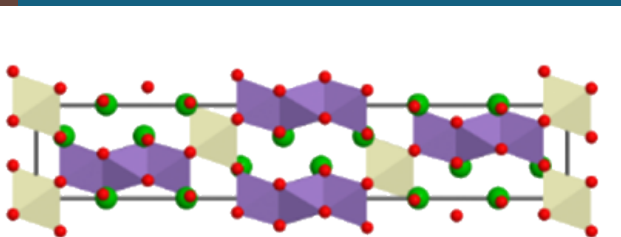




Sandia
National
Laboratories

SAND2021-4899C

Pathways to Renewable Fuels Using Concentrated Sunlight



PRESENTED BY

Anthony McDaniel

Spring MRS meeting, April 20, 2021



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2 Acknowledgements



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

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- Andrea Ambrosini, Eric Coker, James Park, Joshua Sugar, Jamie Trindell

National Renewable Energy Laboratory

- Robert T. Bell, David Ginley, Dan Plattenberger, Philip Parilla, Sarah Shulda

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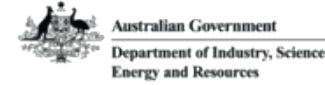
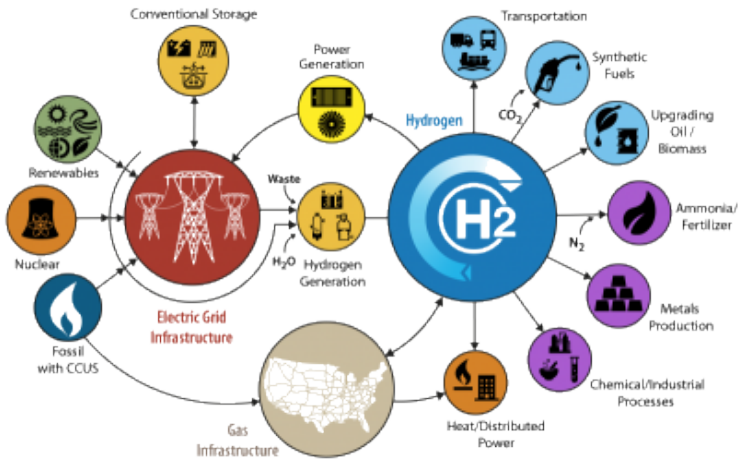
- Tadashi Ogitsu

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Office of
ENERGY EFFICIENCY & RENEWABLE ENERGY

Hydrogen Is Large In The Google-verse



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Australia's National Hydrogen Strategy



2021 Best Countries ▸ See the Worst Countries for Racial Equality

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German Government Agrees on National Hydrogen Strategy

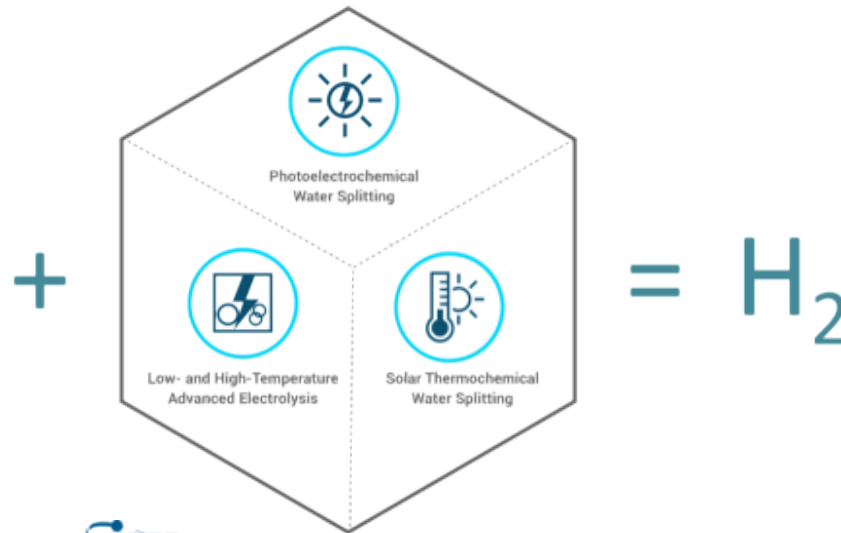


China prepares multi-pronged hydrogen strategy

Global efforts underway to advance “green” hydrogen production.

- Address KEY technology challenges to advance readiness level of large scale, low cost renewable H₂ production

Hydrogen As Far As The Eye Can See



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

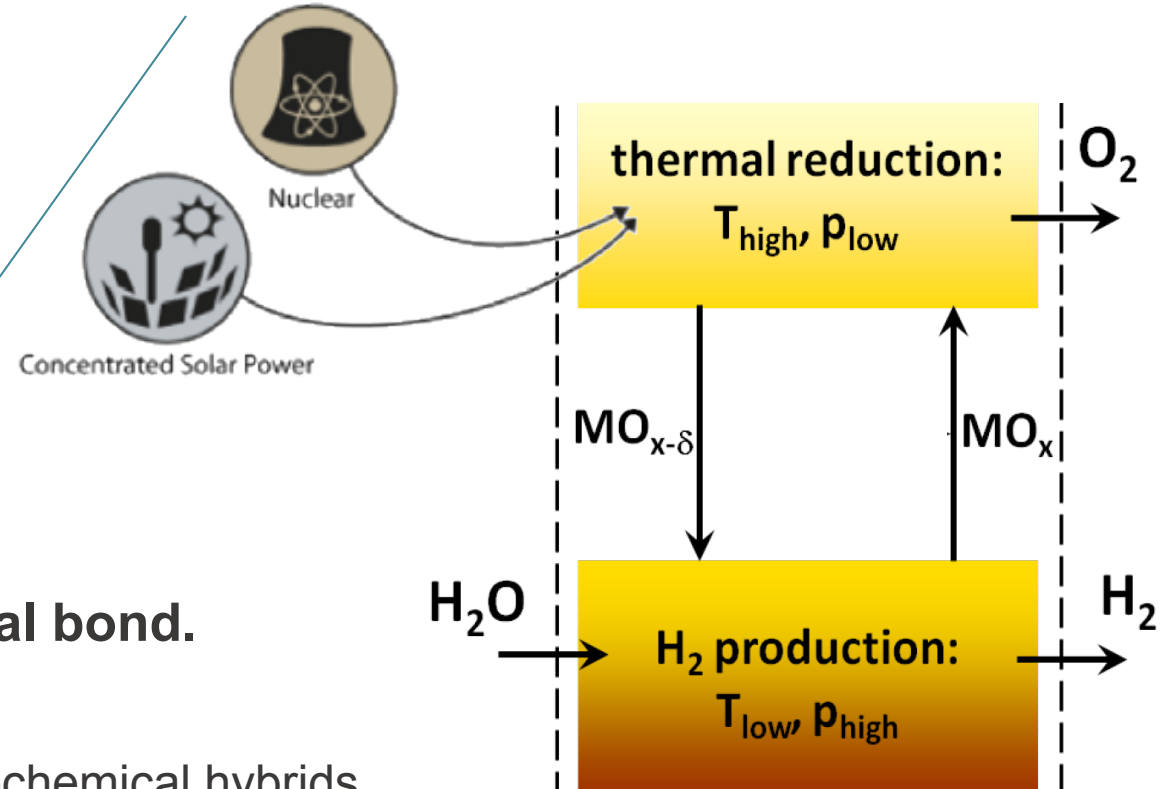
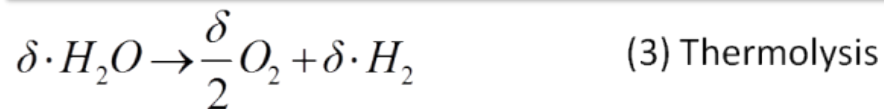
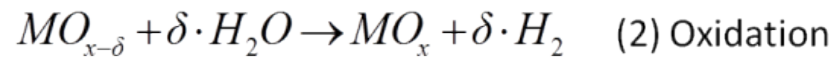
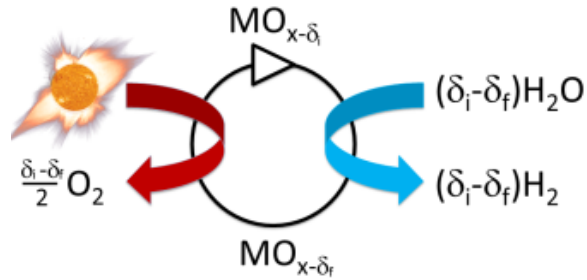
- Electrolysis, photoelectrochemical, thermochemical, microbial

DOE's HydroGEN Advanced Water Splitting Materials consortium (H₂AWSM):

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

Solar Thermochemical Water Splitting Is A Simple Concept: Heat + H₂O In, H₂ + O₂ Out

R. Perret, SAND Report (SAND2011-3622), Sandia National Laboratories, 2011.
 G. J. Kolb, R. B. Diver, SAND Report (SAND2008-1900), Sandia National Laboratories, 2008.
 S. Abanades, P. Charvin, G. Flamant, P. Neveu, *Energy*, **31**, 2805–2822 (2006).



Direct storage of solar energy in a chemical bond.

Many hundred cycles proposed.

- Multi-phase, multi-step, thermochemical-electrochemical hybrids

DOE's HydroGEN Advanced Water Splitting Materials (H₂AWSM) consortium is focused on two-step, non-volatile MO_x.

- h2awsm.org

Outline



Searching for a commercially viable metal oxide.

- Navigating a highly constrained requirement space (oxygen storage materials)
- Application of first principles theory to material discovery (H₂AWSM)

An interesting story about layered perovskites.

- Ba₄CeMn₃O₁₂ and Ba₄PrMn₃O₁₂ and polytypes

Summary.

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.

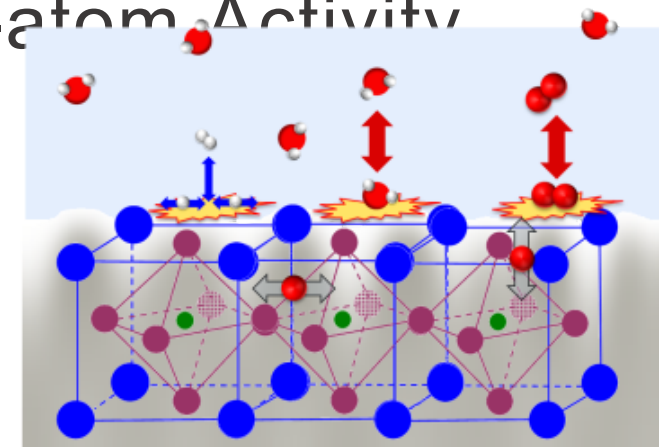
- O-atom “harvested” from H_2O not Air
- Bulk phenomena largely govern O-atom exchange with environment

Material subject to extreme environments.

- Redox cycling on the order of seconds
- Large thermal stress per cycle
 - $800\text{ }^\circ\text{C} < T < 1450\text{ }^\circ\text{C}$; $\Delta T_{RATE} \sim 100\text{ }^\circ\text{C/sec}$
- Large chemical stress per cycle
 - $10^{-14}\text{ atm} < p_{O_2} < 10^{-1}\text{ atm}$

Water splitting at extremely low p_{O_2} .

- Strongly reducing “oxidizing” atmosphere



“O” activity in
 $H_2O:H_2$

$\mu_{gas} > \mu_{solid}$

$\mu_{gas} \sim 10^{-13}\text{ atm}$

A Brief History Of Non-Stoichiometric Materials...



spinel

Fe²⁺/Fe³⁺ (unsupported) systems:

High redox capacity ($\Delta\delta > 0.1$)

Moderate $T_R < 1400$ °C

WS-UNTESTED in H₂O:H₂ atm

perovskite

TM²⁺/TM³⁺/TM⁴⁺ (Mn, Fe, Co) systems:

High redox capacity ($\Delta\delta > 0.1$)

Low-to-moderate $T_R < 1400$ °C

WS-PROMISING in H₂O:H₂ atm

fluorite

Ce³⁺/Ce⁴⁺ systems:

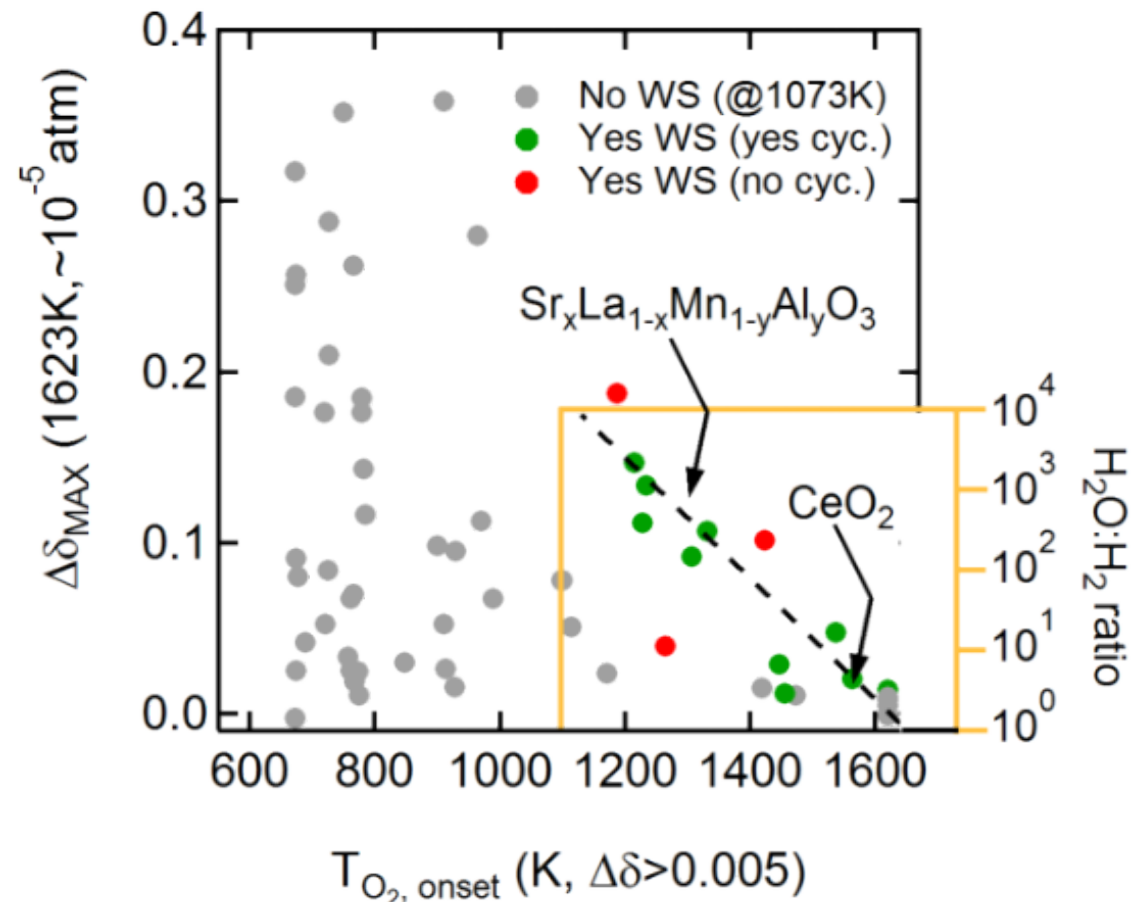
Low redox capacity ($\Delta\delta < 0.08$)

High $T_R > 1500$ °C

WS-“BEST IN CLASS” in H₂O:H₂ atm

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

WS inactive at $T_{O_2, onset} < 1100$ °C
high H₂O:H₂ ratio at $T_{O_2, onset} < 1400$ °C

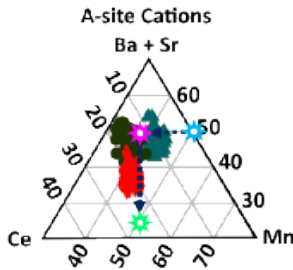
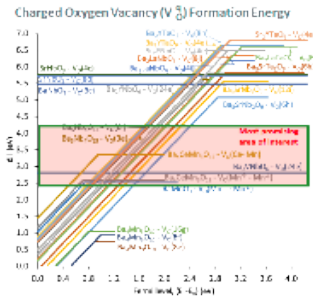


H₂AWSM Projects Are Fulfilling The Vision Of The Consortium/EMN Model (HPC, ML, Theory Guided Material Design)



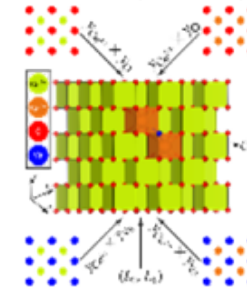
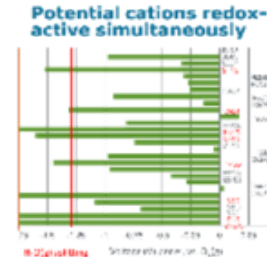
Found RP phases that modify redox thermo.

- DFT screening of defect formation energy
- Thin film combinatorics for compound discovery
- High throughput colorimetric screening



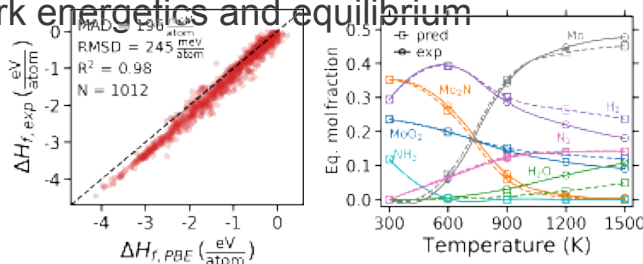
Incorporate second redox active sublattice to modify thermo.

- DFT method to predict $\Delta\delta$ a priori using simple sublattice model formulations
- Discover compounds with optimized thermo (δH , δS)



Use machine-learned models coupled to DFT to discover new redox materials.

- Rapidly screen materials based on machine-learned predicted stability
- Formulate descriptor(s) for predicting reaction network energetics and equilibrium

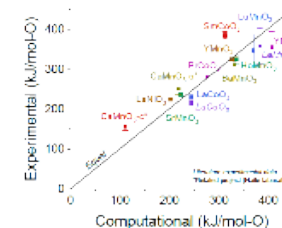


Use high-throughput Density Functional Theory to discover new redox materials.

- Screen $>10^4$ known compounds for ground state stability/synthesizability and favorable thermo at reduction $T < 1400$ °C

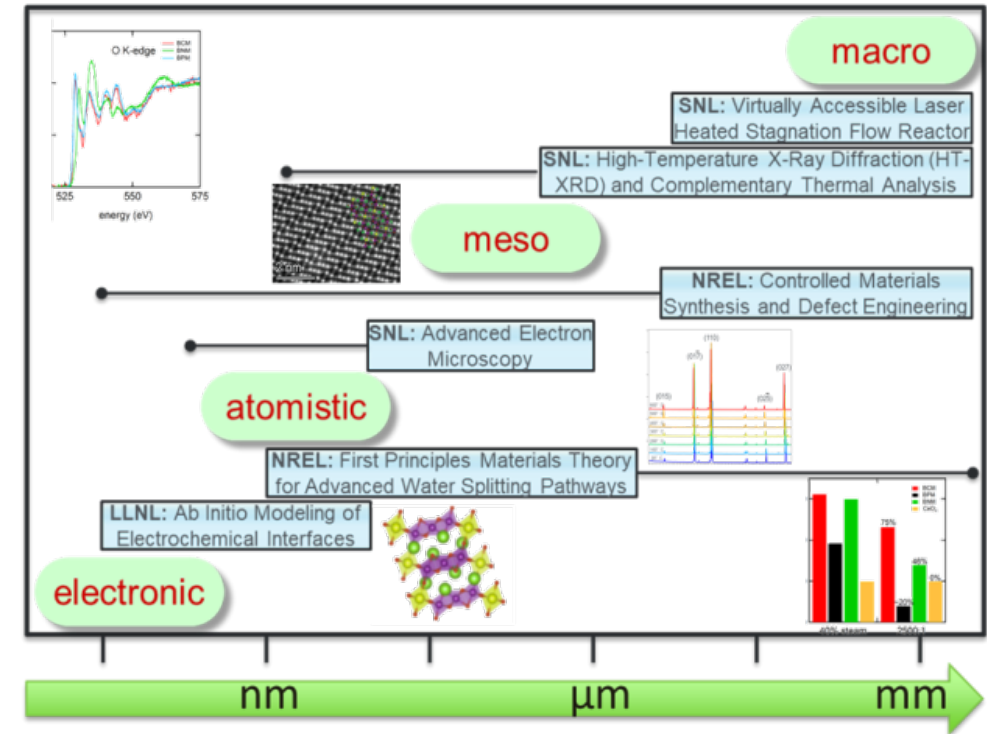
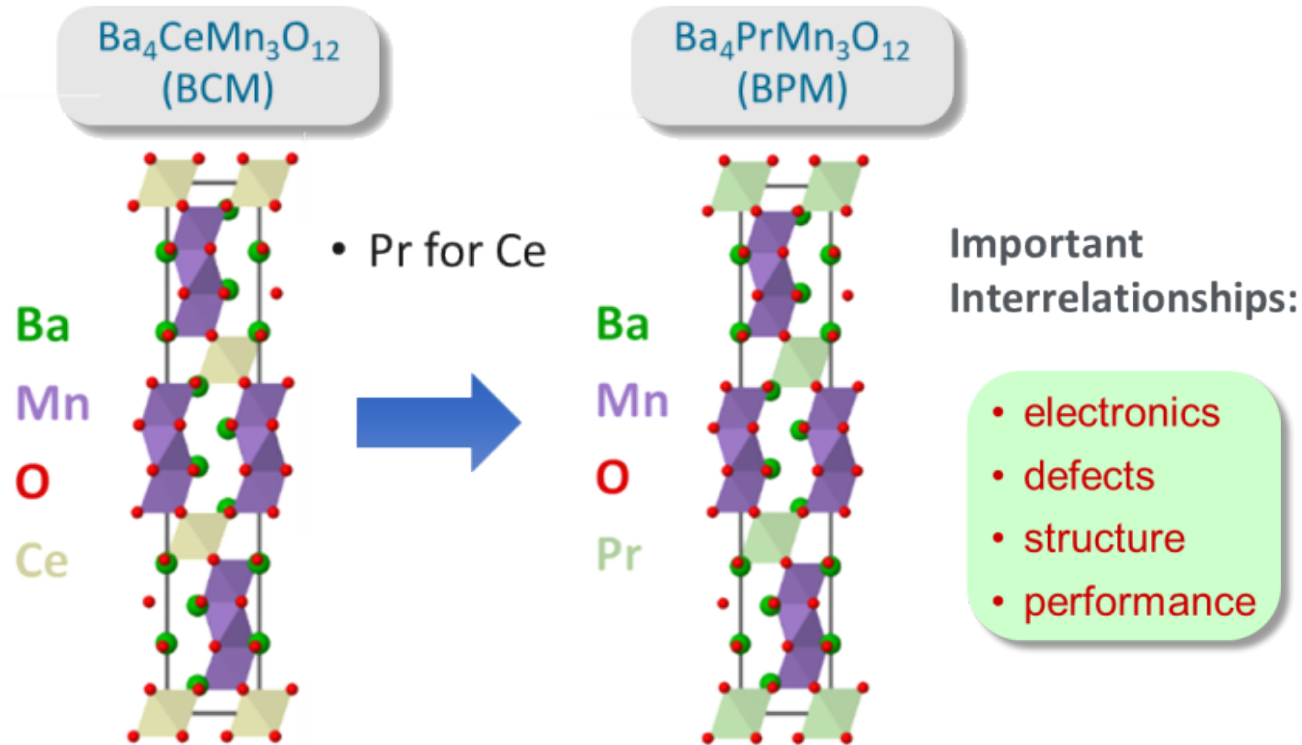


Northwestern University



- One dozen *potential* compounds have been “discovered” using HPC, ML, and DFT
- Water splitting functionality has been verified in several of these predicted formulations
- Validated high-throughput computational tools are now in place to rapidly expand the known material space

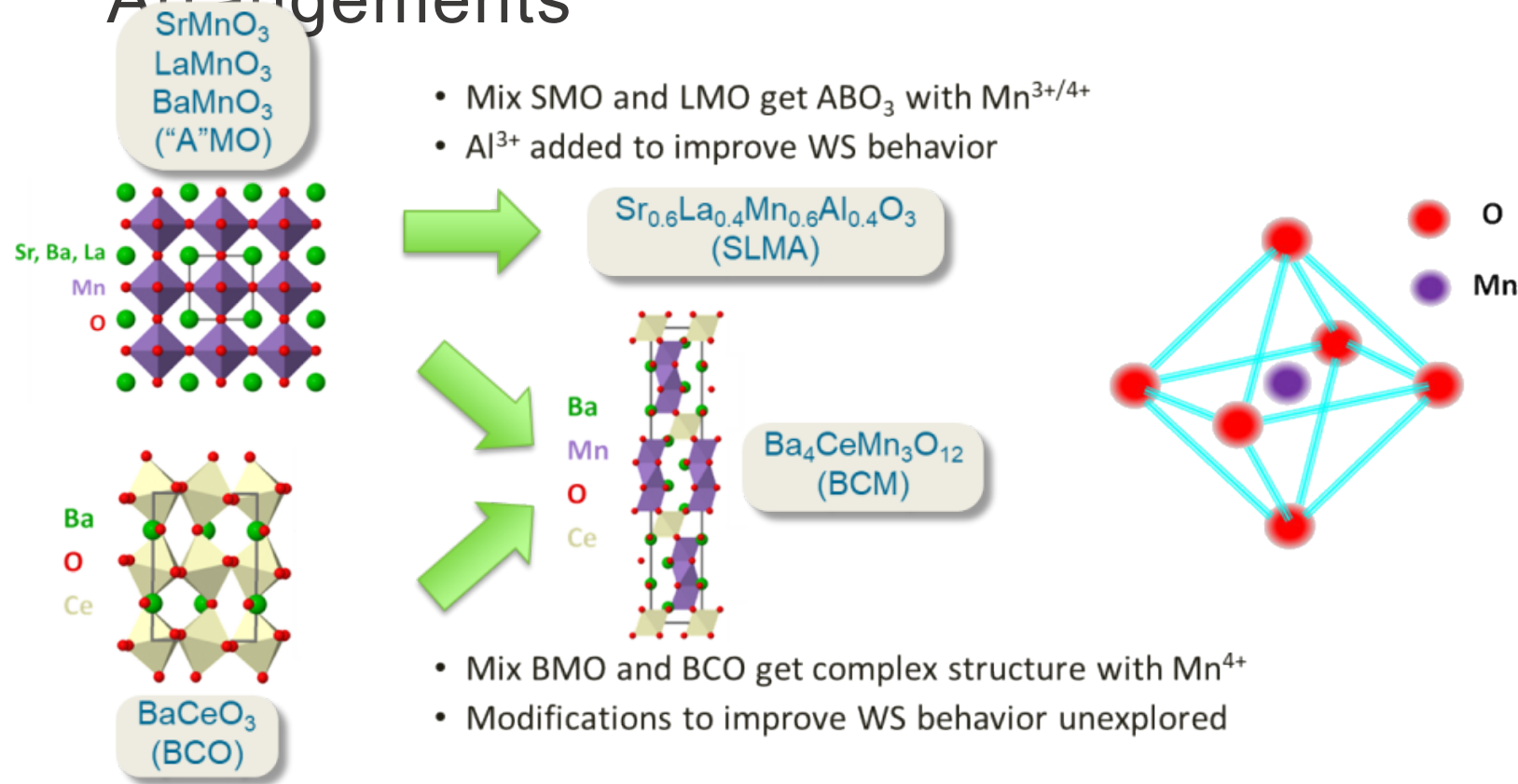
An Interesting Story About Layered Perovskites



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 water splitting activity

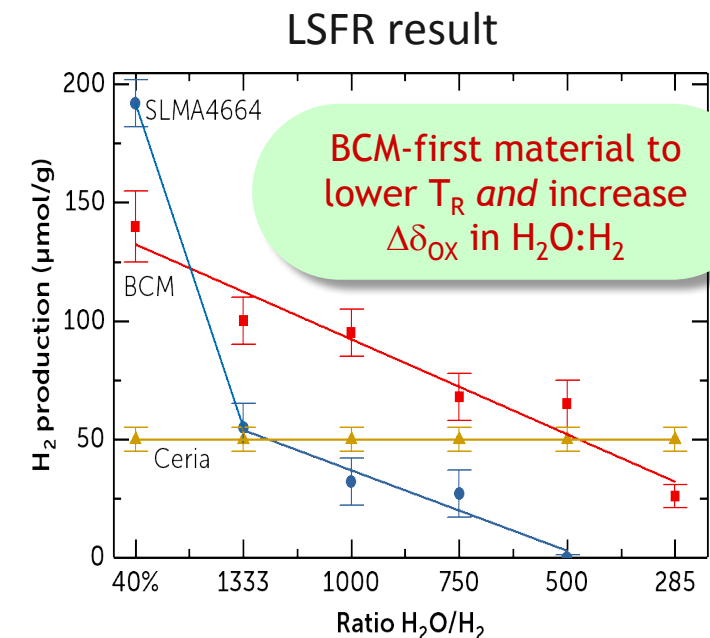
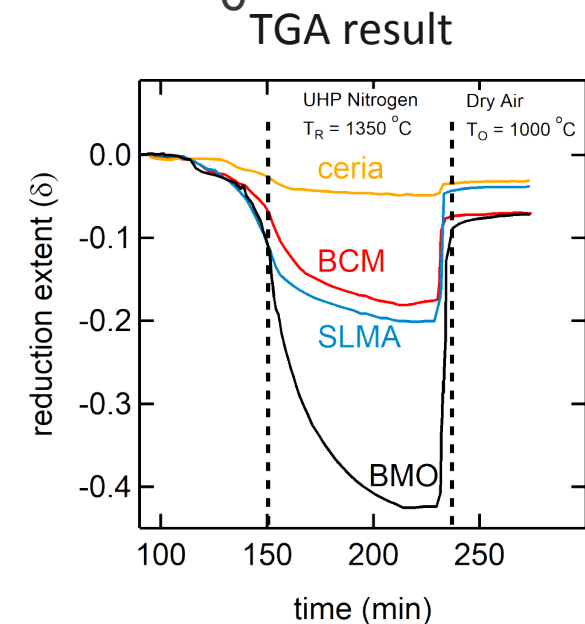
Redox Functionality Extremely Sensitive To MnO_6 Arrangements



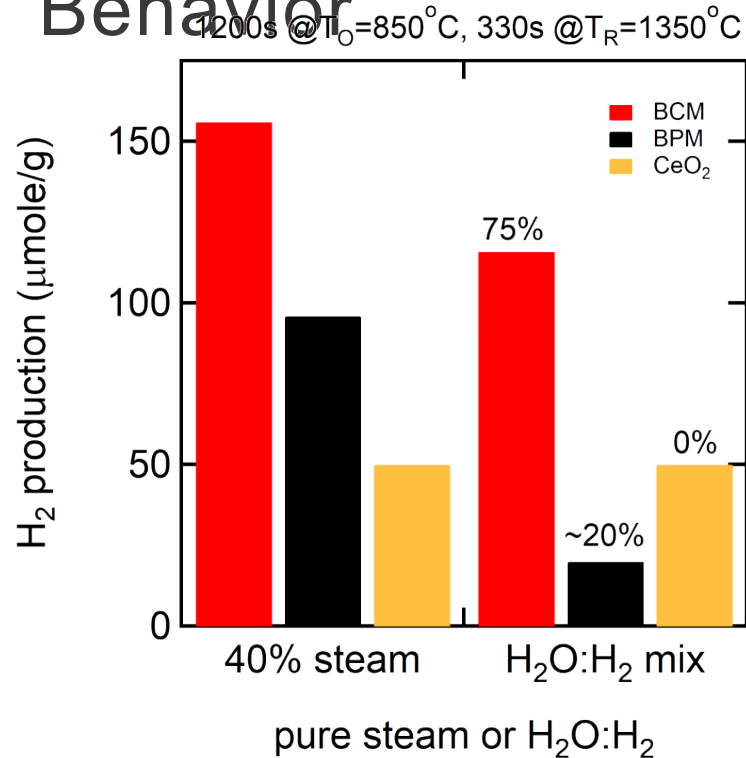
SMO, LMO, BMO, and BCO are ABO_3 perovskites that do not split water.

- MnO_6 in SMO, LMO, BMO, and SLMA form a 3-D interconnected network of corner-sharing octahedra.

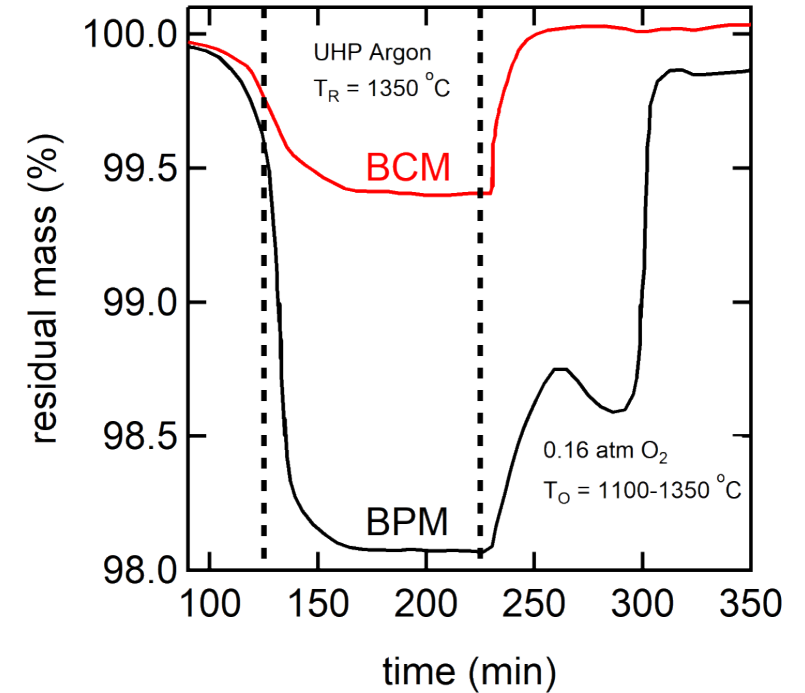
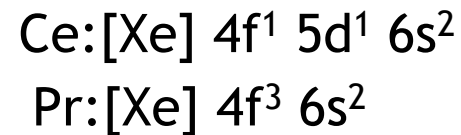
MnO_6 in BCM form a disconnected network of face-sharing octahedron trimers



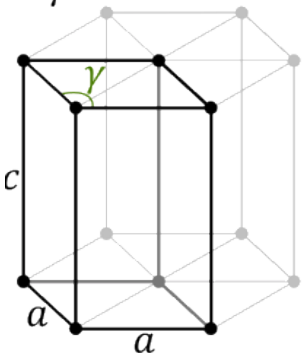
Swapping Pr For Ce Dramatically Changes Redox Behavior



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



#166 $R\bar{3}m$
 $\gamma = 120^\circ$



BXM (X = Ce, Pr) are structurally identical.

- Oxidation state $\text{Pr}^{+4} = \text{Ce}^{+4}$; $\Delta_{\text{radii}} \sim -2\%$
- Identical ground state crystallography, different electronic structure

O₂ redox capacity of BCM << BPM (measured by TGA).

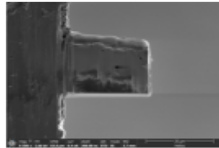
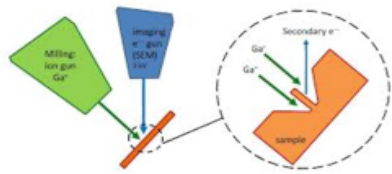
$\Delta\delta_{\text{ox}}$ for BPM << BCM in 40% H₂O and H₂O:H₂ mixture.

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

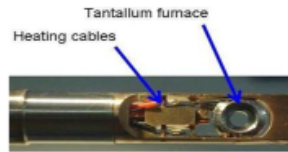


theory needed to resolve interrelationships between structure and performance

Precision FIB Cutout



GATAN Hot Stage



FIB precision sample prep.

- Orient FIB cutout along low index crystal planes

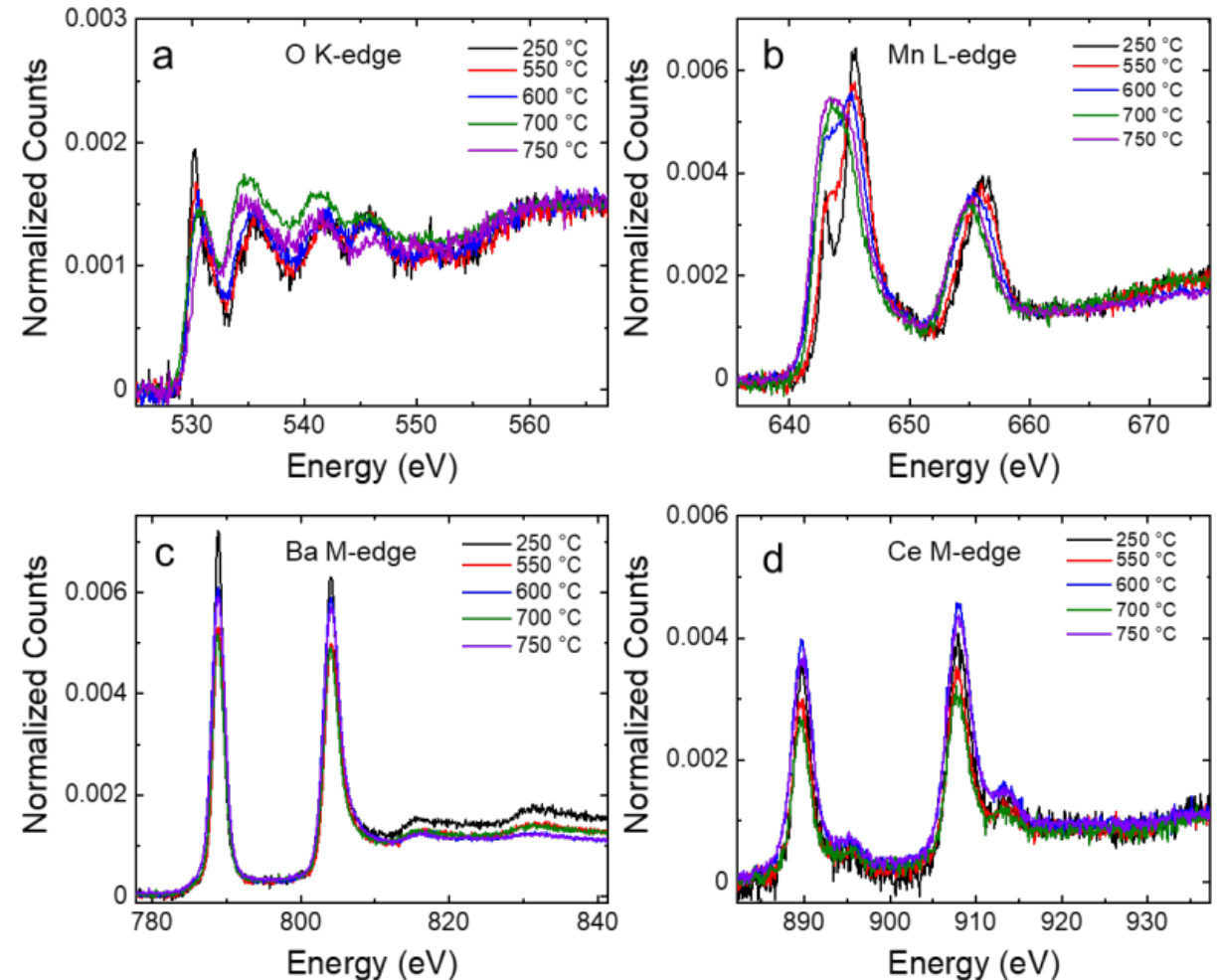
Heating rates $\gg 100$ °C per second.

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

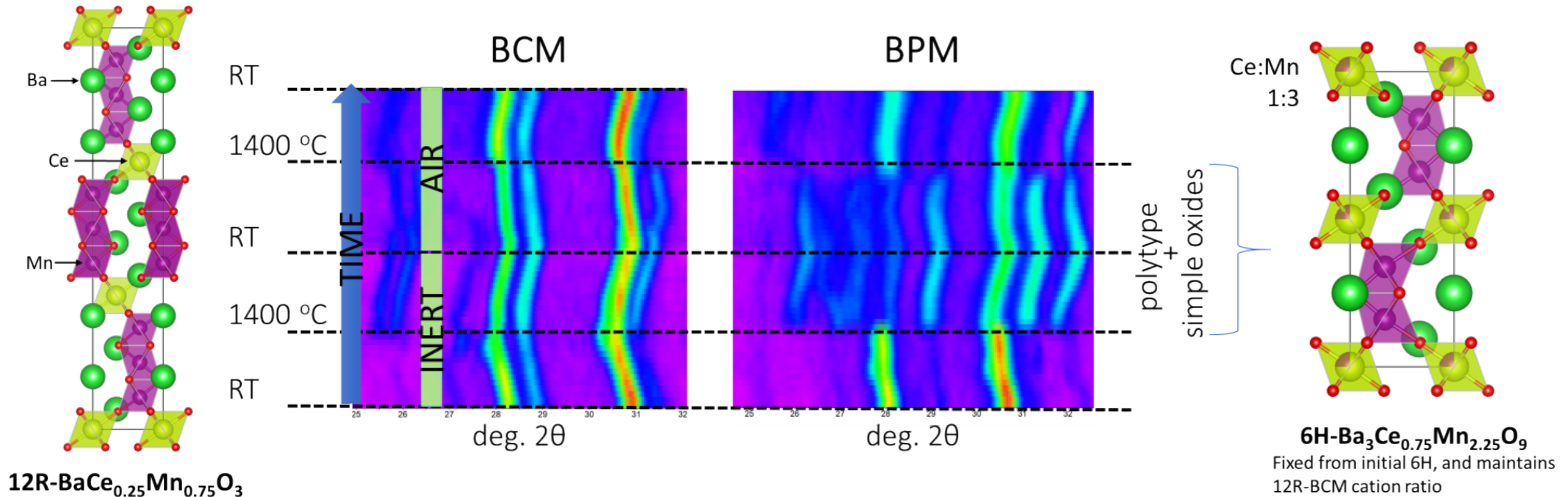
- Features in O K-edge and Mn L-edge change shape and intensity
- Coordination chemistry and Mn oxidation state change

Trend-wise loss of intensity in Ce electronic states.

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



HT-XRD Experiments Reveal Different Redox Crystallography Within BXM Family



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

- MnO₆ timer reduced to a dimer, partial occupancy of Mn on Ce site increases configurational entropy

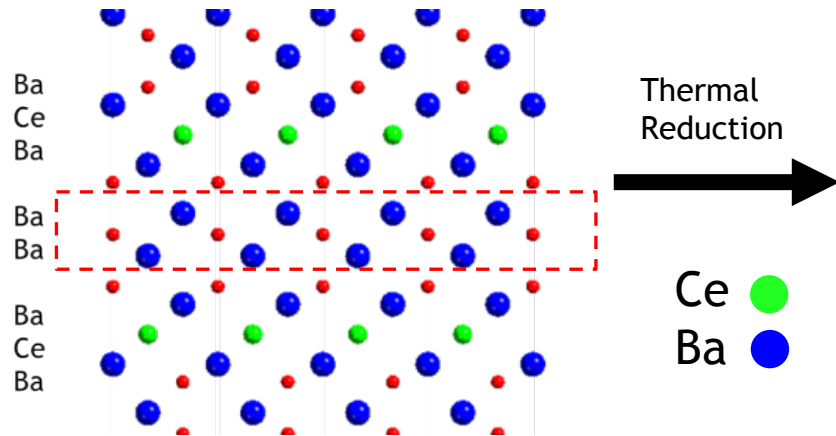
BPM clearly exhibits more complicated redox phase behavior.

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

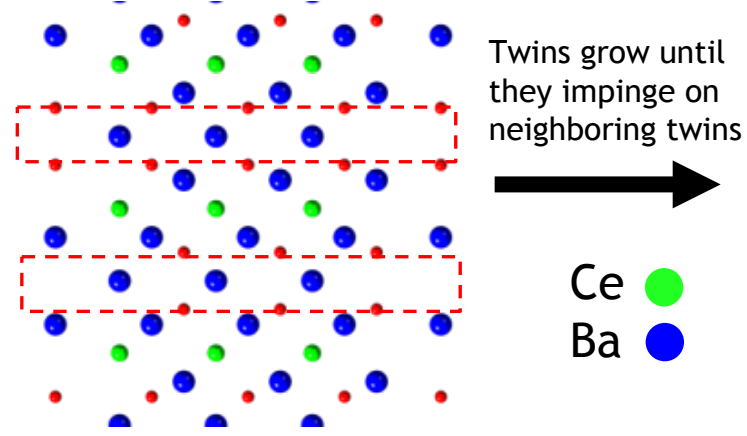
HR-STEM Reveals Structural Transformations In BCM



12R

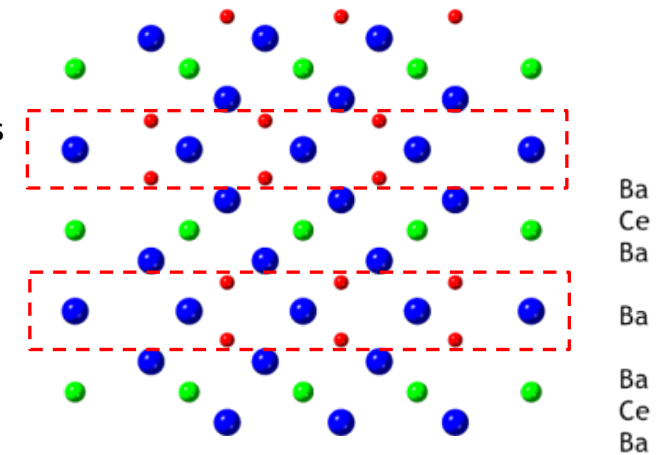


Twin

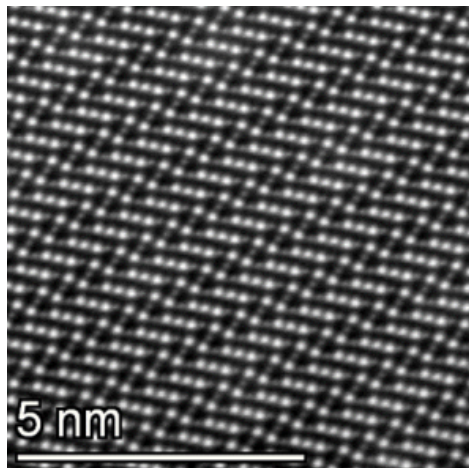


Twins grow until
they impinge on
neighboring twins

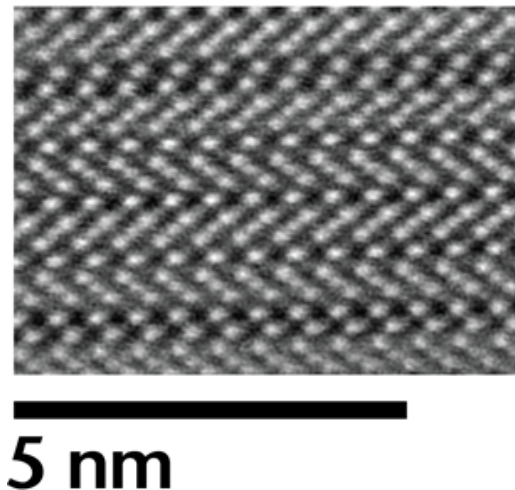
6H



Perfect crystal before cycling



Twins that develop
during reduction



6H structure resembles
repeated twins

- Calculations show that there is a reduced oxygen vacancy formation energy at the twins.
- The nucleation and growth of twinned regions could provide a mechanism for 6H formation.

1:3 Ce:Mn cation ratio in 12R is
maintained by 6H

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.

- Hot Stage HR/STEM with EELS
- Operando HT-XRD

Ba₄CeMn₃O₁₂ is the first perovskite material discovered that lowers thermal reduction temperature while maintaining “decent” $\Delta\delta_{\text{ox}}$ in H₂O:H₂ mixtures.

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

Substituting Pr for Ce dramatically degrades redox behavior.

- Isostructural variant with ONE additional valence electron
- Ba₄PrMn₃O₁₂ redox behavior is much more complex than Ce variant
- BPM is the perfect 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



Thank You

