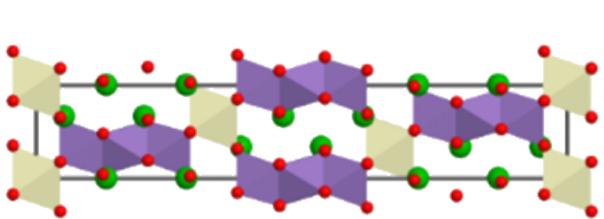




# Pathways to Renewable Fuels Using Concentrated Sunlight



*PRESENTED BY*

Anthony McDaniel

Spring MRS meeting, April 20, 2021

# Acknowledgements



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

### **Sandia National Laboratories**

- 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

### **Lawrence Livermore National Laboratory**

- Tadashi Ogitsu

## **Funding provided by DOE's Hydrogen and Fuel Cell Technologies Office**

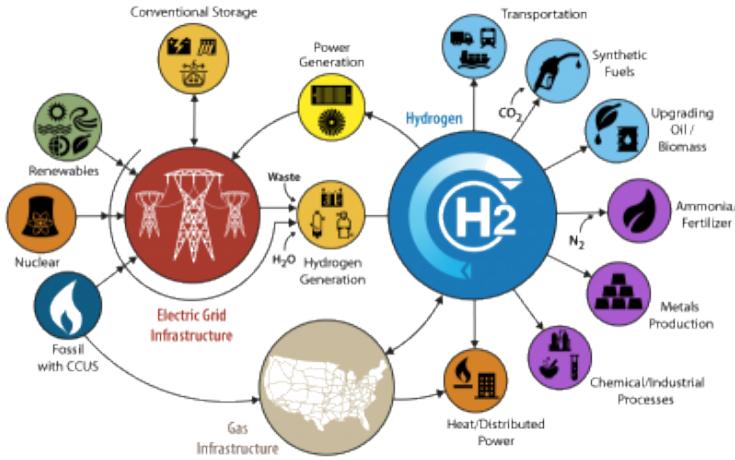


Office of  
ENERGY EFFICIENCY & RENEWABLE ENERGY

### 3 Hydrogen Is Large In The Google-verse

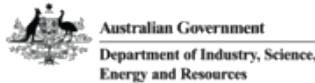


U.S. Department of Energy



**Global efforts underway to advance “green” hydrogen production.**

- Address KEY technology challenges to advance readiness level of large scale, low cost renewable H<sub>2</sub> production



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

### Australia's National Hydrogen Strategy



2021 Best Countries » See the Worst Countries for Racial Equality

Home / News / Business News

### German Government Agrees on National Hydrogen Strategy



China prepares multi-pronged hydrogen strategy

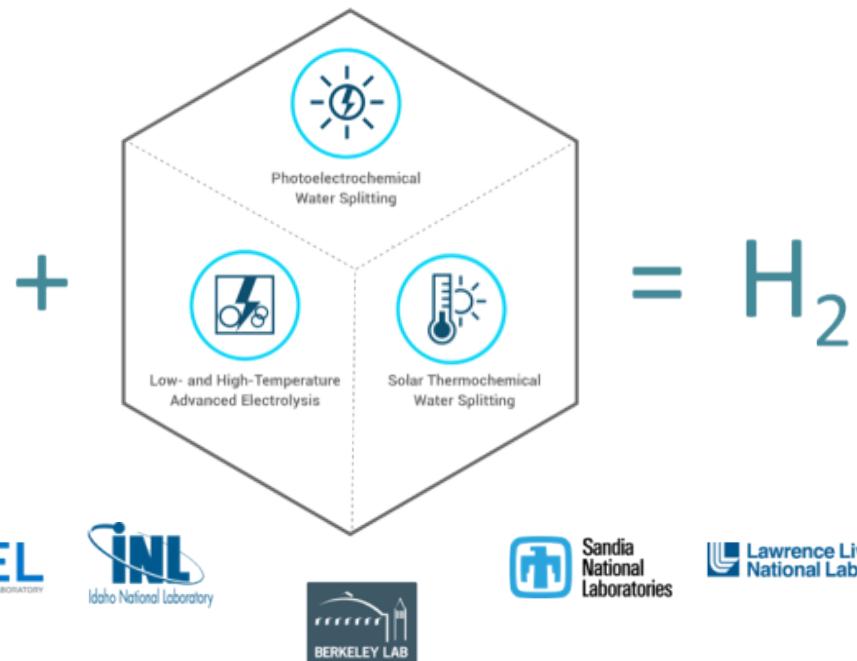
# Hydrogen As Far As The Eye Can See

11 Labs

10 Companies

39 Universities

2 Funding Agencies



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

- Electrolysis, photoelectrochemical, thermochemical, microbial

**DOE's HydroGEN Advanced Water Splitting Materials consortium (H<sub>2</sub>AWSM):**

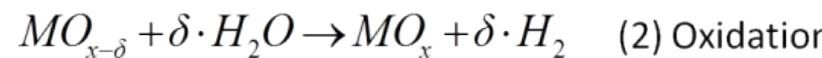
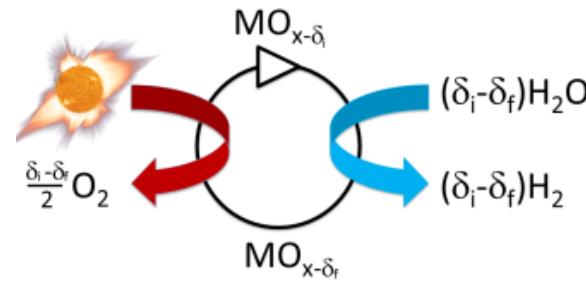
- Enables access to 5 core National Laboratories through collaborations with awarded projects
- Experimental facilities, computational resources, subject matter experts

# Solar Thermochemical Water Splitting Is A Simple Concept: Heat + H<sub>2</sub>O In, H<sub>2</sub> + O<sub>2</sub> Out

R. Petet, 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).



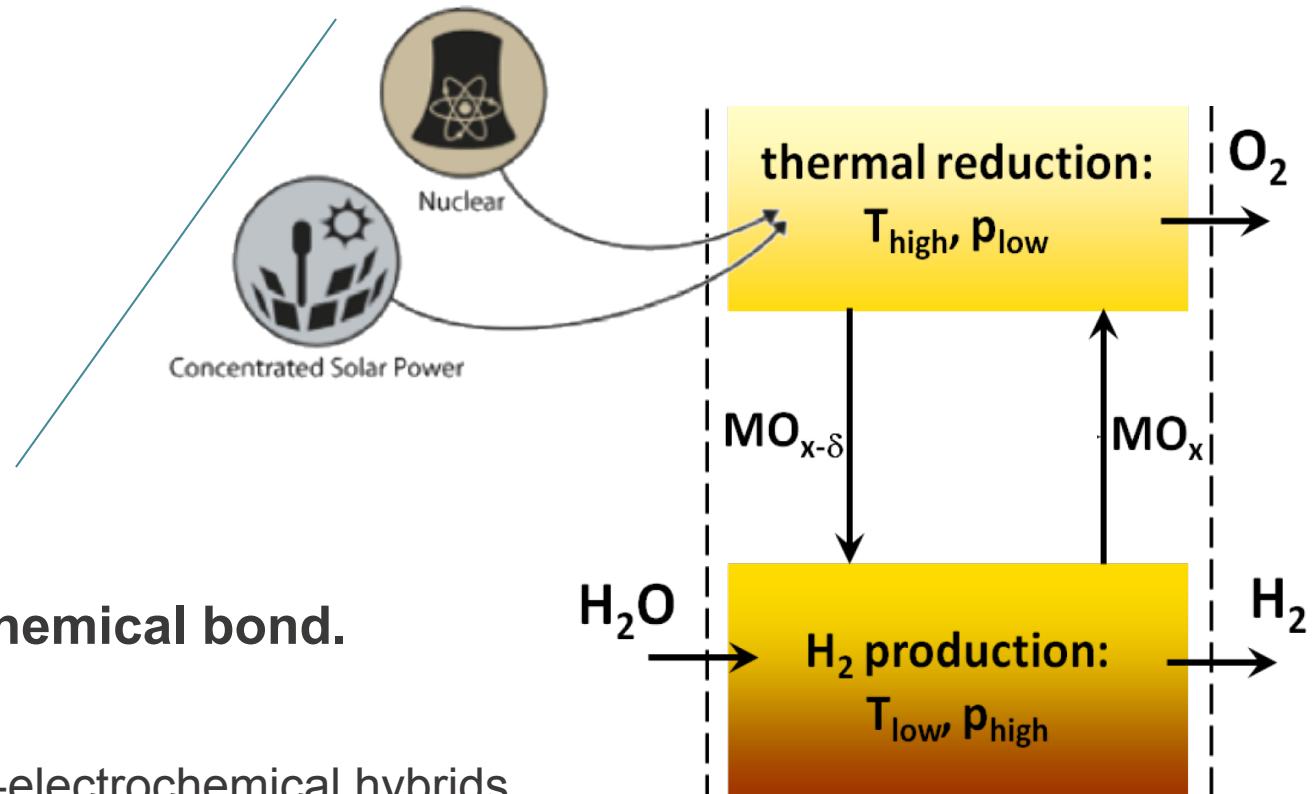
**Direct storage of solar energy in a chemical bond.**

**Many hundred cycles proposed.**

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

**DOE's HydroGEN Advanced Water Splitting Materials (H<sub>2</sub>AWSM) consortium is focused on two-step, non-volatile MO<sub>x</sub>.**

- [h2awsm.org](http://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 (H<sub>2</sub>AWSM)

## **An interesting story about layered perovskites.**

- Ba<sub>4</sub>CeMn<sub>3</sub>O<sub>12</sub> and Ba<sub>4</sub>PrMn<sub>3</sub>O<sub>12</sub> 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.

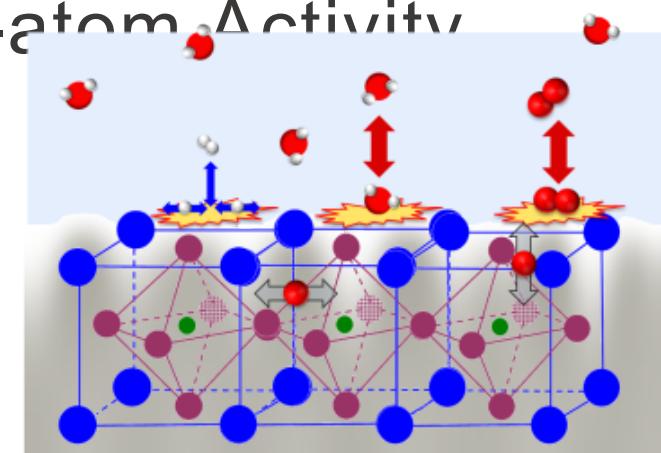
- O-atom “harvested” from  $H_2O$  not Air
- Bulk phenomena largely govern O-atom exchange with environment

## 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

### Fe<sup>2+</sup>/Fe<sup>3+</sup> (unsupported) systems:

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

Moderate  $T_R < 1400$  °C

WS-UNTESTED in H<sub>2</sub>O:H<sub>2</sub> atm

## perovskite

### TM<sup>2+</sup>/TM<sup>3+</sup>/TM<sup>4+</sup> (Mn, Fe, Co) systems:

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

Low-to-moderate  $T_R < 1400$  °C

WS-PROMISING in H<sub>2</sub>O:H<sub>2</sub> atm

## fluorite

### Ce<sup>3+</sup>/Ce<sup>4+</sup> systems:

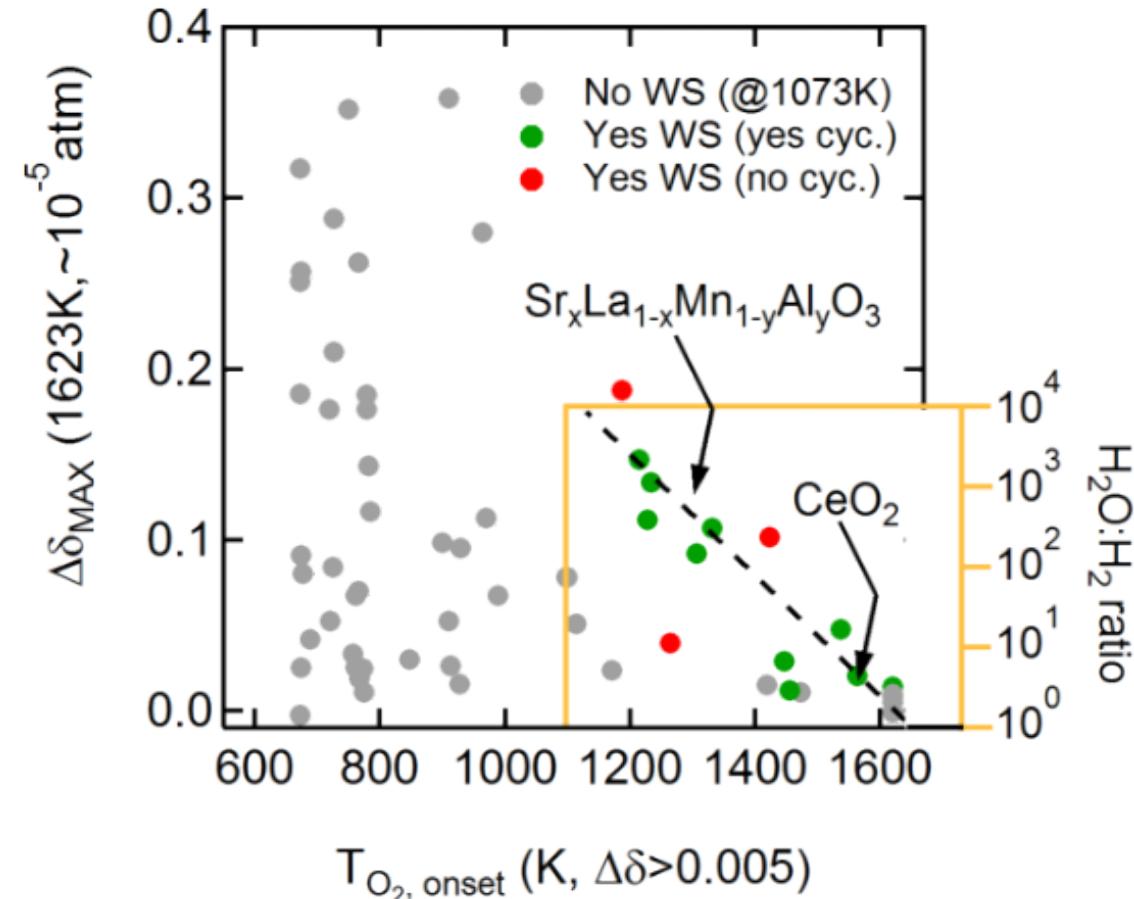
Low redox capacity ( $\Delta\delta < 0.08$ )

High  $T_R > 1500$  °C

WS-“BEST IN CLASS” in H<sub>2</sub>O:H<sub>2</sub> atm

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

WS inactive at  $T_{O_2, onset} < 1100$  °C  
high H<sub>2</sub>O:H<sub>2</sub> ratio at  $T_{O_2, onset} < 1400$  °C



# $H_2$ AWSM Projects Are Fulfilling The Vision Of The Consortium/EMN Model (HPC, ML, Theory Guided Material Design)



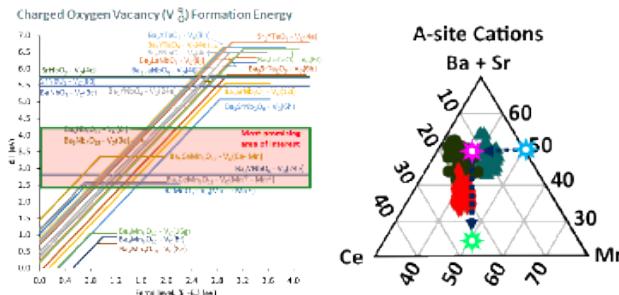
## Found RP phases that modify redox thermo.

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



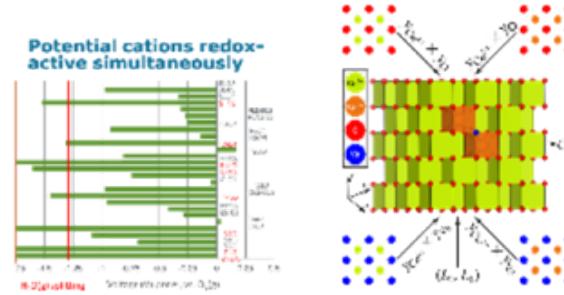
## Use machine-learned models coupled to DFT to discover new redox materials.

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



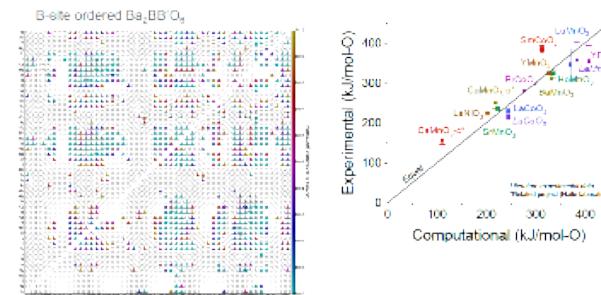
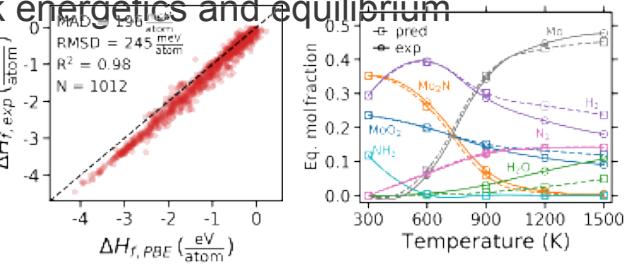
## Incorporate second redox active sublattice to modify thermo.

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



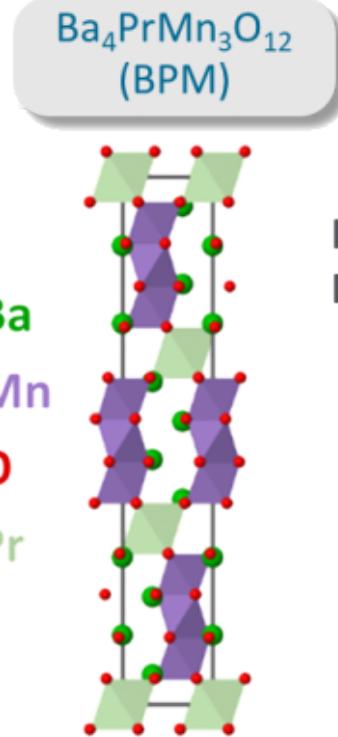
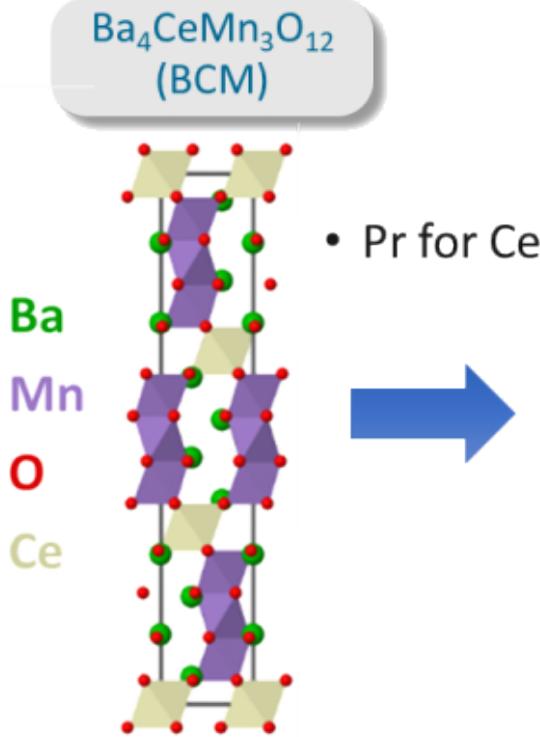
## Use high-throughput Density Functional Theory to discover new redox materials.

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



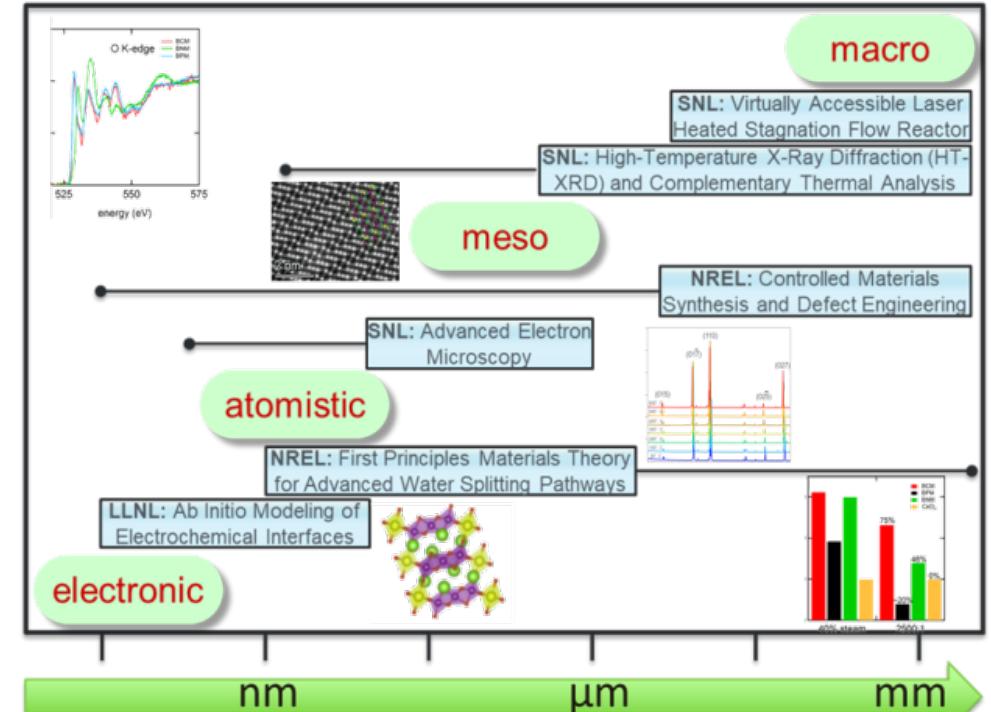
- One dozen *potential* compounds have been “discovered” using HPC, ML, and DFT
- Water splitting functionality has been verified in several of these predicted formulations
- Validated high-throughput computational tools are now in place to rapidly expand the known material space

# An Interesting Story About Layered Perovskites



Important  
Interrelationships:

- electronics
- defects
- structure
- performance

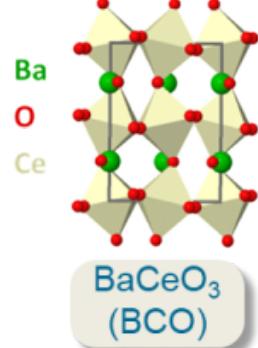
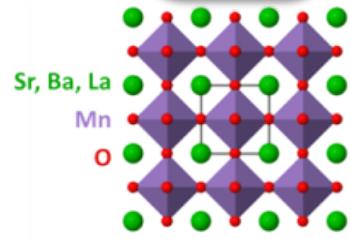


## Objectives:

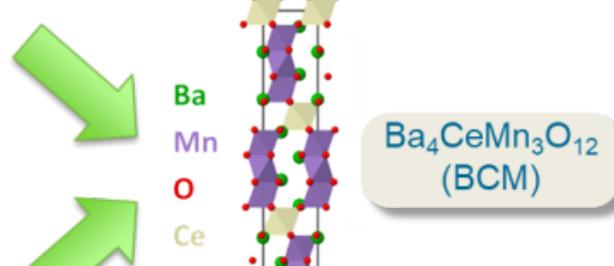
- Discover and synthesize model perovskite system
- Develop and exercise multi-length-scale observation platforms and methods
- Apply first principles theory to derive atomistic understanding of water splitting activity

# Redox Functionality Extremely Sensitive To $\text{MnO}_6$ Arrangements

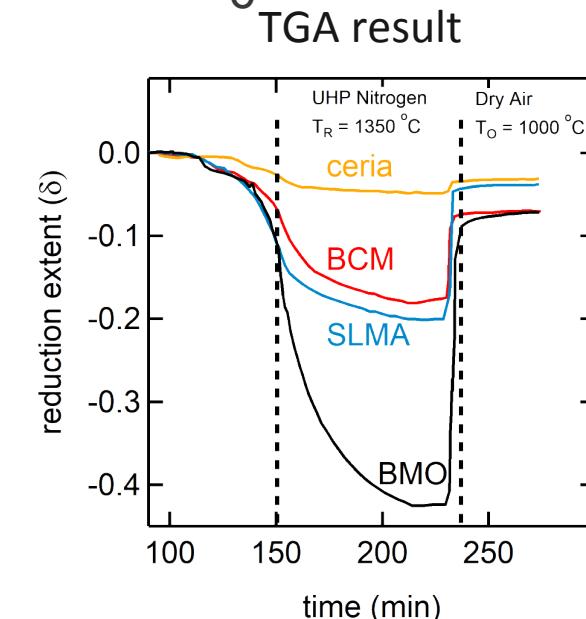
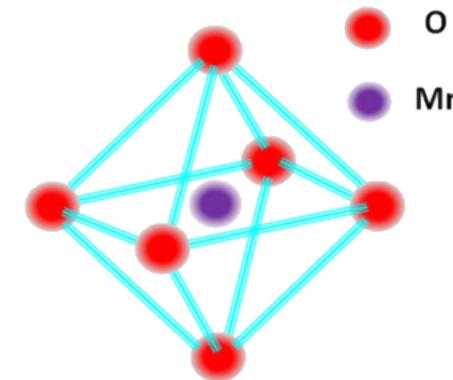
$\text{SrMnO}_3$   
 $\text{LaMnO}_3$   
 $\text{BaMnO}_3$   
 ("A"MO)



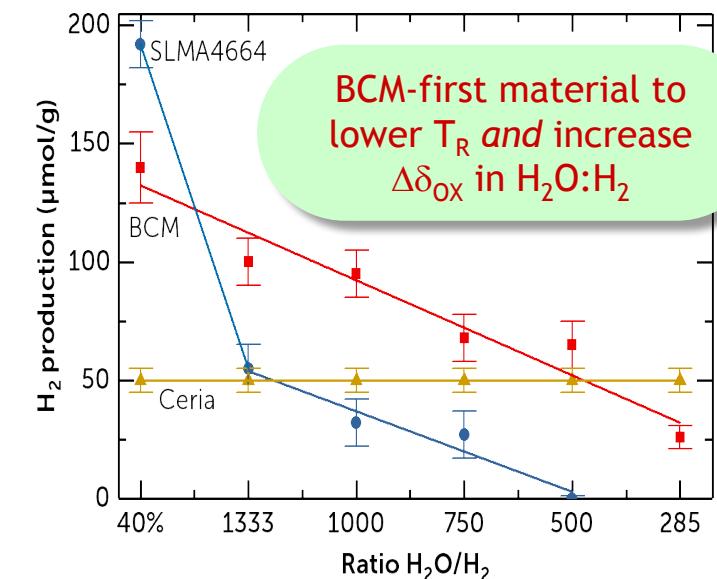
- Mix SMO and LMO get  $\text{ABO}_3$  with  $\text{Mn}^{3+}/4+$
- $\text{Al}^{3+}$  added to improve WS behavior



- Mix BMO and BCO get complex structure with  $\text{Mn}^{4+}$
- Modifications to improve WS behavior unexplored



**LSFR result**



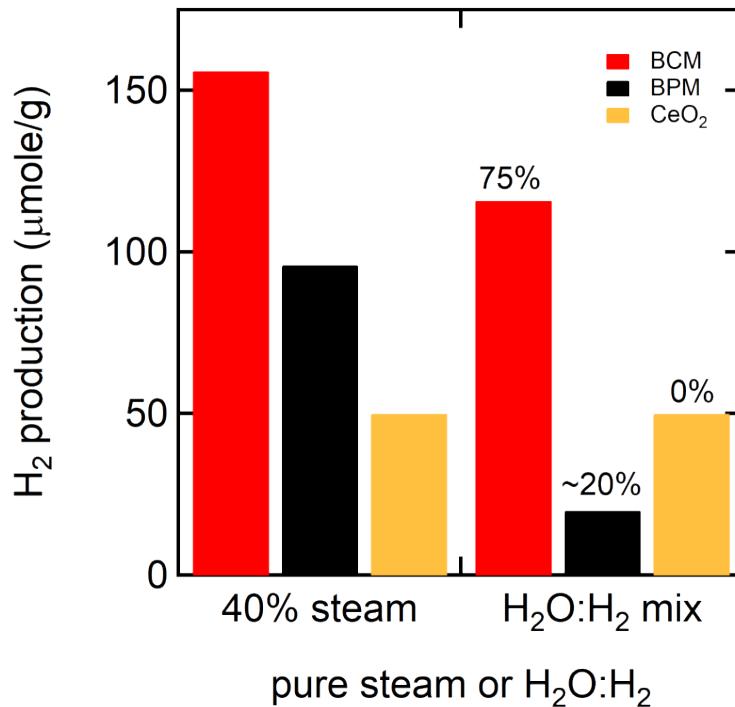
**SMO, LMO, BMO, and BCO are  $\text{ABO}_3$  perovskites that do not split water.**

- $\text{MnO}_6$  in SMO, LMO, BMO, and SLMA form a 3-D interconnected network of corner-sharing octahedra.

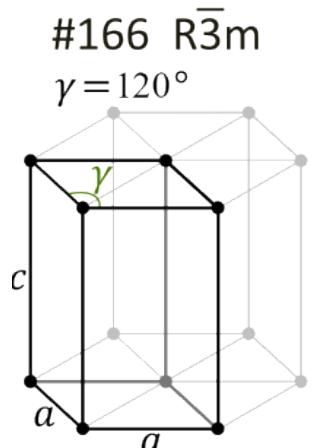
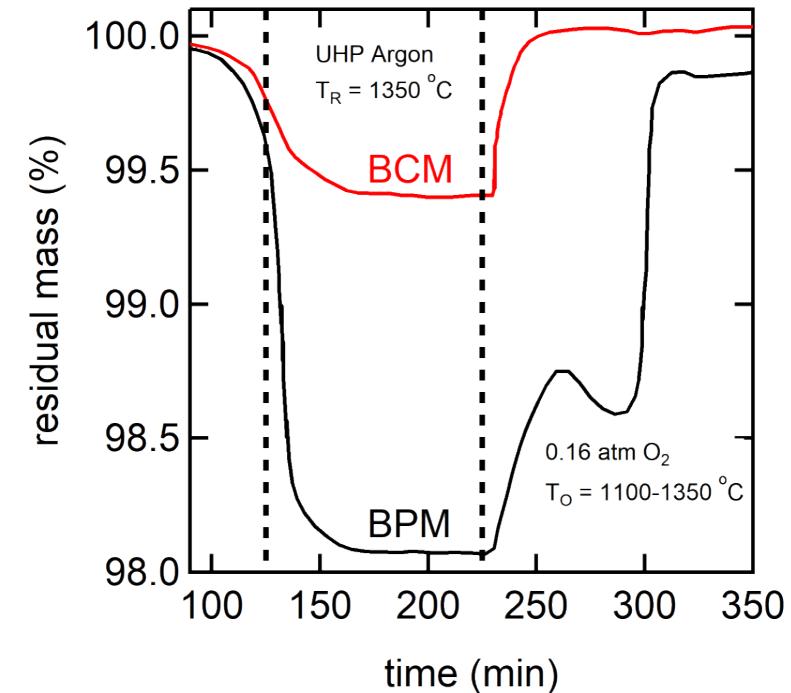
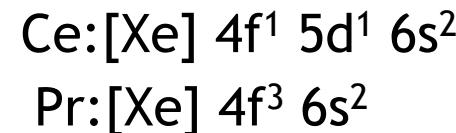
**$\text{MnO}_6$  in BCM form a disconnected network of face-sharing octahedron trimers**

# Swapping Pr For Ce Dramatically Changes Redox Behavior

1200s @  $T_O = 850^\circ\text{C}$ , 330s @  $T_R = 1350^\circ\text{C}$



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



**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

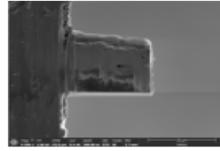
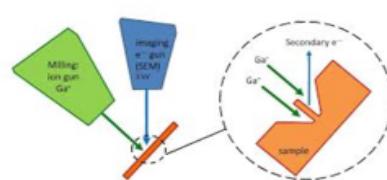
**O<sub>2</sub> redox capacity of BCM << BPM (measured by TGA).**

$\Delta\delta_{\text{ox}}$  for BPM << BCM in 40% H<sub>2</sub>O and H<sub>2</sub>O:H<sub>2</sub> mixture.

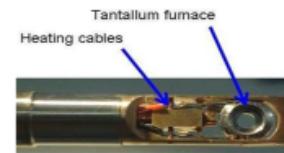
# Hot Stage In Situ Vacuum Reduction of BCM: Electron Energy Loss Spectroscopy (EELS) Probes Local Electronic States



Precision FIB Cutout



GATAN Hot Stage



theory needed to resolve interrelationships between structure and performance

## FIB precision sample prep.

- Orient FIB cutout along low index crystal planes

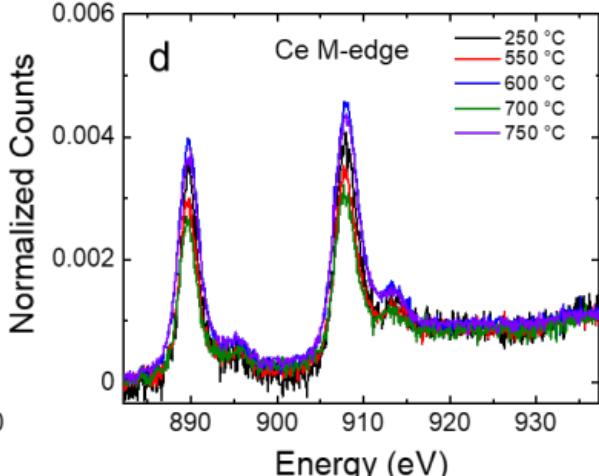
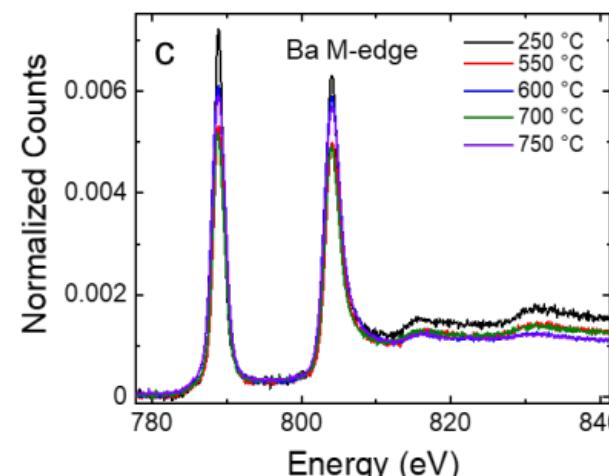
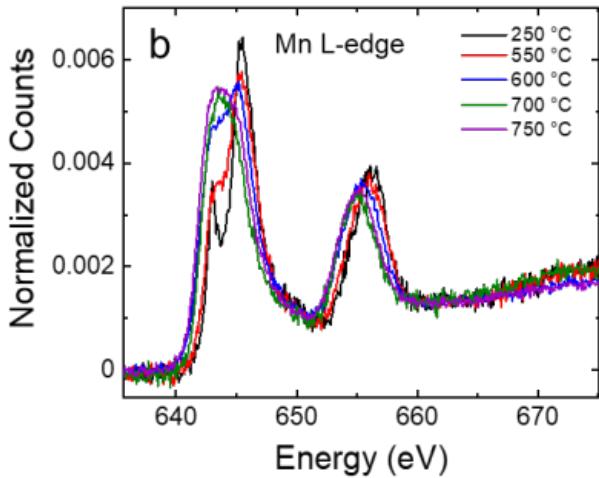
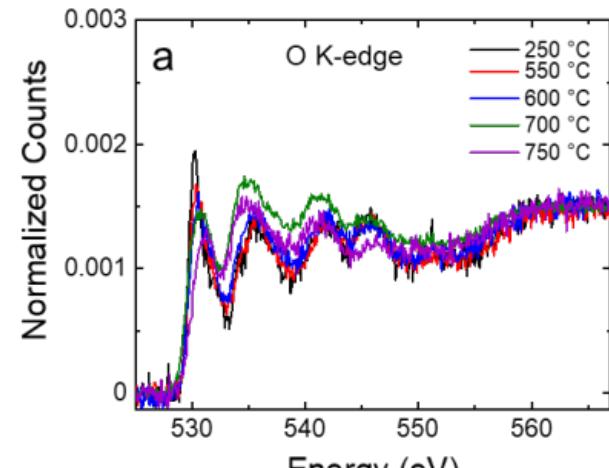
## Heating rates $>> 100 \text{ }^{\circ}\text{C}$ per second.

## Clear and obvious changes to electronic structure local to $\text{MnO}_6$ manifold in BCM.

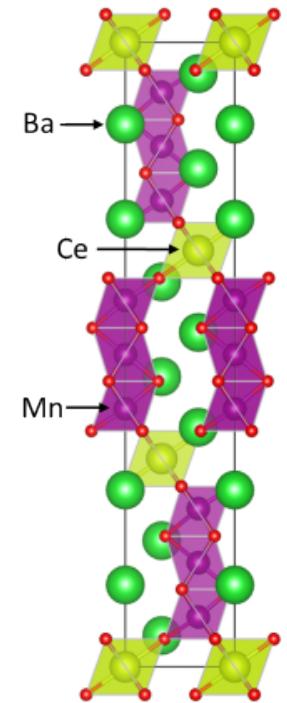
- Features in O K-edge and Mn L-edge change shape and intensity
- Coordination chemistry and Mn oxidation state change

## Trend-wise loss of intensity in Ce electronic states.

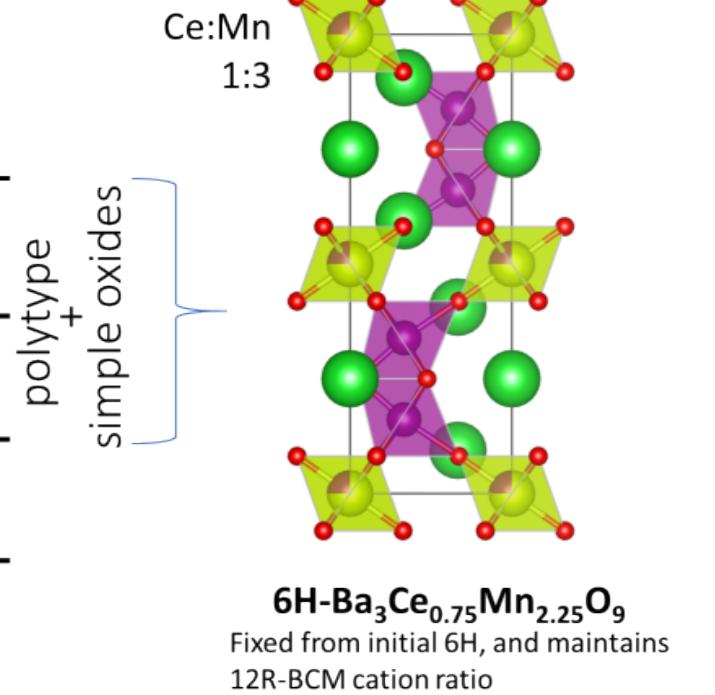
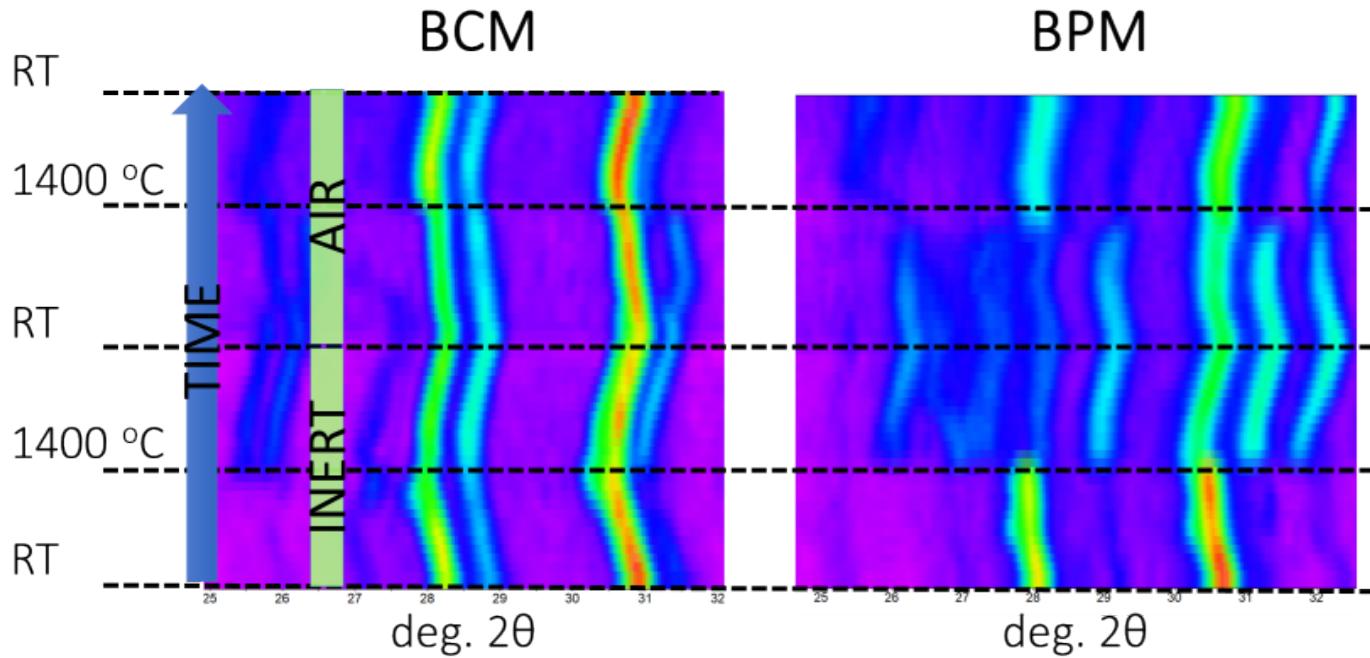
- Unclear to what extent O 2p – Ce 4f manifold



# HT-XRD Experiments Reveal Different Redox Crystallography Within BXM Family



12R- $\text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3$



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

- MnO<sub>6</sub> timer reduced to a dimer, partial occupancy of Mn on Ce site increases configurational entropy

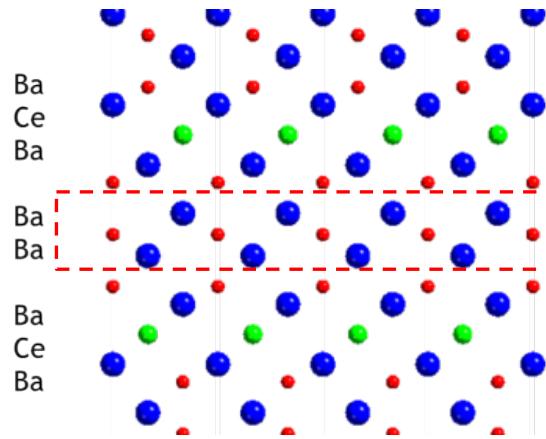
**BPM clearly exhibits more complicated redox phase behavior.**

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

# HR-STEM Reveals Structural Transformations In BCM



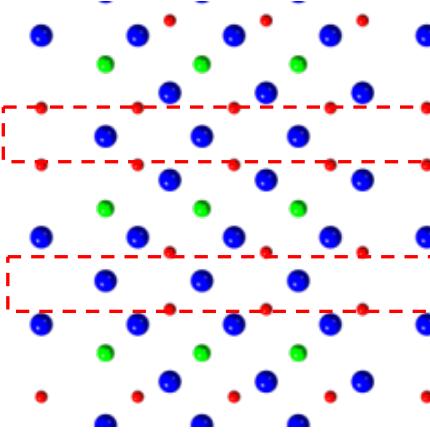
## 12R



Thermal  
Reduction

Ce  
Ba

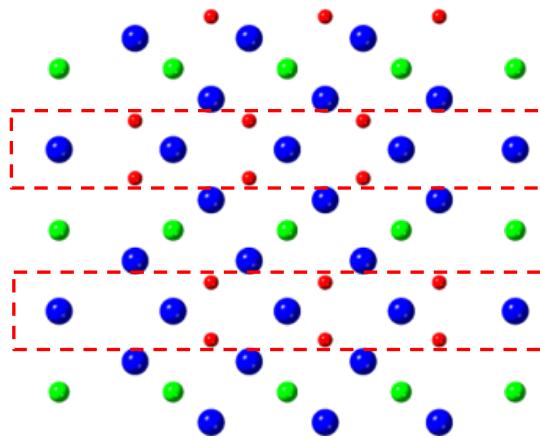
## Twin



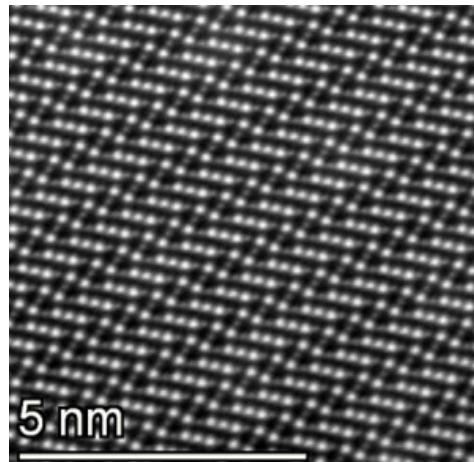
Twins grow until  
they impinge on  
neighboring twins

Ce  
Ba

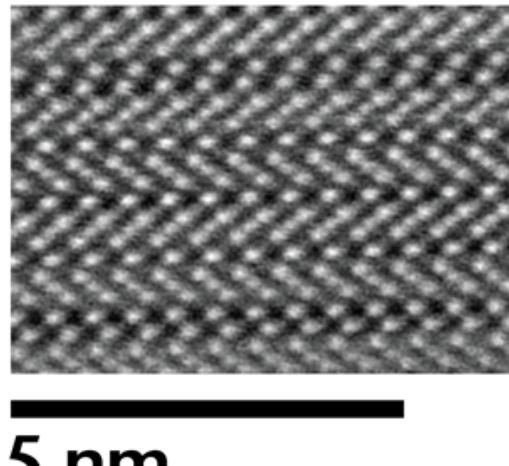
## 6H



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 mechanisms 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

$\text{Ba}_4\text{CeMn}_3\text{O}_{12}$  is the first perovskite material discovered that lowers thermal reduction temperature while maintaining “decent”  $\Delta\delta_{\text{ox}}$  in  $\text{H}_2\text{O}:\text{H}_2$  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
- $\text{Ba}_4\text{PrMn}_3\text{O}_{12}$  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

