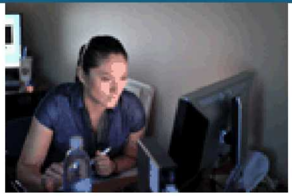
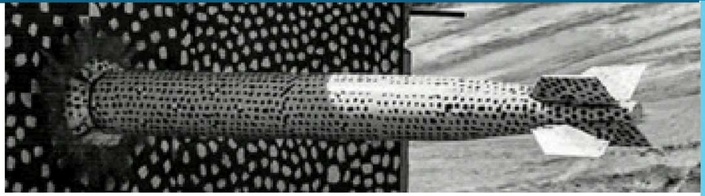
SAND2019-14549C

Exploring the Low-Temperature Carbon Monoxide Oxidation and Thermochemical Water Splitting Capabilities of High Entropy Oxides

2019 MRS Fall Meeting

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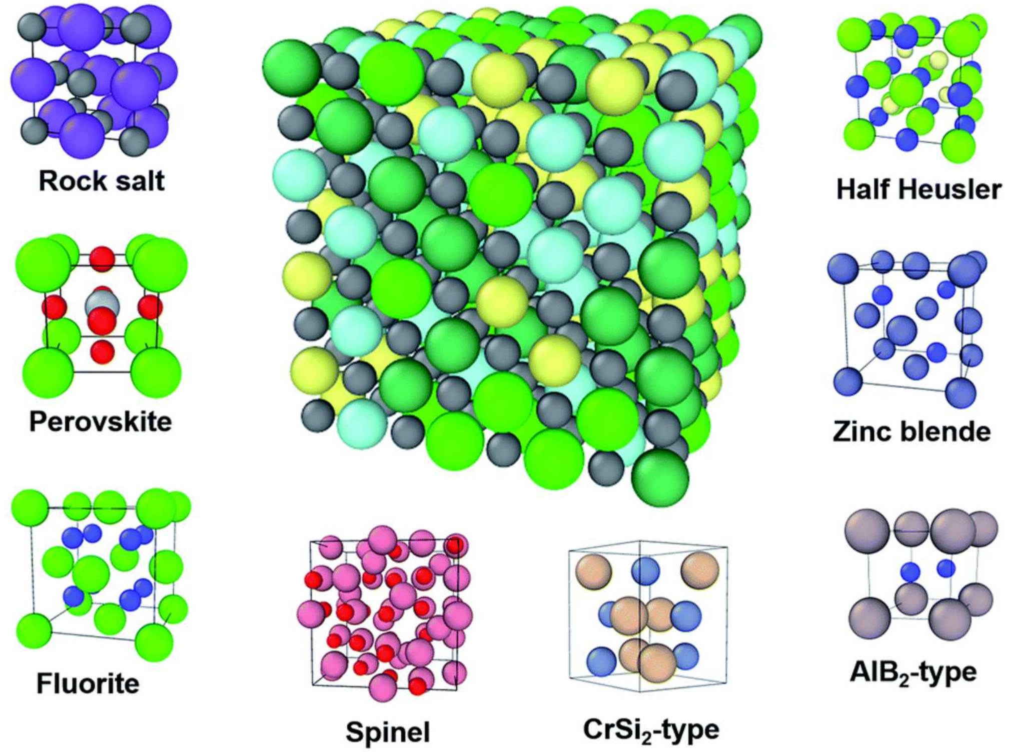
Introduction - High Entropy Oxide



Structural Diversity of High Entropy Ceramics

High Entropy Oxide (HEO)

- Single-phase multi-cation oxide stabilized by configurational entropy
- High configurational entropy due to randomly distributed elements on same lattice site
- Engineer chemical and defect structure of oxides

Previous reported applications

Rock salt-based HEO (Mg,Co,Ni,Cu,Zn)O

- Li-storage capability
- Catalytic CO oxidation

Polycation oxides (PCO) $(Mg,Fe,Co,Ni)O_x$

- High-temperature water splitting

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Sarkar, A. *et al. Adv. Mater.* **2019**, 1806236.
Zhai, S. *et al. Energy Environ. Sc.* **2018**, *11*, 2172.
Djenadic, R. *et al. Mater. Res. Lett.* **2017**, *5*, 102.
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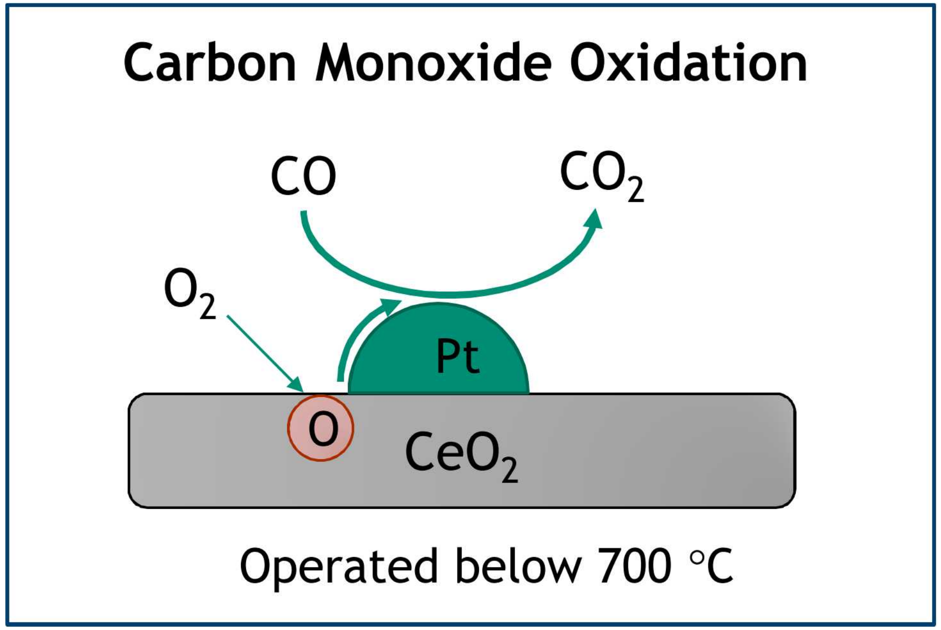
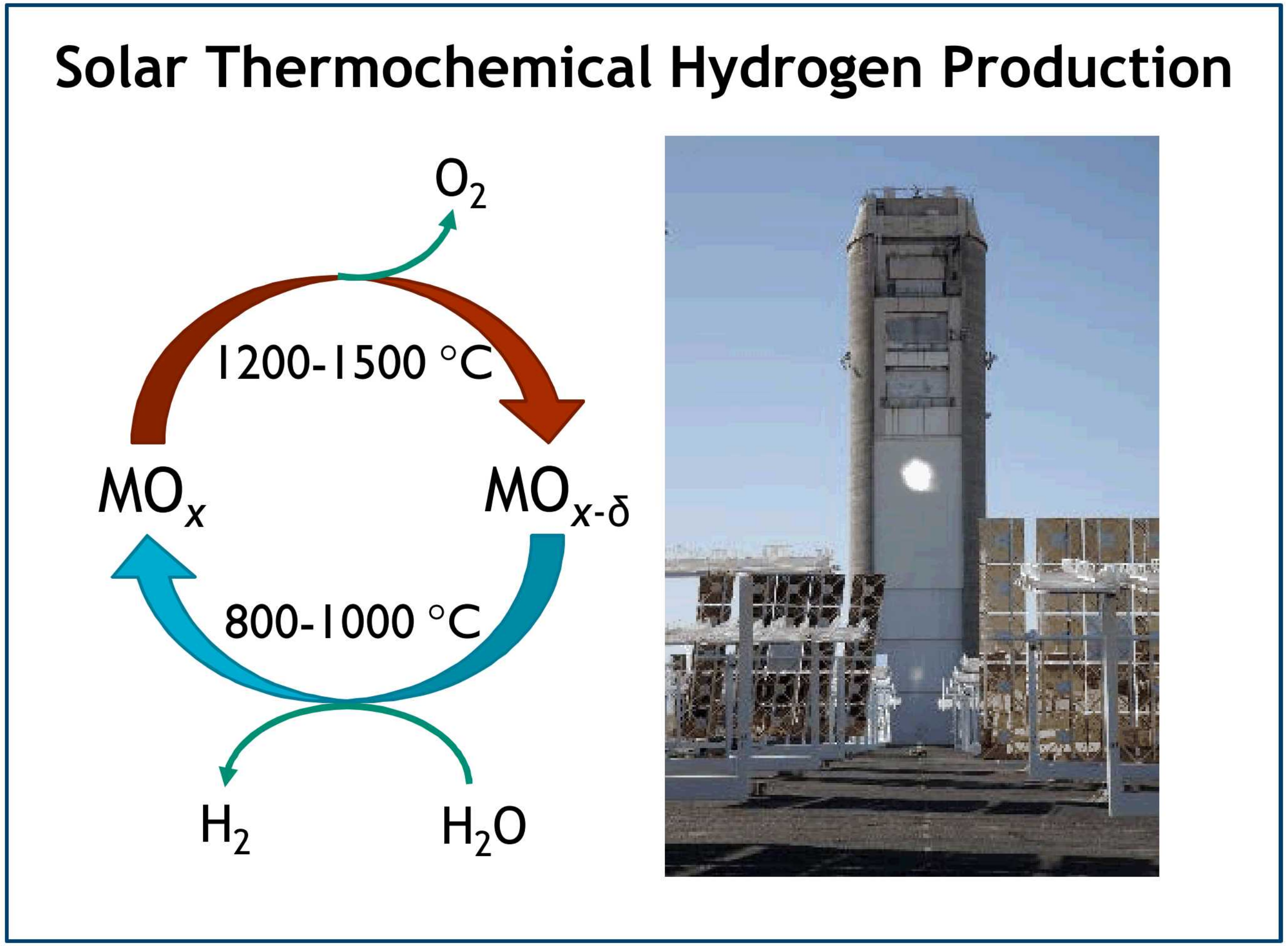
Different Catalytic and Surface-Mediated Processes



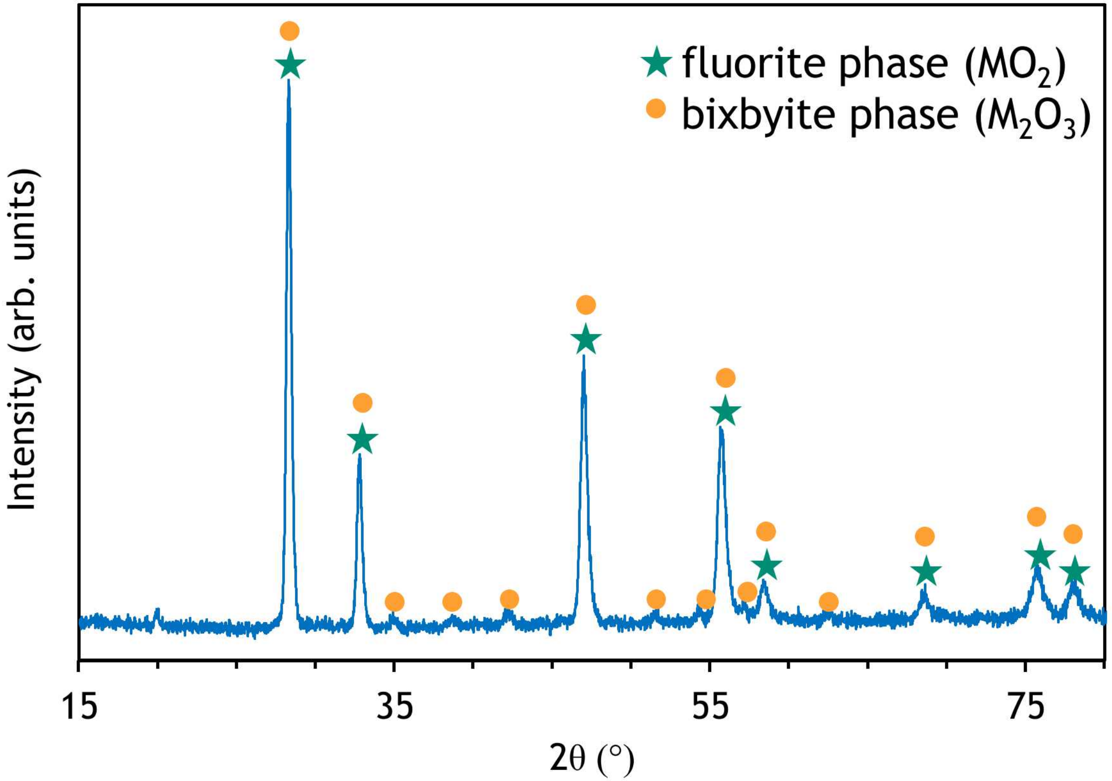


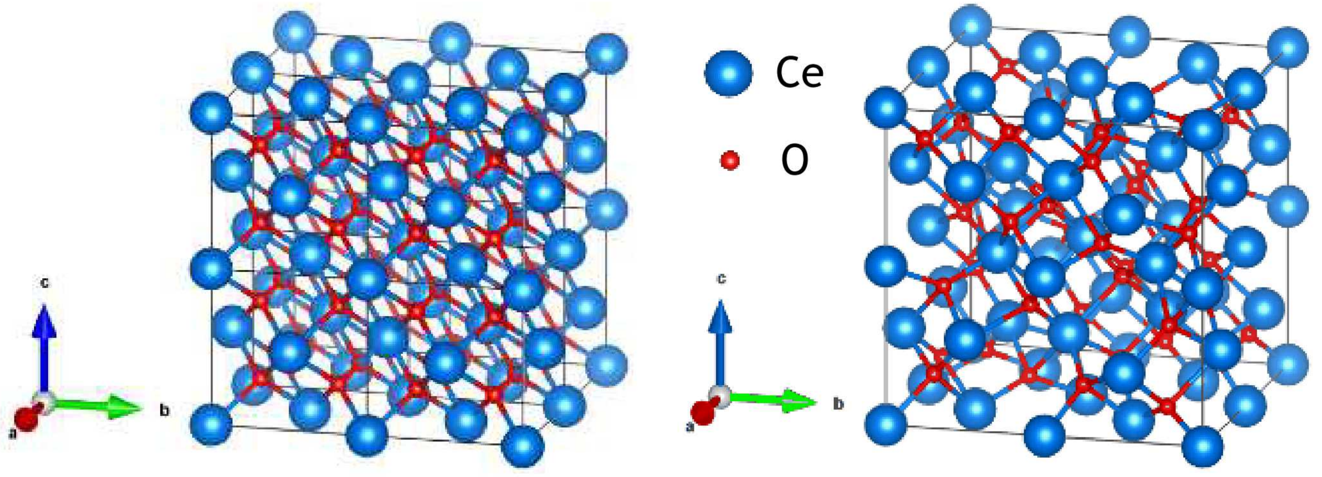
- CeO_2 studied heavily for both reactions
- Explore these reactions with high entropy oxide with fluorite structure
  $(Ce_{0.2}La_{0.2}Pr_{0.2}Sm_{0.2}Y_{0.2})O_2$

https://energy.sandia.gov/energy/renewable-energy/solar-energy/csp-2/nsttf/

Synthesis of (Ce,La,Pr,Sm,Y)O_2 High Entropy Oxide

Reacting stoichiometric amount of CeO_2, La_2O_3, Y_2O_3, Pr_6O_{11}, Sm_2O_3 at 1500 °C in air





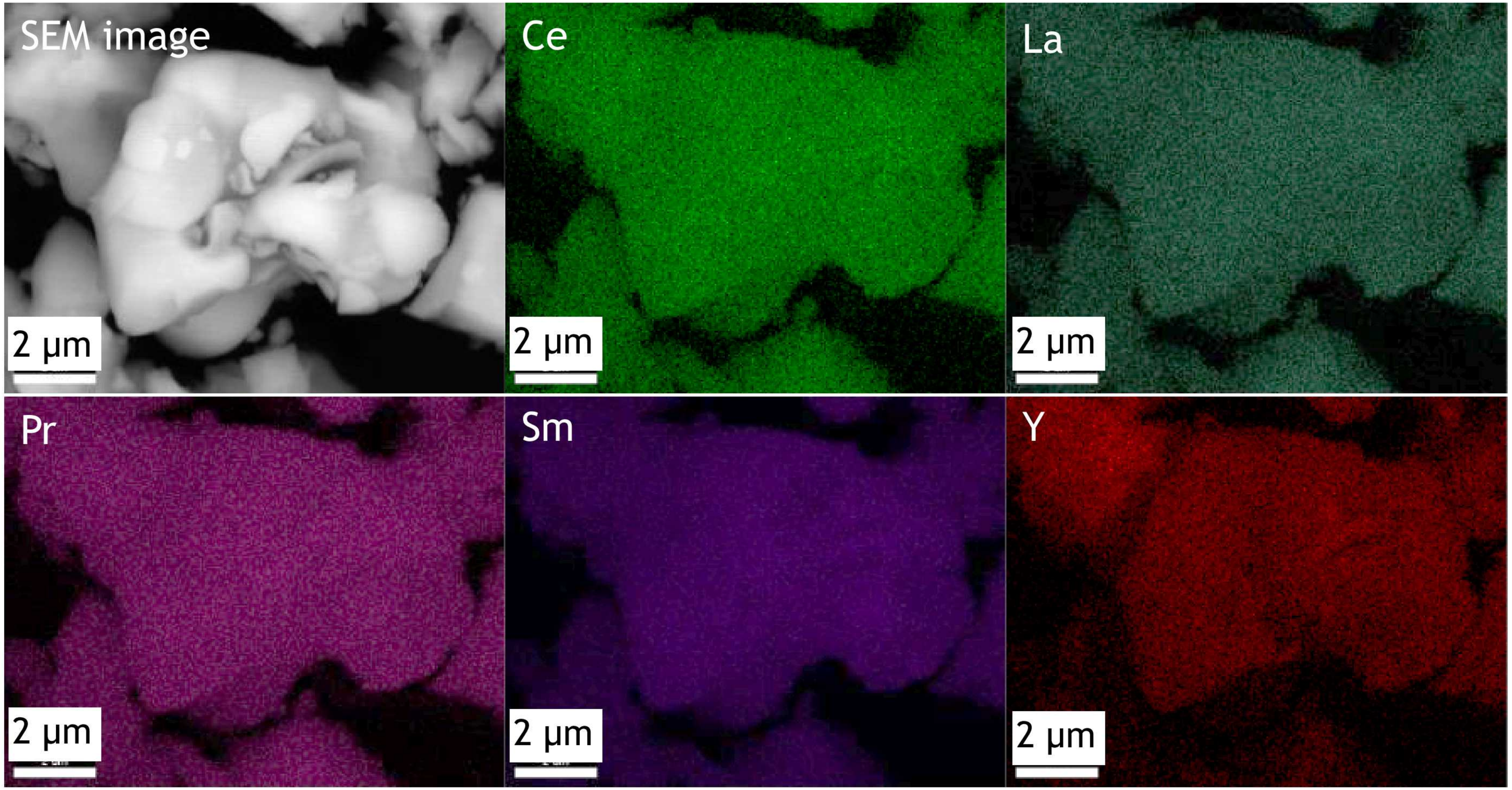
Fluorite Structure (CeO_2) Bixbyite Structure (Ce_2O_3)

Bixbyite: comparable to 2×2×2 fluorite supercell with oxygen removed

- XRD pattern reveals mainly fluorite phase with bixbyite phase.
- Bixbyite phase was still present even after heating at 1500 °C under O_2

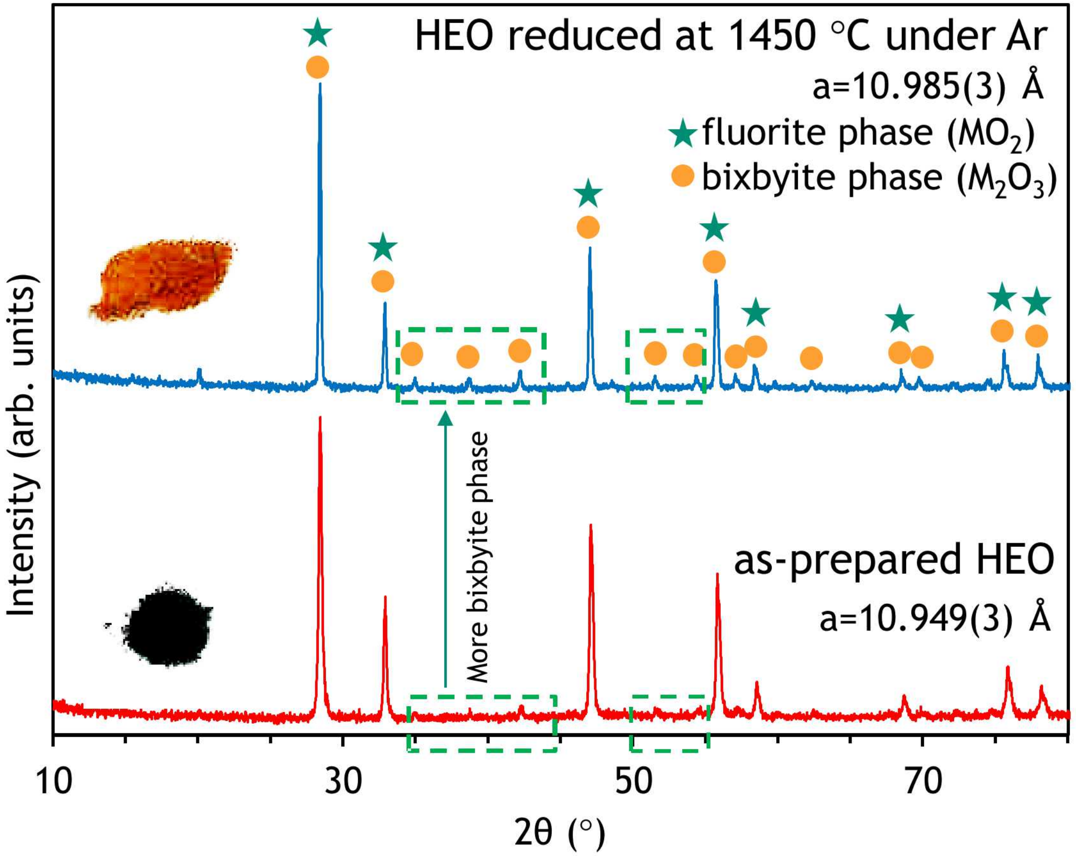
SEM/EDS of $(Ce,La,Pr,Sm,Y)O_2$

Homogeneous distribution of the metal cations was observed under EDS mapping in SEM.



SEM/EDS Mapping

Oxygen Defects on (Ce,La,Pr,Sm,Y)O_2 High Entropy Oxide

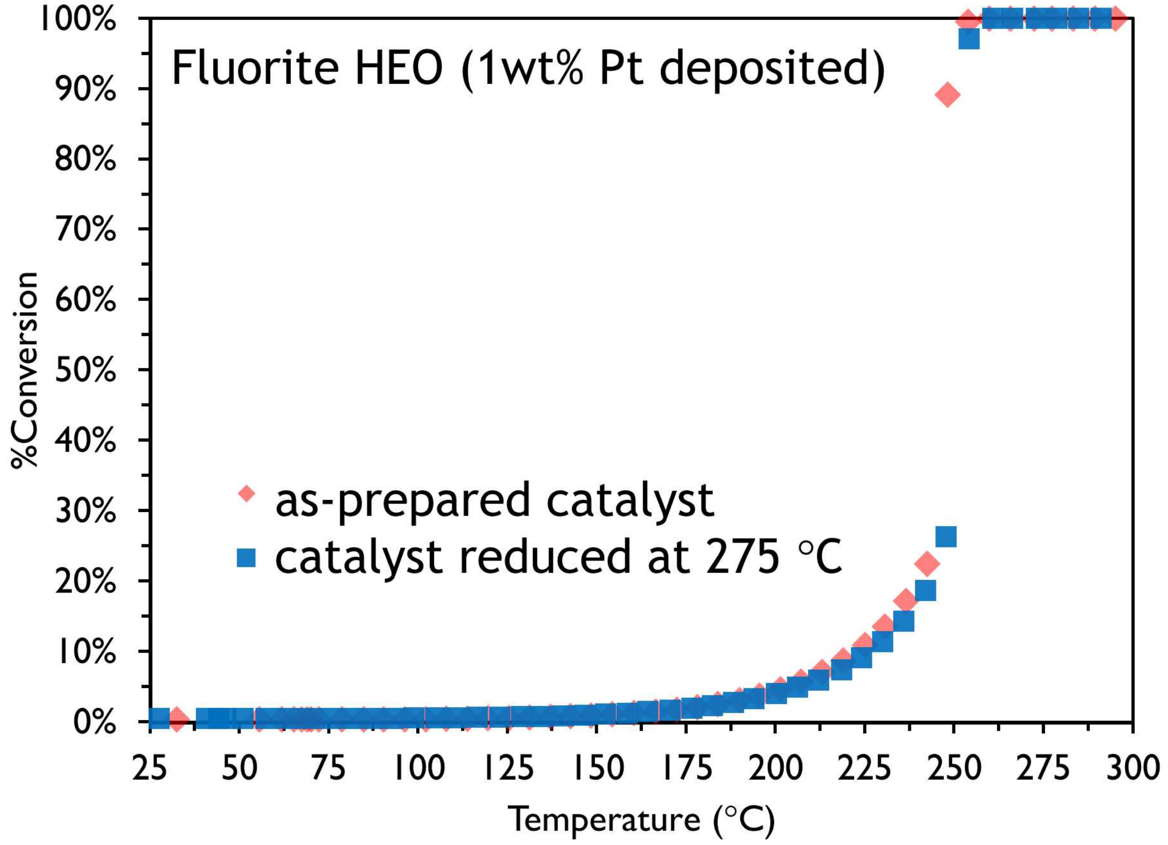


After heating sample at 1450 °C under Ar,

- Lattice expanded by ~0.04 Å
- Fluorite phase converted to bixbyite phase

- Oxygen deficient phase can be utilized in different catalytic reactions.
- Possible to prepare different oxygen deficient phases by heating and quenching at different temperatures.

Low-Temperature CO Oxidation Catalytic Performance



Light-off Curve for CO Oxidation

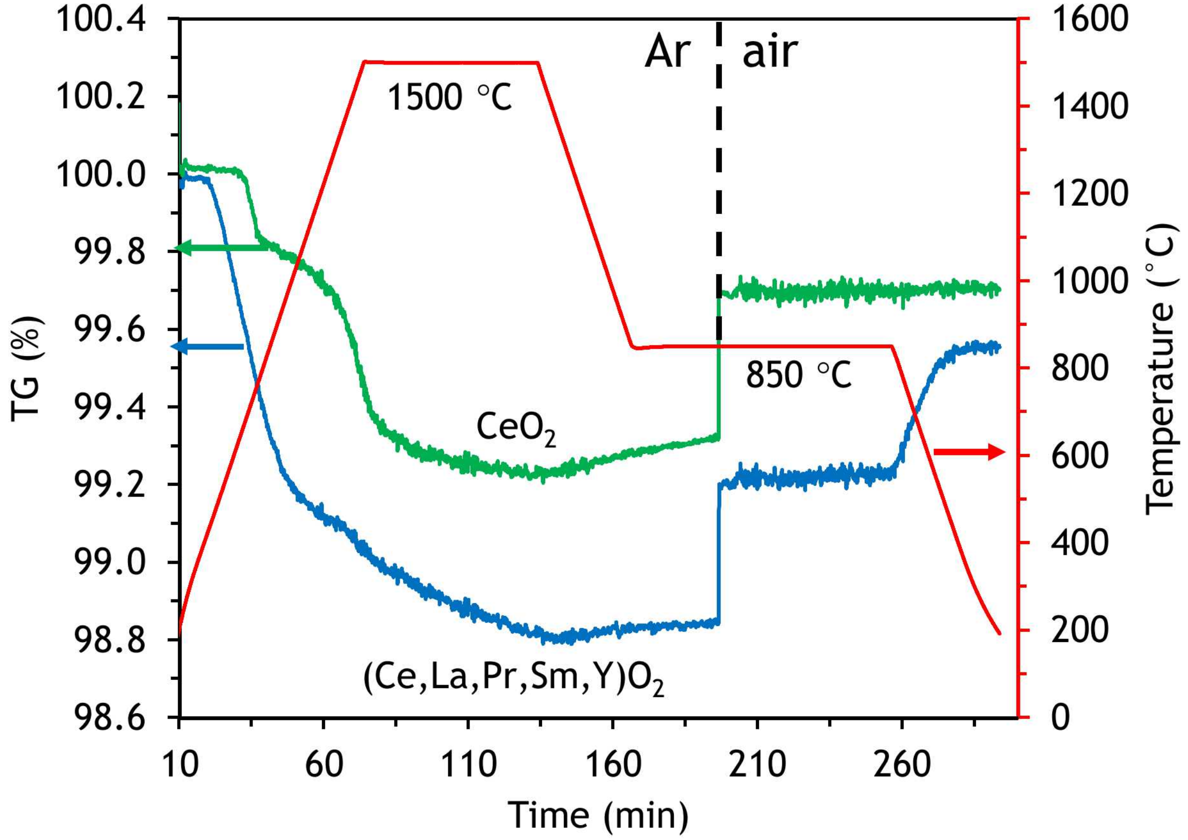
CO Oxidation with 1wt% Pt deposited

- High conversion efficiency at ~250 °C
- After reduction at 275 °C, no change in catalyst performance observed.

- Pt is either stable on the surface of the support, or stable in the lattice
- High redox stability is promising for high temperature catalytic reactions.

Dr. Andrew De La Riva
University of New Mexico

Oxygen Redox Behavior



TGA plot for oxygen redox behavior

Exploring oxygen redox behavior of HEO comparing to CeO_2

Reduction at 1500 °C under Ar

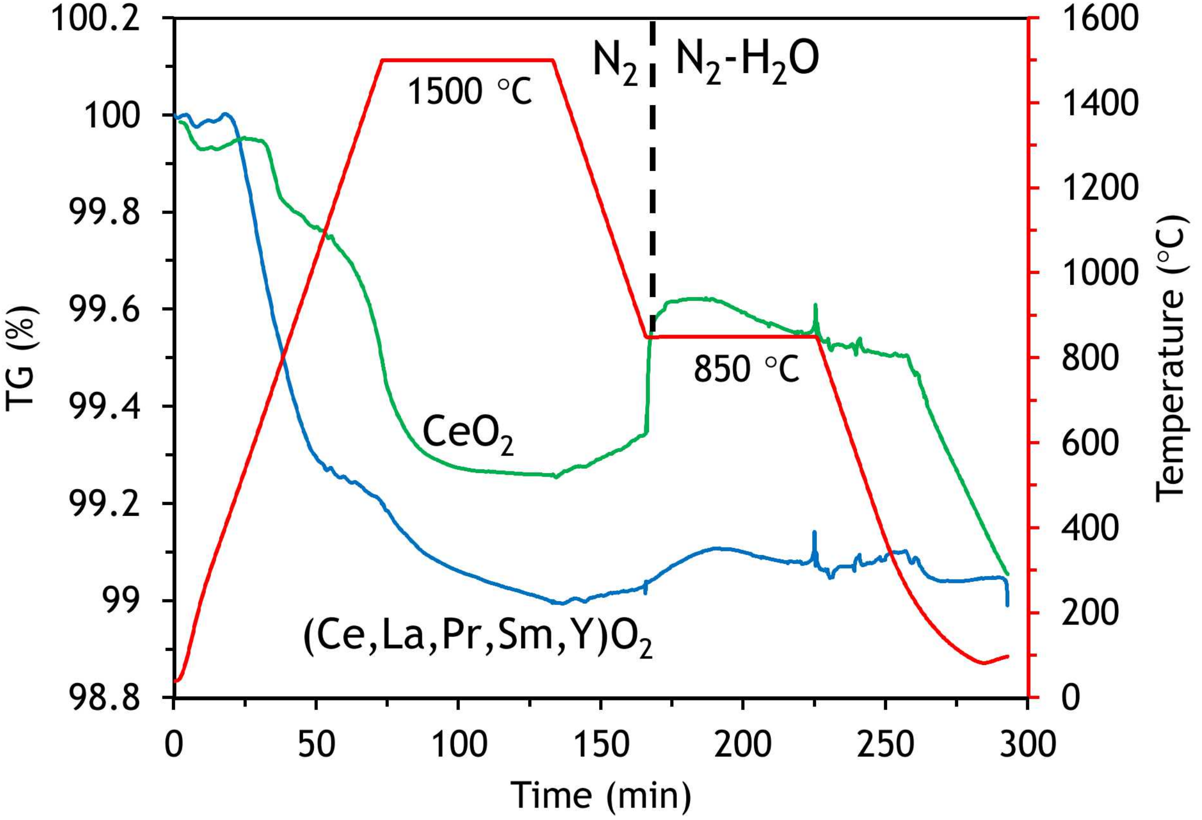
- HEO (blue) reduces more than CeO_2 (green)

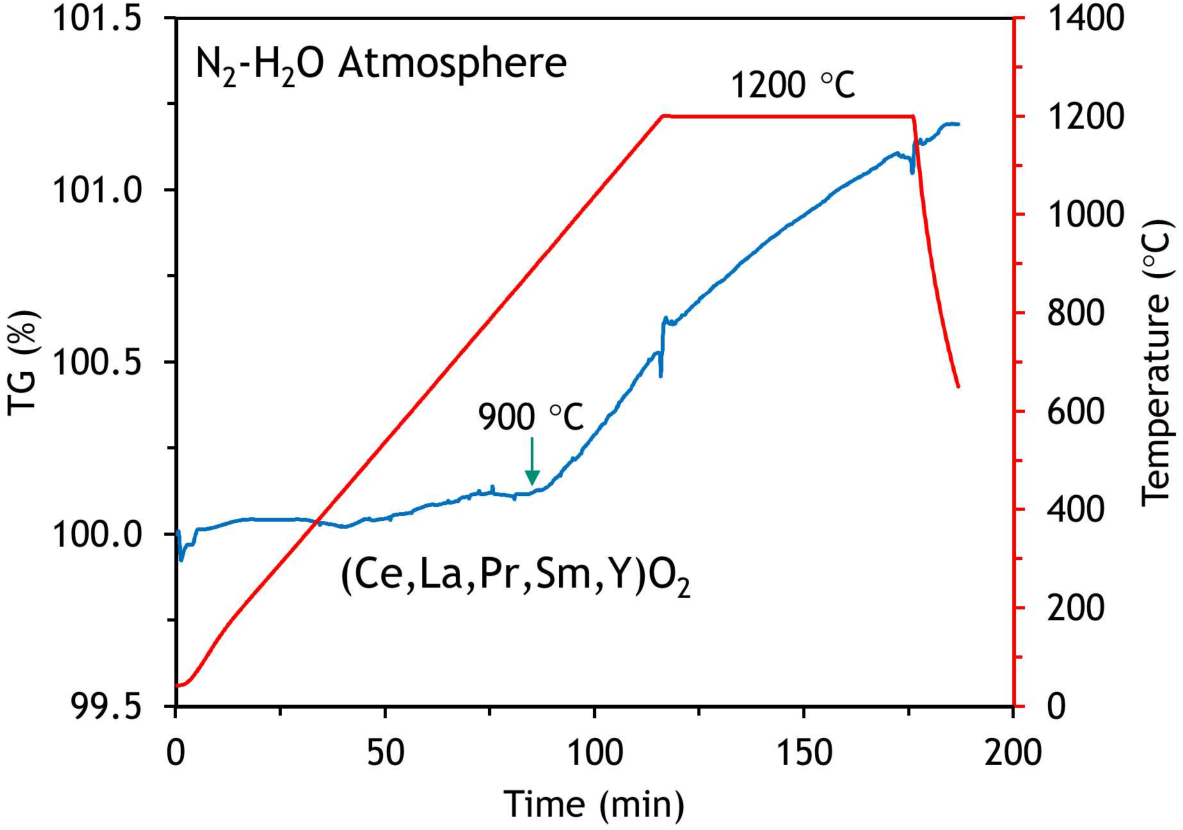
Oxidation at 850 °C under air

- Similar oxidation behavior at 850 °C for both HEO and CeO_2
- Further oxidation observed for HEO while cooling down.

HEO readily reduces and oxides more than CeO_2

High-Temperature Water Splitting





Same temperature program as before, but replacing air with steam-N_2.
While CeO_2 splits water rapidly, HEO shows slow water splitting.

The HEO was further tested by heating to 1200 °C under steam-N_2.
Water splitting occurs more above 900 °C with slow kinetics – phase change between fluorite and bixbyite

Summary/Acknowledgement

(Ce,La,Pr,Sm,Y)O_2 prepared via solid state synthesis

Catalytic CO Oxidation

- Good redox stability observed for HEO with Pt deposited
- Possible support derivation by inducing oxygen vacancies
  - fluorite vs. bixbyite phase

High-Temperature Water Splitting

- Greater extent of reduction for HEO than CeO_2
- Slower water splitting kinetics
  - Phase transition between fluorite and bixbyite structure
- Develop better understanding on temperature-dependent phase change

Collaborator

David Rademacher

UNM

Dr. Andrew De La Riva
Dr. Abhaya K. Datye

HydroGEN
Advanced Water Splitting Materials

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LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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