SAND2021-12736C

Uniting Experiment and Computational Modeling to Elucidate Structure-Property Relationships of Water Splitting Materials

240th Electrochemical Society Conference

Jamie Trindell[1], Sarah Shulda[2], Robert Bell[2], James Park[3], Eric Coker[3], Subhayan Roychoudhury[4], David Prendergast[4], David Ginley[2], Anthony McDaniel[1,4], Joshua Sugar[1]

[1] Sandia National Laboratory, Livermore CA

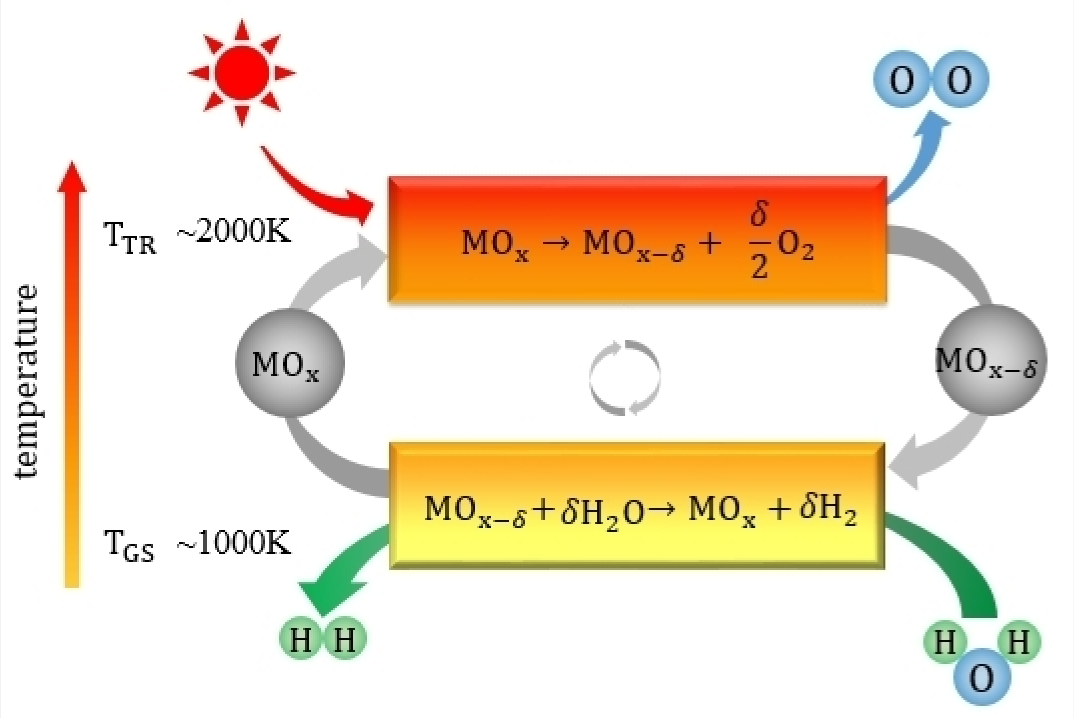
[2] National Renewable Energy Laboratory, Golden CO

[3] Sandia National Laboratory, Albuquerque NM

[4] Molecular Foundry, Berkeley, CA

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Solar Thermochemical Hydrogen (STCH) Production



High-conversion water splitting (HCWS)
A yield ~20% at H_2O/H_2 < 10 is very desirable

Two-step cycle:

1. High temp reduction → O_2
2. Low-temp oxidation in steam → H_2

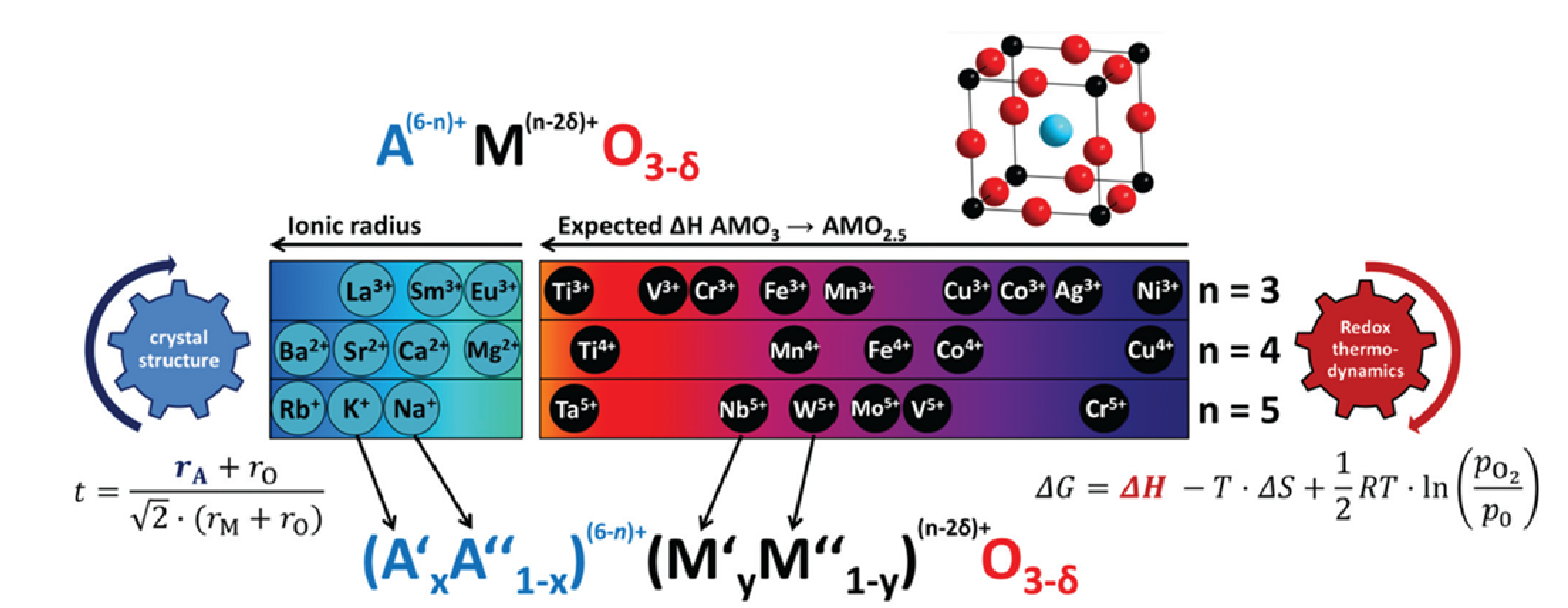
Key factors in material design:

1. Stability
2. Redox capacity ($\Delta\delta$)
   - oxygen vacancy formation energy (E_V)
3. H_2 yield (mole H_2/mole O-atom in solid)
   - ease of reoxidation in steam

Practical limits of STCH materials?

- Temp required for reduction
- H_2-tolerance during oxidation

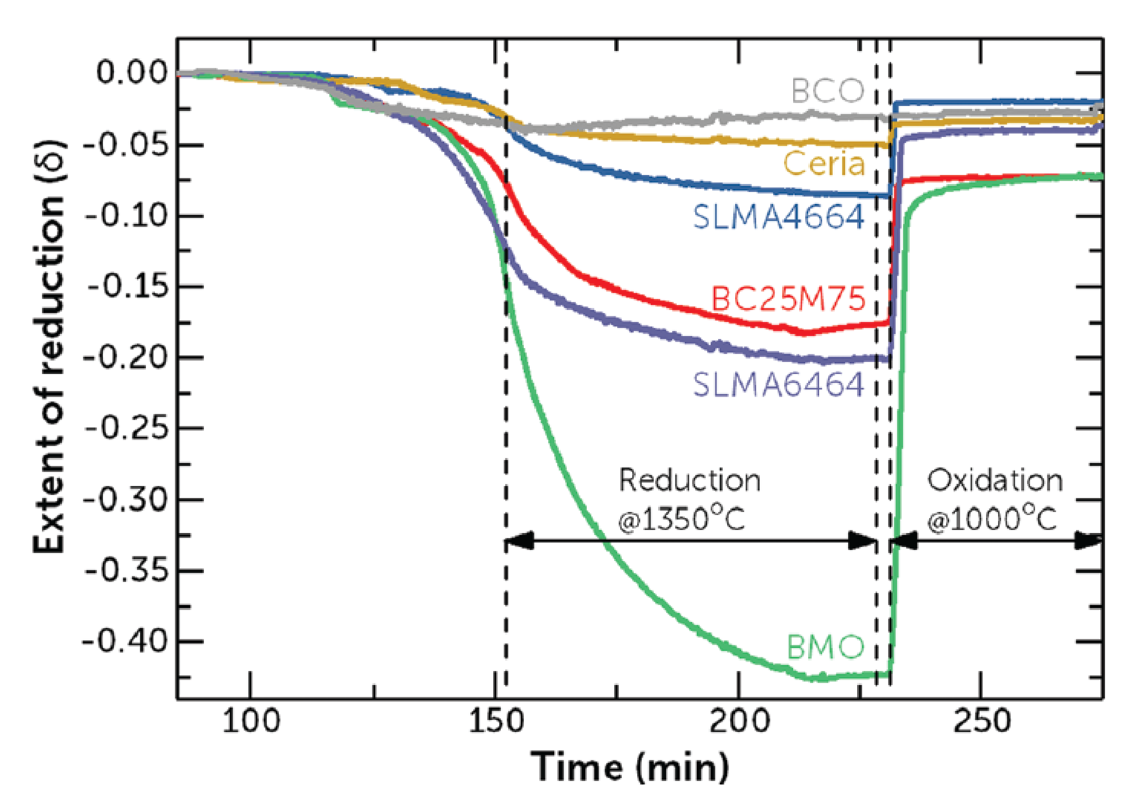
STCH Production Materials : Perovskites

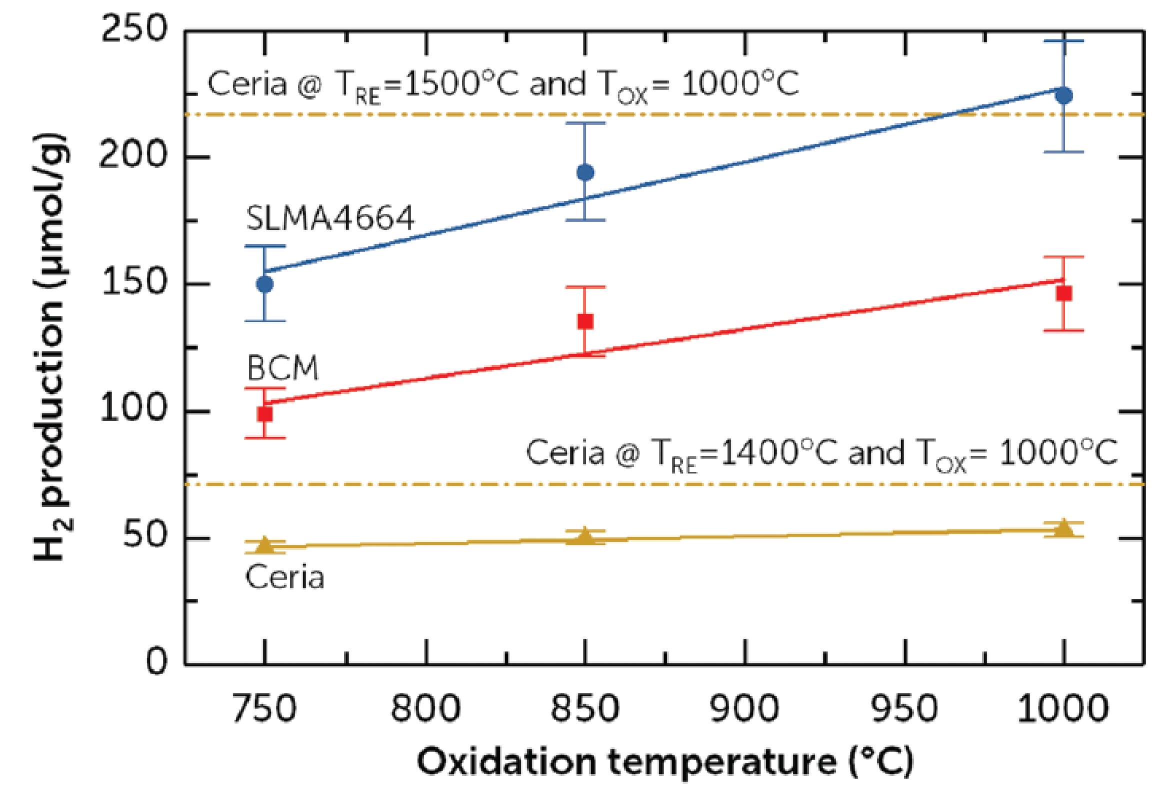


- CeO_2 is the 'benchmark' STCH cycle material
  - × T_r = 1500°C
  - ✓ Retains performance in H_2O/H_2 environment
- $Sr_xLa_{1-x}Mn_yAl_{1-y}O_3$ is the highest performing perovskite to-date
  - ✓ T_r = 1350°C
  - × Loses performance in H_2O/H_2 environment

How do we improve material design?
1. Extensive materials characterization
2. Computational modeling

$BaCe_{0.25}Mn_{0.75}O_3$ (BCM)



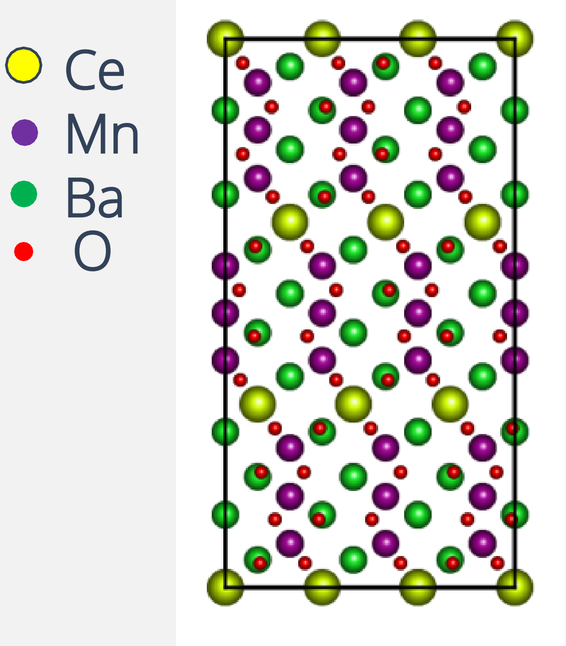


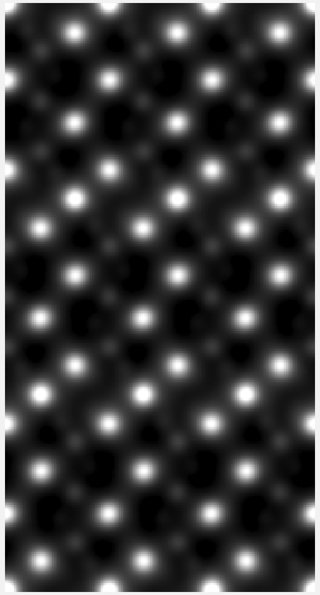
CeO_2 (Ceria)
$BaCeO_x$ (BCO)
$BaMnO_x$ (BMO)
SrLaMnAlO_x (SLMA)

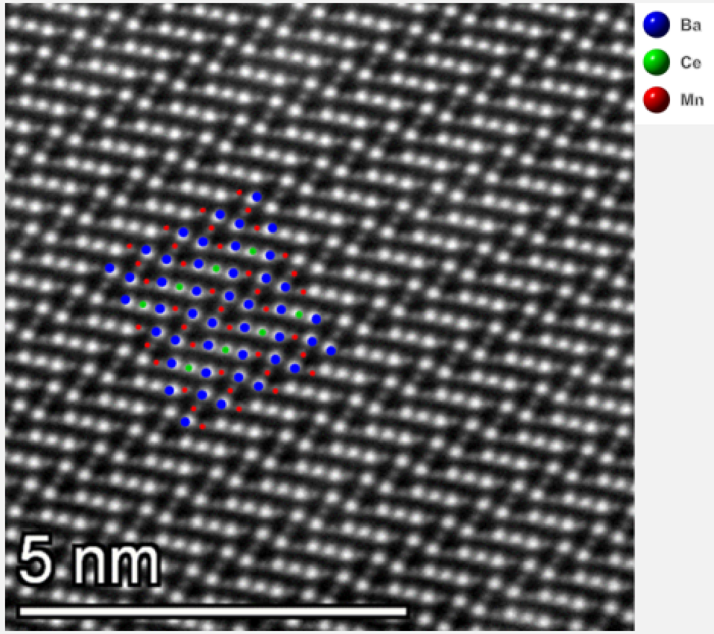
Advantages of BCM :
- exhibits fast kinetics
- lower reduction temperature relative to CeO_2
- higher tolerance for H_2 during re-oxidation than SLMA

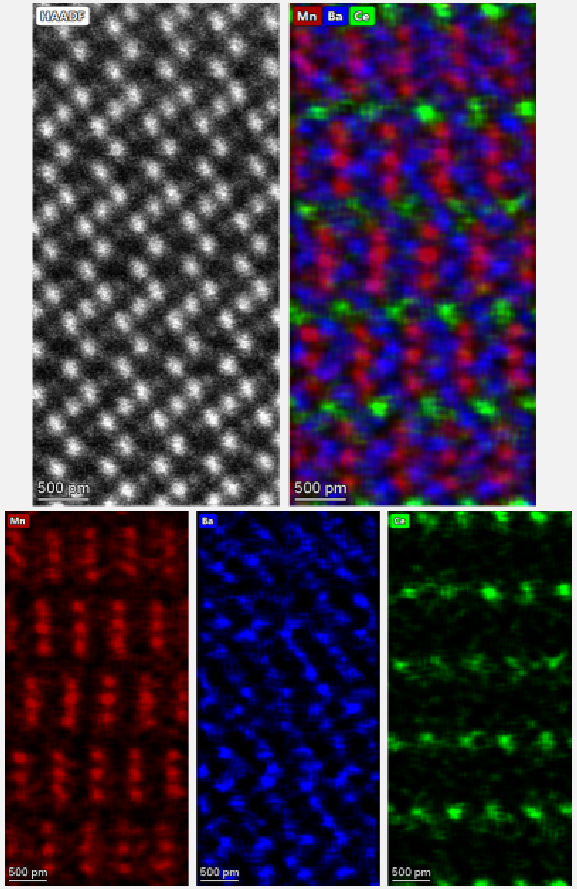
Energy Environ. Sci., **2019**, *12*, 1369.

$BaCe_{0.25}Mn_{0.75}O_3$: 12R Polytype



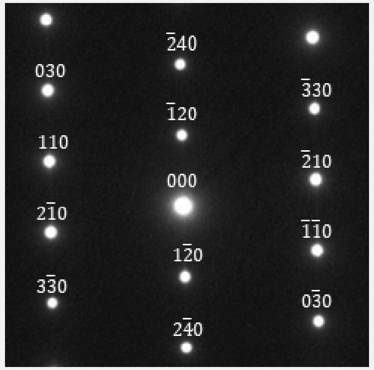


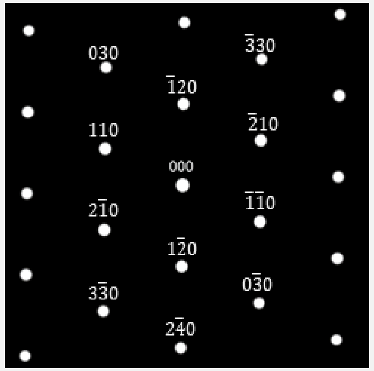




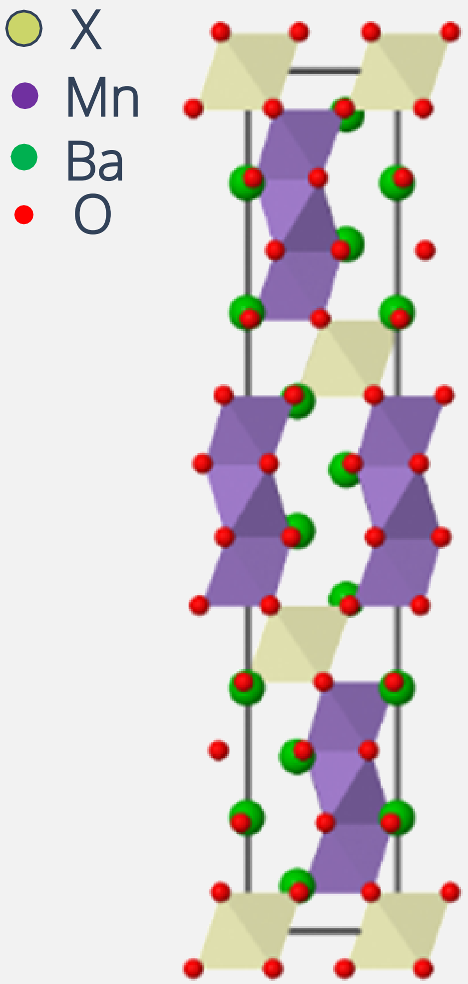
- Characterization Methods :

1. Thermogravimetric Analysis (TGA)
2. Synchrotron X-ray Diffraction (XRD)
3. X-ray Absorption Spectroscopy (XAS)
4. Selected-area electron diffraction (SAED)
5. Energy dispersive spectroscopy (EDS)
6. Electron energy loss spectroscopy (EELS)
7. Atomic-resolution imaging





$BaX_{0.25}Mn_{0.75}O_3$ (BXM; X = Ce, Pr, Nb)

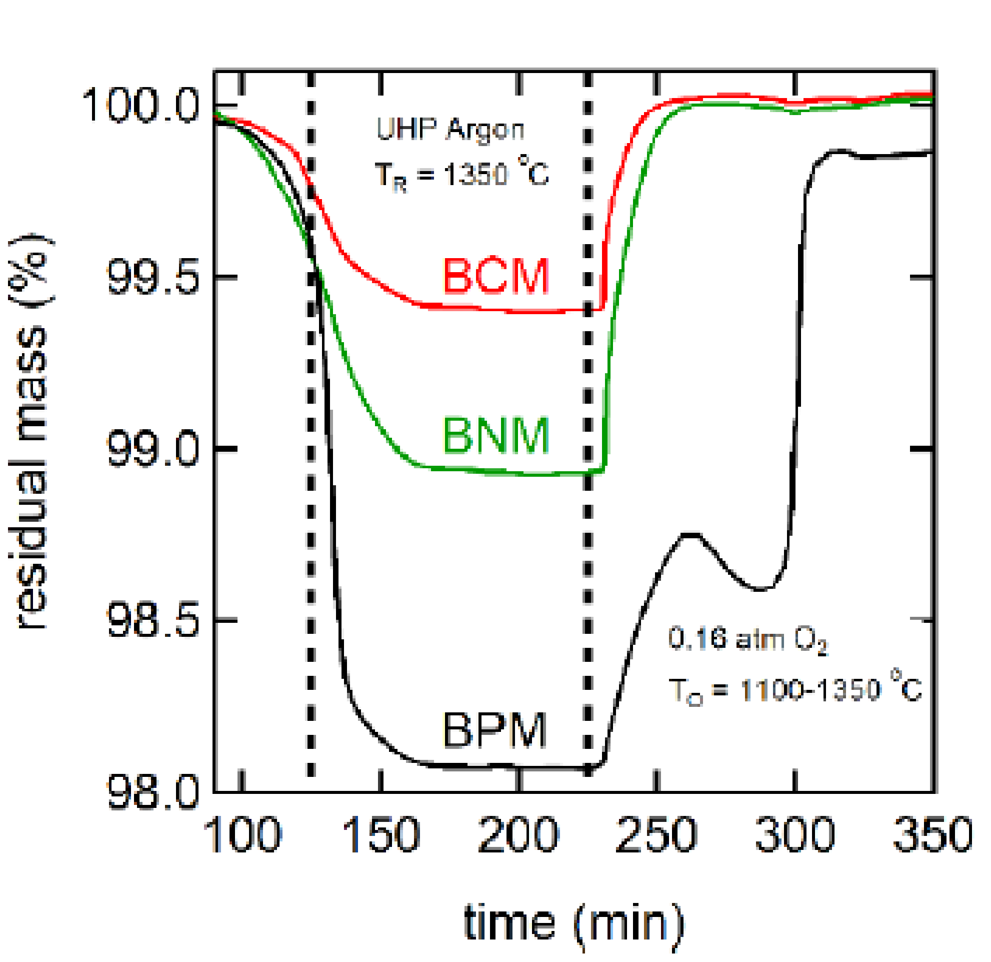


12R

- Substitution of Ce results in similar 12R polytype with different redox capacities:

BCM < BNM < BPM

Ce = [Xe] $4f^2 6s^2$
Pr = [Xe] $4f^3 6s^2$
Nb = [Kr] $4d^4 5s^1$

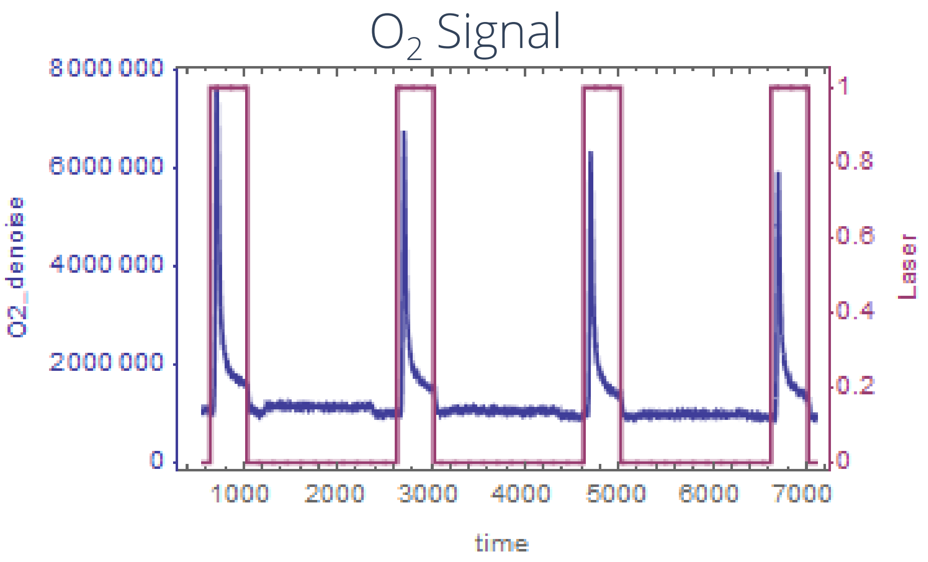


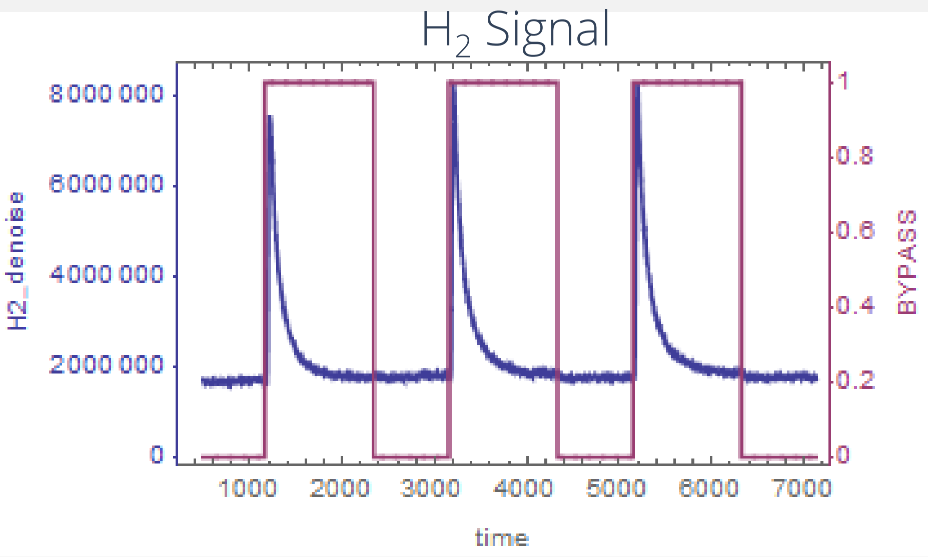
Experimental Conditions

1. WS in 40% H_2O
2. WS in $H_2O:H_2$ 1333:1

<u>One Cycle</u>

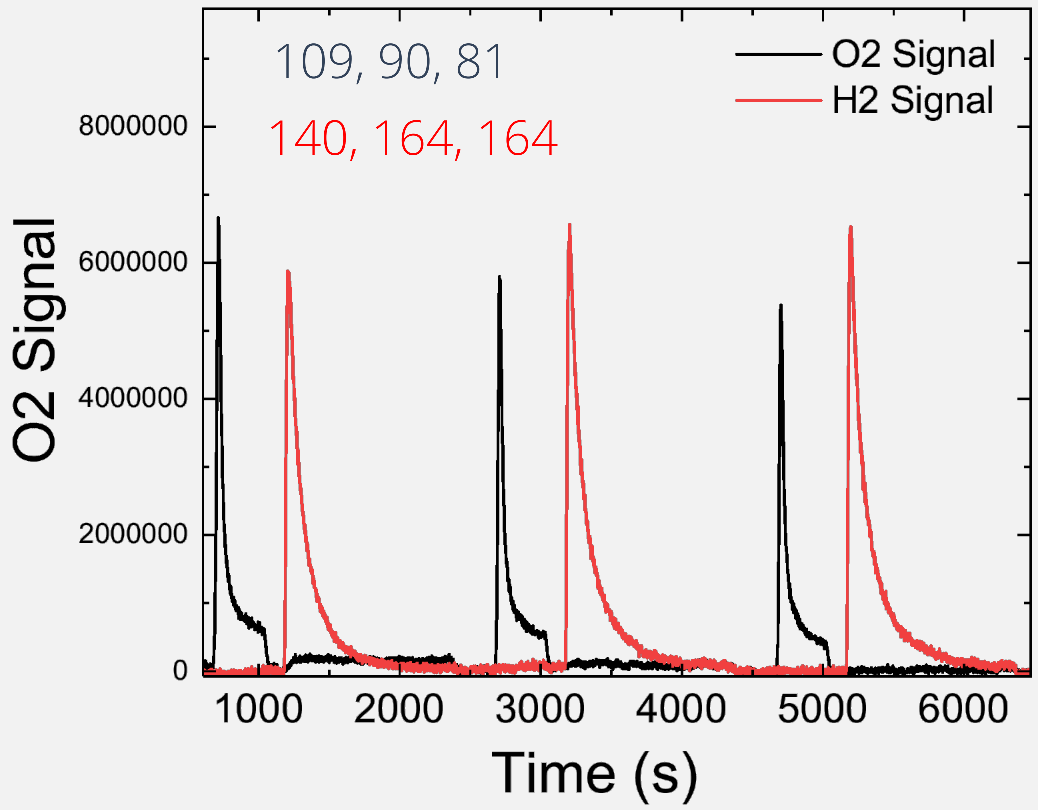
1. Reduction
   T_r = 1350°C for 330s
2. Oxidation
   T_o = 850°C for 1200s



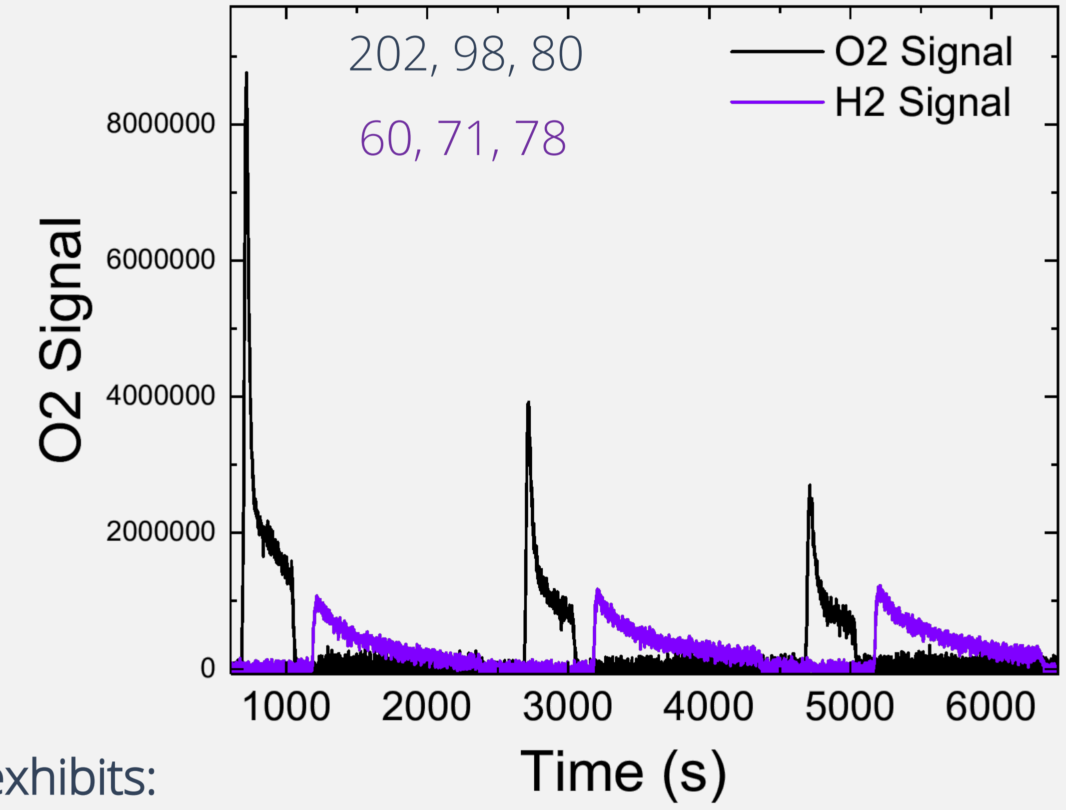


H_2 Production in 40% H_2O : BCM vs. BPM

BCM



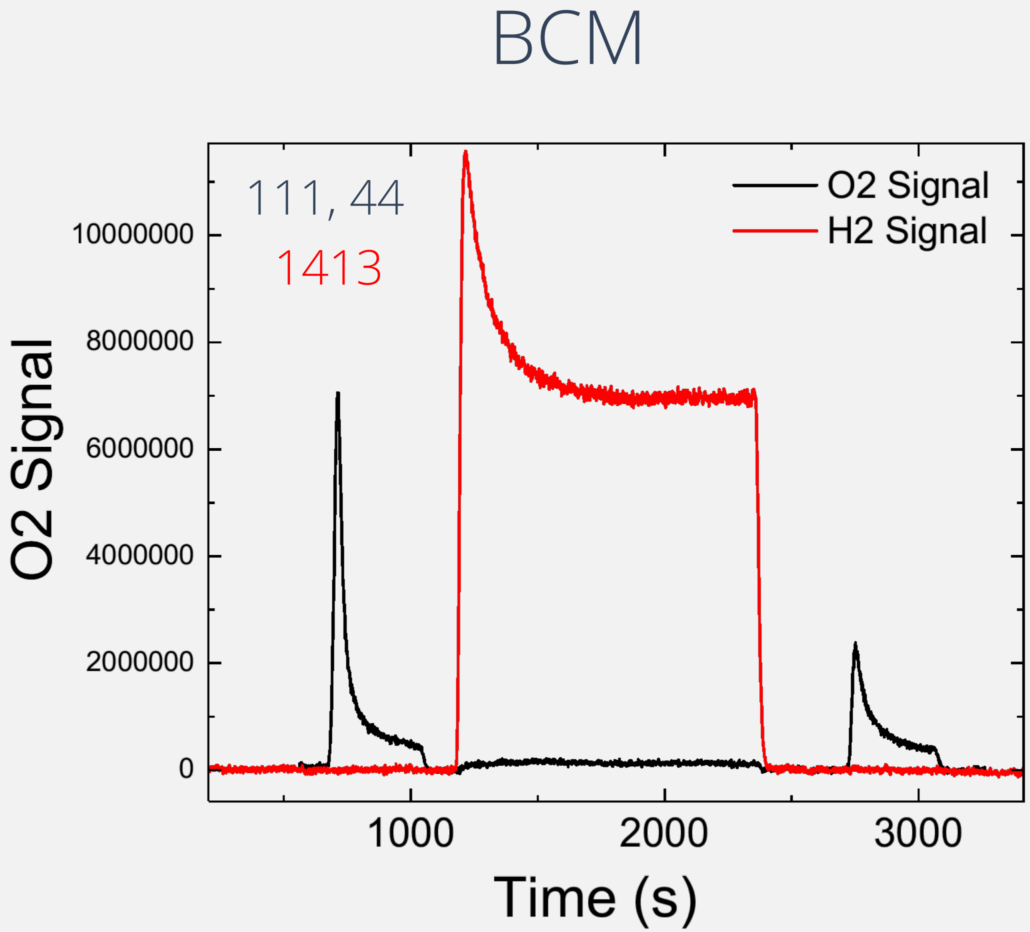
BPM

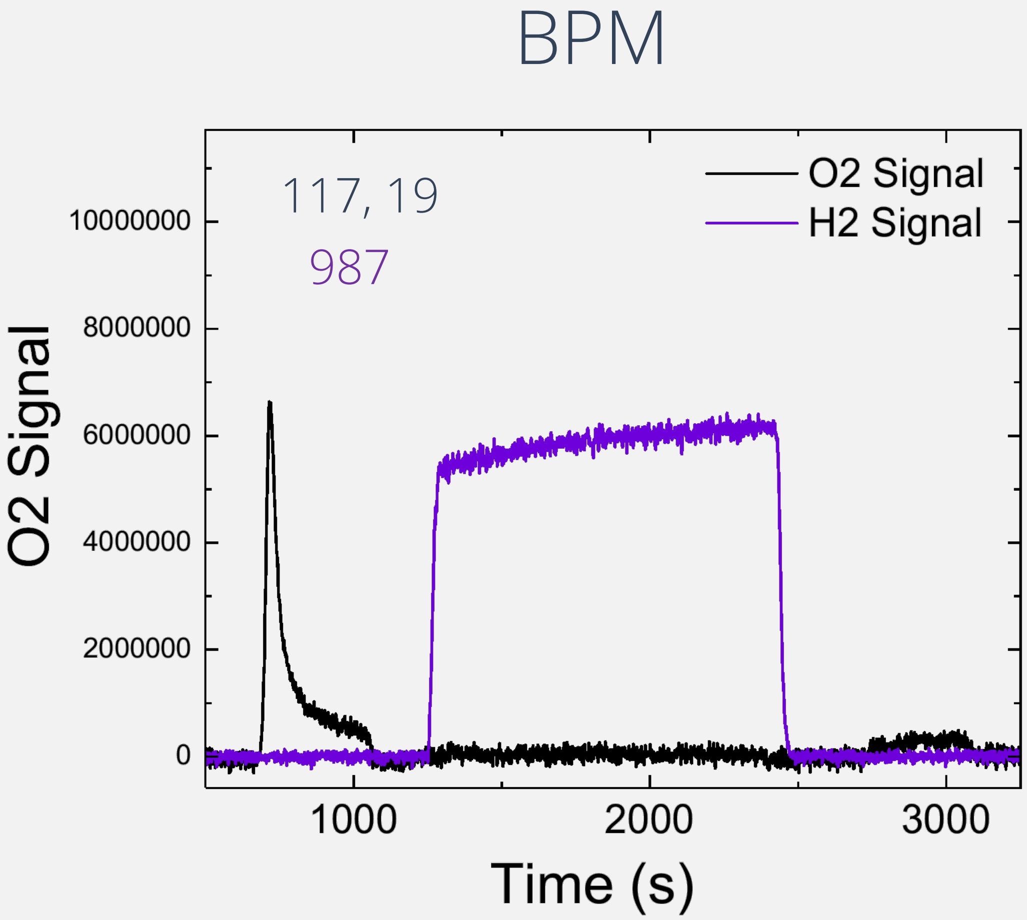


BPM exhibits:

- Slower kinetics
- Lower redox capacity (delta)
- Lower H_2 yield (mol H2/mol O solid)

HCWS Data for $H_2O:H_2$ 1333:1

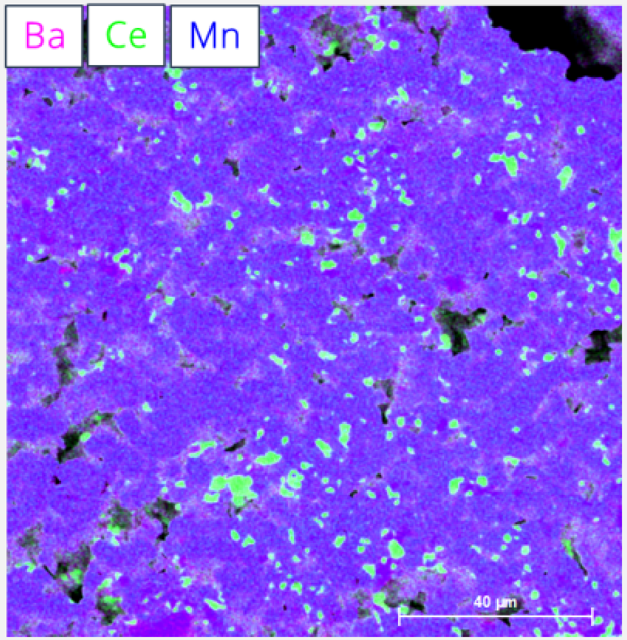




Why does BPM lose redox capacity during HCWS in $H_2O:H_2$ 1333:1?

Post-WS Characterization : SEM-EDS

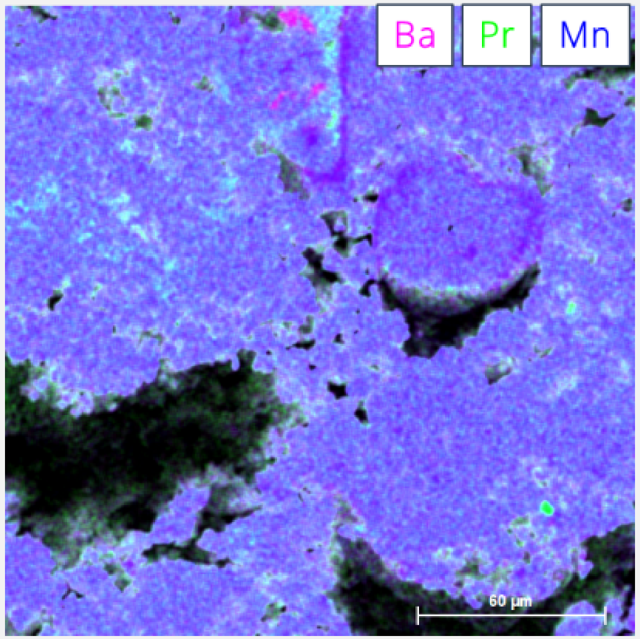
BCM



Phases:
- BCM
- BMO
- BCO

BCM After WS	
Bulk BCM (Ba : Ce : Mn)	1 : 0.20 : 0.75
BMO (Ba : Mn)	1 : 0.66
BCO (Ba : Ce)	1 : 0.71
BCM #2 (Ba : Ce : Mn)	N/A

BPM

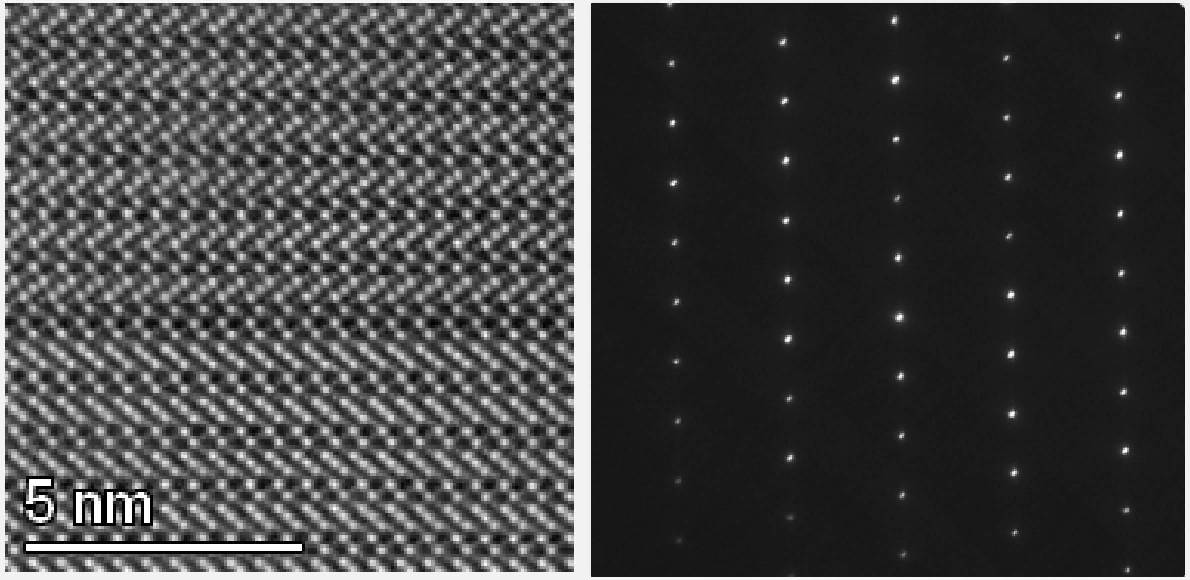


Phases:
- BPM
- BMO
- *Multiple* BPM phases

BPM After WS	
Bulk BPM (Ba : Ce : Mn)	1 : 0.24 : 0.61
BMO (Ba : Mn)	1 : 0.58
BPM #2 (Ba : Ce : Mn)	1 : 0.49 : 0.35
BPM #3 (Ba : Ce : Mn)	1 : 0.38 : 0.51

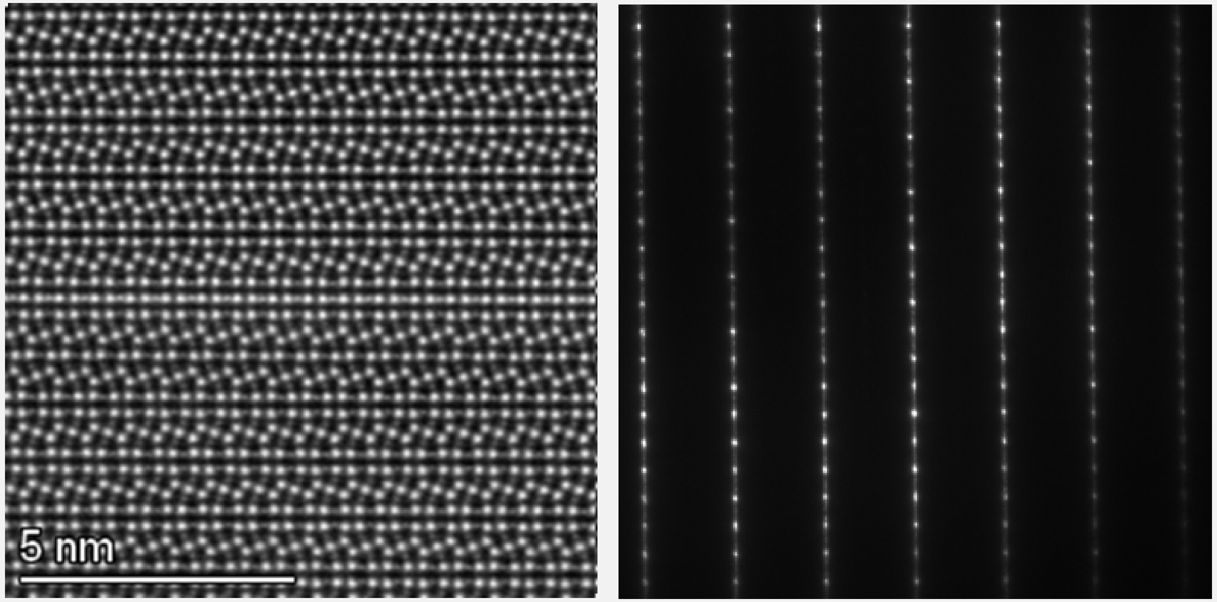
Post-WS Characterization : HAADF-STEM Imaging

BCM



12R

BPM



Not 12R

BPM undergoes an unknown phase change during cycling

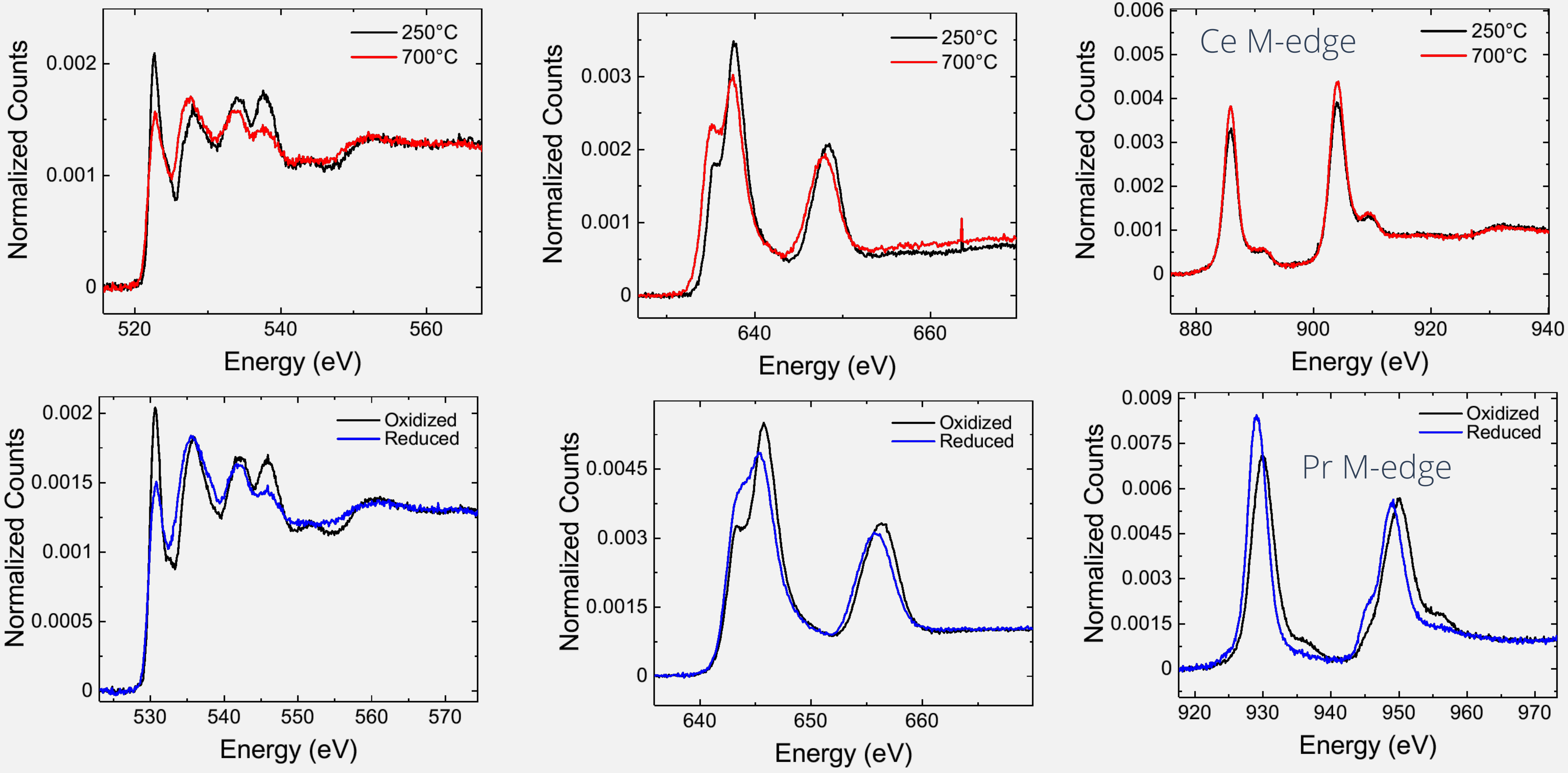
What is the mechanism of this transformation?

Post-WS Characterization : STEM-EELS

O K-edge | Mn L-edge

BCM

BPM



- Extent of Mn reduction → BPM>BCM
- Dual reduction of Pr in BPM

Summary

1. BCM shows good capacity for HCWS
2. BMO, BCO, and a minor secondary BCM phase form during cycling
3. Defects form during thermal cycling but no overall phase change observed
4. Ce does not reduce

1. BPM loses redox capacity during HCWS
2. Multiple BPM phases form
3. BPM undergoes a phase transition from 12R to a currently *unknown* phase
4. Pr reduces