phase transformations more complex

Summary: Rich And Interesting Behavior At The Atomic Scale

Examined the behavior of a complex layered perovskite to unravel structure – property relationships important to high performing thermochemical water splitting materials.

- Forensic and in situ Hot Stage HR/STEM with EELS
- Operando HT-XRD
- DFT

$Ba_4CeMn_3O_{12}$ is the first perovskite material demonstrated that lowers thermal reduction temperature while maintaining "decent" $\Delta\delta_{OX}$ in H_2O:H_2 mixtures.

- High configurational entropy upon reduction is important, the 12R – 10H – 6H transition provides a clue

Substituting Pr for Ce dramatically degrades redox behavior.

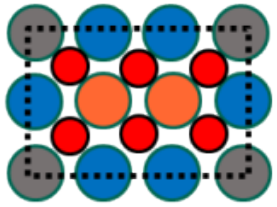
- Isostructural variant with ONE additional valence electron
- $Ba_4PrMn_3O_{12}$ redox behavior is much more complex than Ce variant
- BPM is a good model system to unravel the details of electronic effects in these materials and gain an understanding of atomistic processes that engender favorable water-splitting thermodynamic behavior

Searching *Beyond* Perovskite Space For A Commercially Viable Metal Oxide Using DFT+ML

Computational Search For $\Delta H_d(V_O) \in [2.3, 4.0]$ eV Rapidly Encounters Scaling Issues

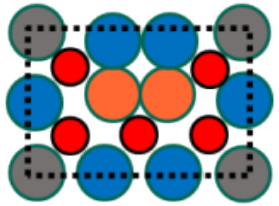
Need the vacancy formation enthalpy, ΔH_d, of all N symmetry sites:

Relaxed host energy, E_h

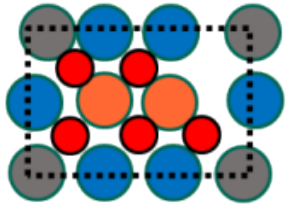


Relaxed defect energy, E_d

N=1 defect



N=2 defect

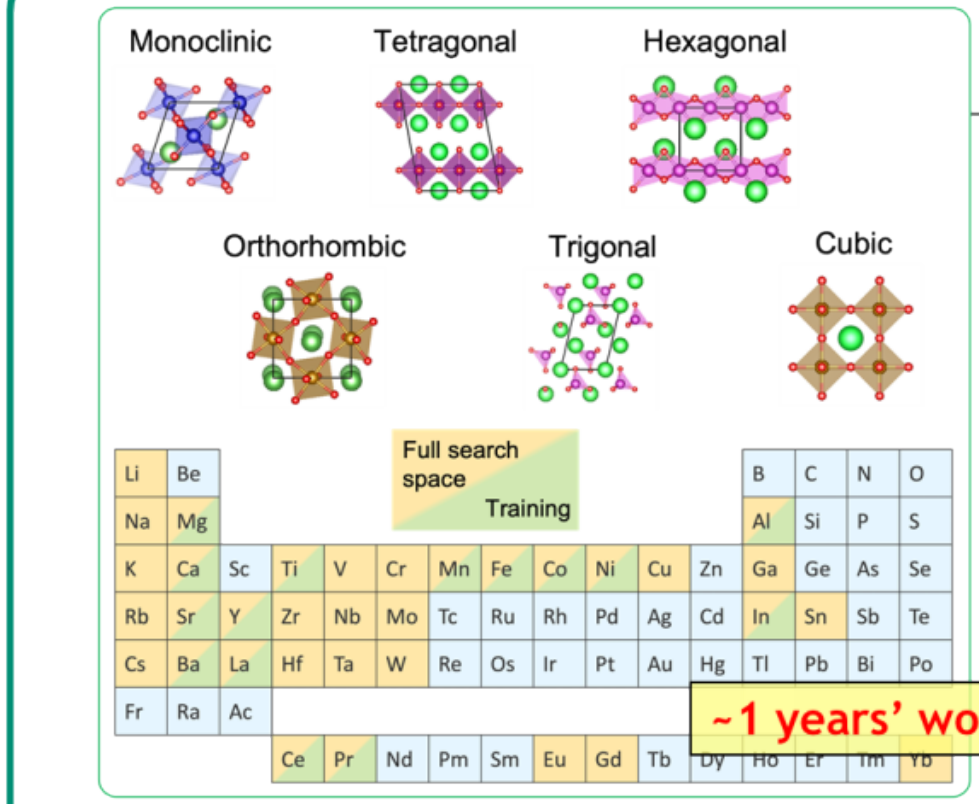


$$\Delta H_d = E_d - E_H + \sum_i n_i \mu_i^{ref}$$

- Defect Formation Energy
- Relaxed Defect Supercell Energy
- and Host
- Atomic Reference Energy

Requires N+1 DFT relaxations

First-principles DFT workflow is robust but costly (using NRELMatDb hosts)



DFT workflow

A. Material Space

Diversity in Training:
63 space groups
51 unique stoichiometries
14 cations

B. Host Calculations

Relaxed structure,
Atomic spin and oxidation state,
Enthalpy of formation,
Bandgap, Electron effective mass

C. Defect Calculations

Calculated oxide space:
~200 host structures
~1500 defect relaxations

~1 years' work

Existing oxide space:
~10,000s host structures
~1Ms defect relaxations

100+ years' work… so more efficient model needed

Use Graph Neural Network (GNN) Model To Perform "Automated Feature Extraction" Directly from Host Crystal Structure

Interpret crystal structures as a graph.

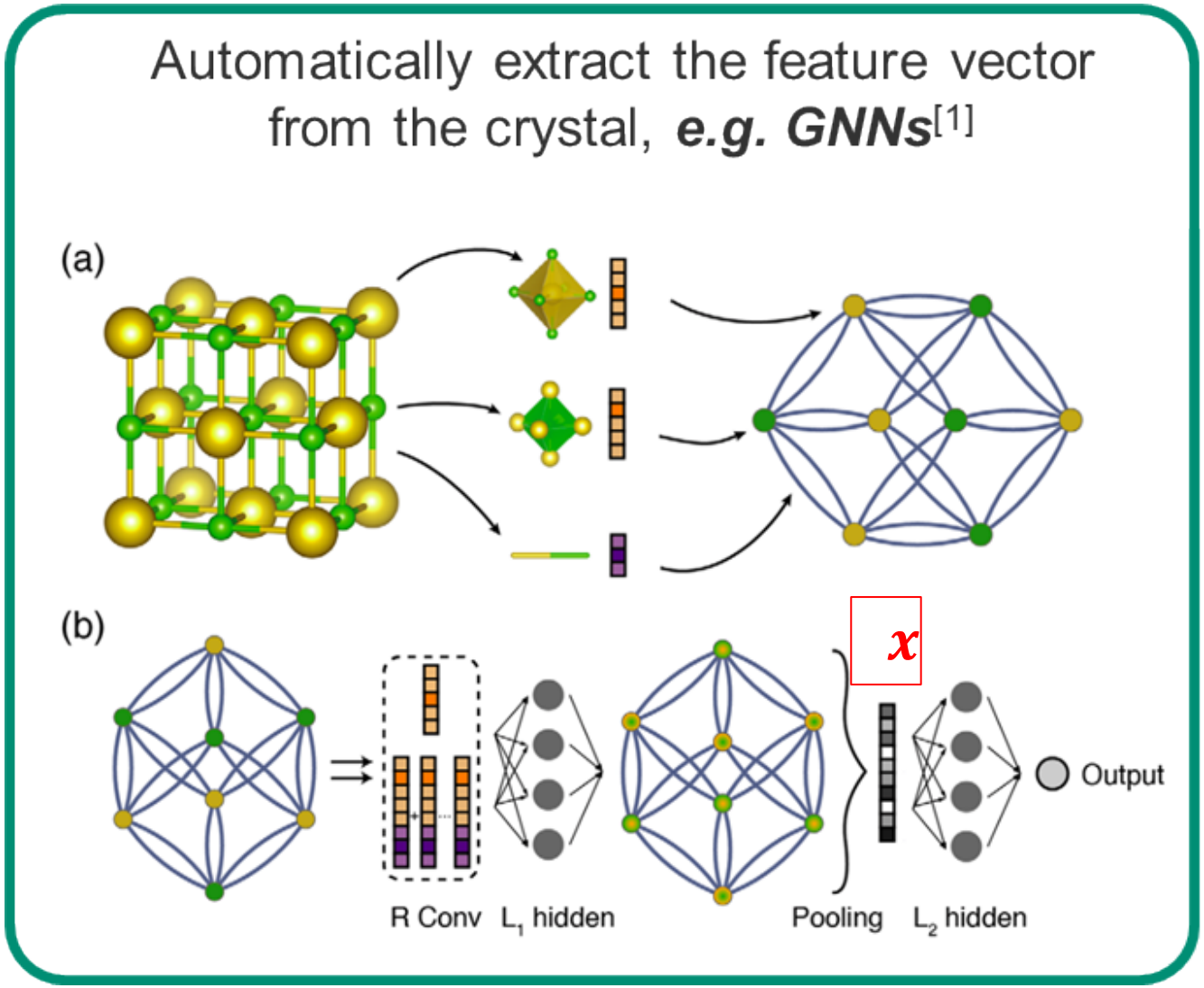
- Nodes = Atoms, "Bonds" = Edges
- Pass information between neighboring nodes

Pool atom features to create crystal feature vector (χ).

Input host properties.

- Relaxed host crystal structure
- Optional: atom oxidation state, atom magnetic moment, compound formation enthalpy, bandgap, e- effective mass

Output the atom site-specific defect formation energy without knowing the relaxed defect structure.

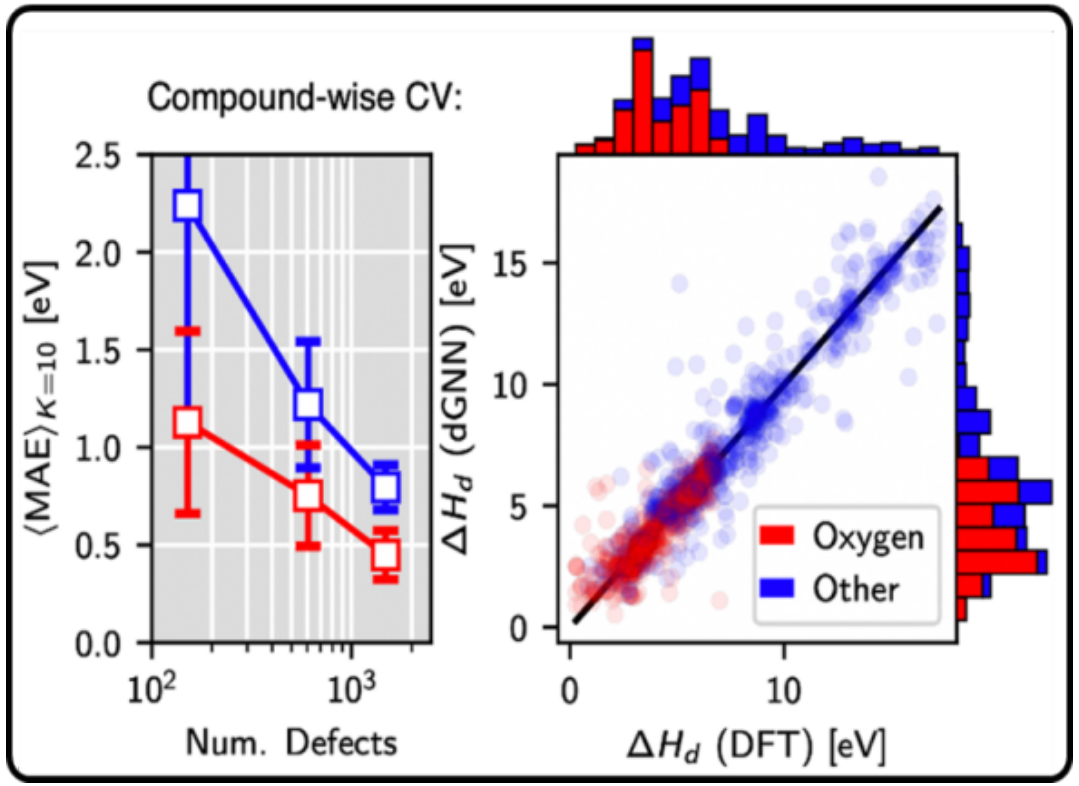


[1] Xie, et al. *P.R.L.* 120 (14), **2018**

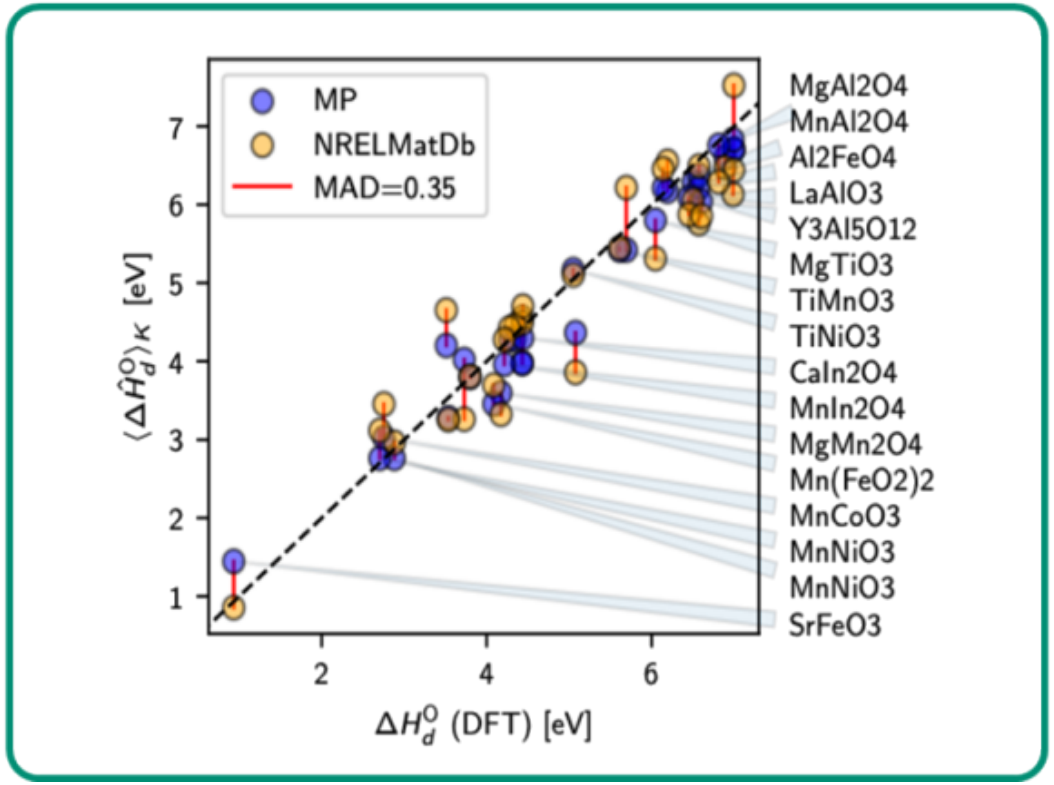
Defect GNN Approach Validated For Use In High-throughput Screening Exercise*

[*] https://doi.org/10.26434/chemrxiv-2022-frcns

Benchmark accuracy has been met for HT screening



NRELMatDb vs. Materials Project (MP) structure inputs



Expected ΔH_d MAE for unseen compounds <450 meV.

- Robust prediction of O and non-O vacancies.

Robust to small variations in structure.

Can screen using a different database (MP) than training set.

MAE = mean absolute error

ML Screens 10,000's Of MP Structures In Minutes

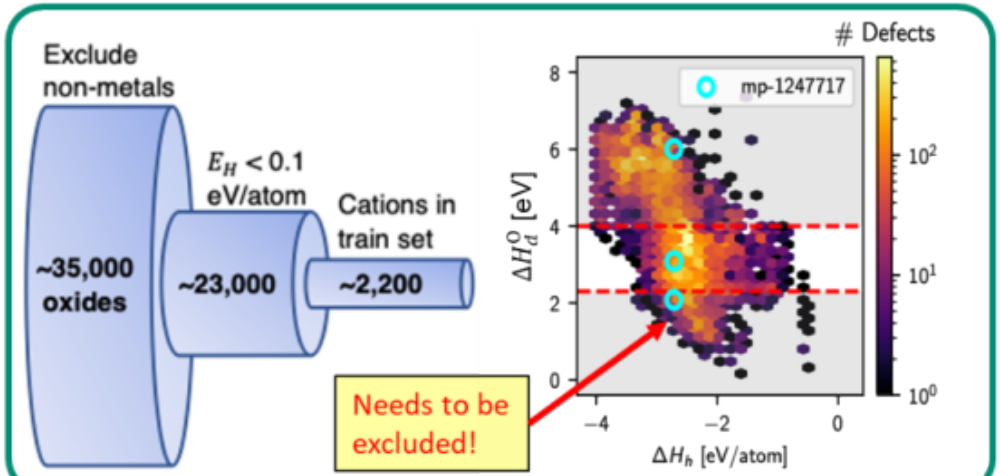
(1) Co-design of host defects and stability for water-splitting

Metric	Requirement
Frac. of defects w/ΔH_d^O > 2.3 eV	$x_{\min} = 1$
Frac. of defects w/$\Delta H_d^O \in$ [2.3, 4.0] eV	$x_{\text{rng}} > 0$
Host stability criteria (ranges intersect)	$\Delta\mu'_{O_2} \cap \Delta\mu_{O_2}^{\phi_H<X} \neq \emptyset$

$\Delta\mu'_{O_2} \equiv \mu_{O_2}$ operating range for STCH

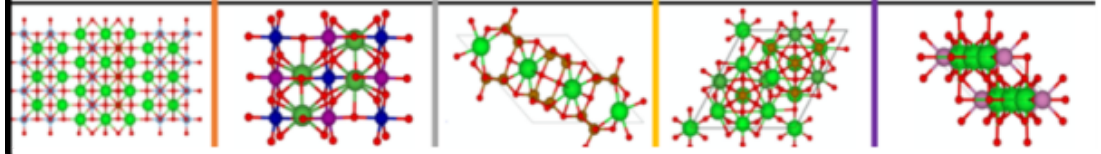
$\Delta\mu_{O_2}^{\phi_H<X} \equiv \mu_{O_2}$ range where host's grand energy above hull (ϕ_H) is < X

(2) Screen the Materials Project for all defects



(3) Identify and filter increasingly promising targets

197 formulas (48 training)	114 formulas (33 training)	34 formulas (17 training)	16 formulas (11 training)	9 formulas (9 training)
➢ $x_{\min,1} = 1$ ➢ $x_{\text{rng},1} > 0$ ➢ $\Delta\mu_{O_2}^{\phi_H<0.1}$	➢ $x_{\min,2} = 1$ ➢ $x_{\text{rng},2} > 0$ ➢ $\Delta\mu_{O_2}^{\phi_H<0.1}$	➢ $x_{\min,3} = 1$ ➢ $x_{\text{rng},3} > 0$ ➢ $\Delta\mu_{O_2}^{\phi_H<0.05}$	➢ $x_{\min,3} = 1$ ➢ $x_{\text{rng},3} > 0$ ➢ $\Delta\mu_{O_2}^{\phi_H=0}$	➢ $x_{\min,3} = 1$ ➢ $x_{\text{rng},3} = 1$ ➢ $\Delta\mu_{O_2}^{\phi_H=0}$
$Sr_6Ti_3FeO_{14}$ (mp-1645141)	La_2MnCoO_6 (mp-19208)	$BaSr(FeO_2)_4$ (mp-1228024)	$Ba_5SrLa_2Fe_4O_{15}$ (mp-698793)	$Ba_3In_2O_6$ (mp-20352)



- Filter candidates with increasingly certain performance
- Mainly identifies known, synthesizable compounds
- ~100 are not AXO_3 , $A_{n+1}X_nO_{3n+1}$, $Fe_{3-n}M_nO_4$, CeO_2 , etc.

Screening workflow on MP structures reduces time from 1,000's of DFT months to minutes.

Rediscovers complex, known water-splitting materials (not in training data) like

Summary: Prospecting Beyond Perovskite Space For A Commercially Viable Metal Oxide Using DFT+ML

Use GNN to predict global defect properties (site-specific ΔH_d) encoded in ground-state crystal structure.

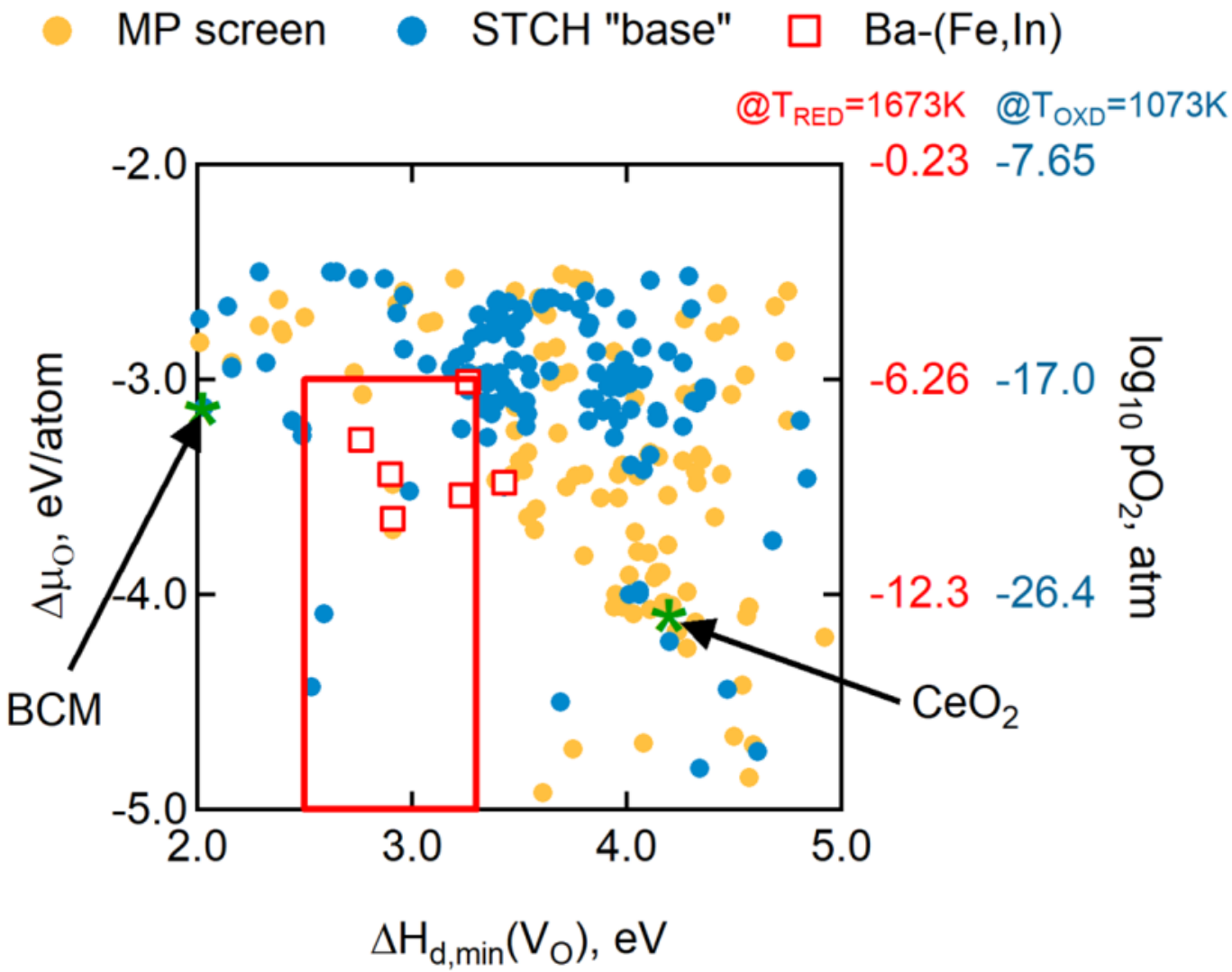
Diverse and unique DFT training space comprised of 200 BINARY and TERNARY oxides.

- 63 unique crystal structures, 51 unique stoichiometries, 14 cations
- Range of oxidation states (2+ to 5+), ionic radii, coordination environments

Identified ~100's of materials, many unknown to STCH community.

- Found quaternaries and quinaries not in training set
- ΔH_d and stability criteria under low pO_2

Conducting second round of DFT defect relaxations to include more cations.



Acknowledgements

HydroGEN Advanced Water Splitting Materials Consortium National Laboratory Solar Thermochemical Water Splitting Research Team:

Sandia National Laboratories

- Andrea Ambrosini, Sean Bishop, Eric Coker, James Park, Andrew Smith, Joshua Sugar, Jamie Trindell, Mathew Witman

National Renewable Energy Laboratory

- Robert Bell, David Ginley, Anuj Goyal, Stephan Lanny, Dan Plattenberger, Philip Parilla, Sarah Shulda

Lawrence Livermore National Laboratory

- Tadashi Ogitsu

SLAC National Accelerator Laboratory

- Nicolas Strange

Funding provided by [illegible] **ogies Office**

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