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HydroGEN Advanced Water Splitting Materials

Supernode: Developing an Atomistic Understanding of the Layered Perovskite $Ba_4CeMn_3O_{12}$ and its Polytypes for Thermochemical Water Splitting

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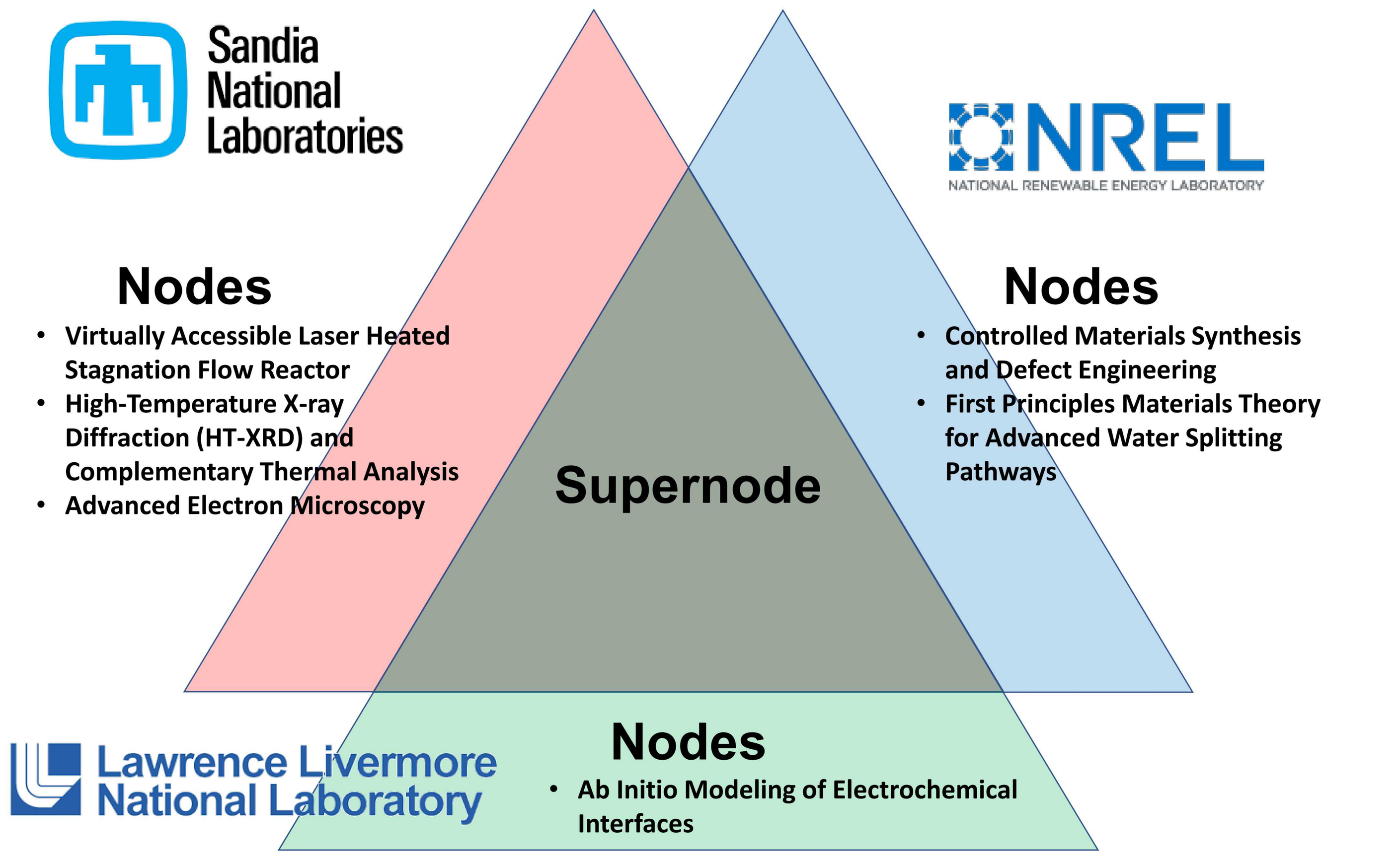
What is a Supernode?

- Combines unique capabilities of several nodes.
- Creates in sum greater capabilities.
- Focuses on ground breaking research.

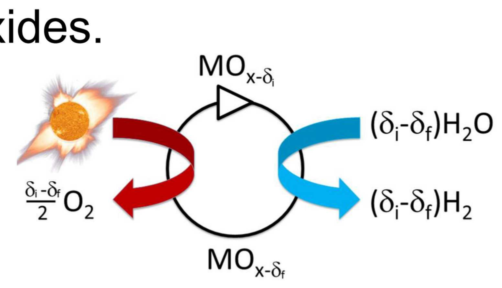
What does this Supernode Do?

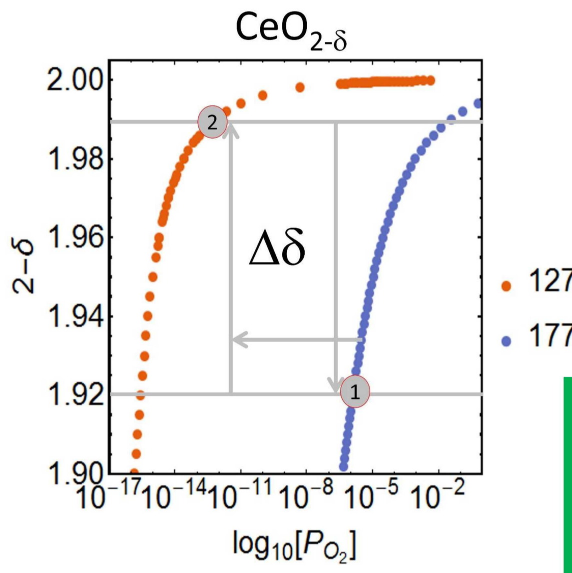
- Synthesizes model Mn-O based compounds.
- Probes material behavior at extreme conditions using operando synchrotron X-ray scattering, hot stage HR/STEM with EELS, and other techniques.
- Models defect thermochemistry, electronic band structure, cation transport, and structural rearrangement with DFT.

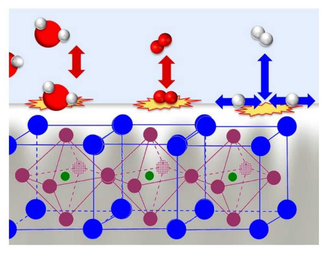


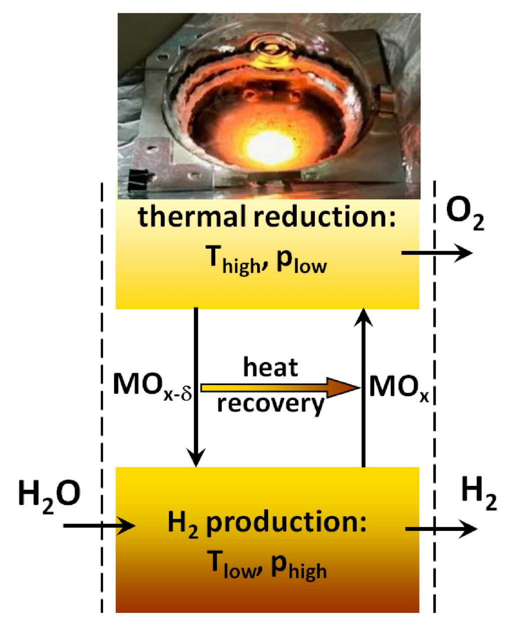
Technology Descriptions

- Water splitting by a high-temperature, two-step thermochemical cycle using nonstoichiometric perovskite oxides.
  - Store solar energy in defected oxide
- Oxygen storage materials with a "twist".







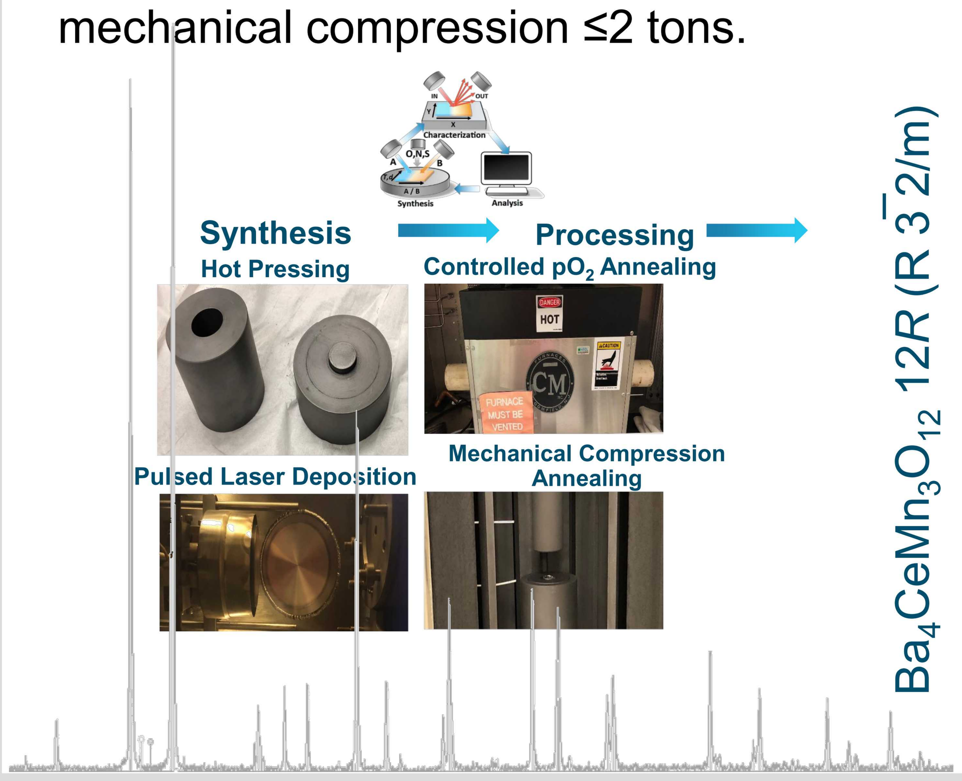


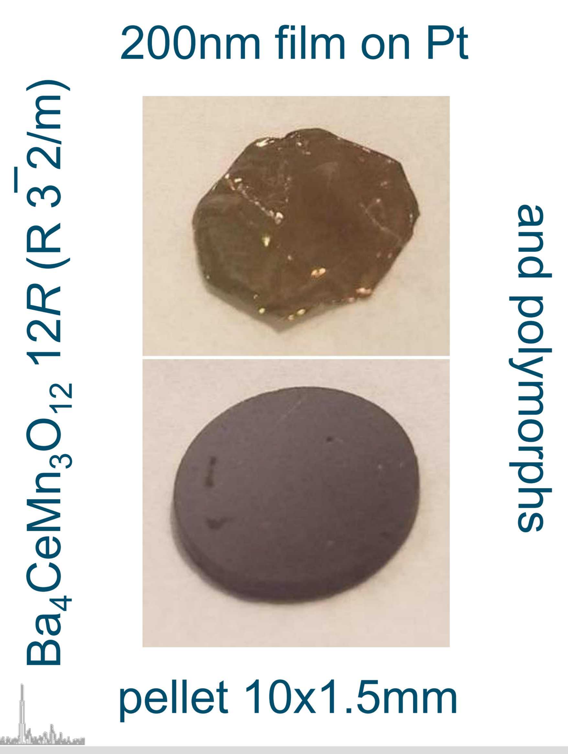
A. H. McDaniel, Current Opinion in Green and Sustainable Chemistry. 4, 37–43 (2017).

Challenge:
- *Deeply reduce at T<1623K*
- *Oxidize at extremely low O_2 pressure.*

Material Synthesis

- Sol-gel modified Pechini method used for bulk synthesis of powders, pellets, and PLD targets.
- Phase selection by controlled anneals at temperatures ≤2273K and mechanical compression ≤2 tons.

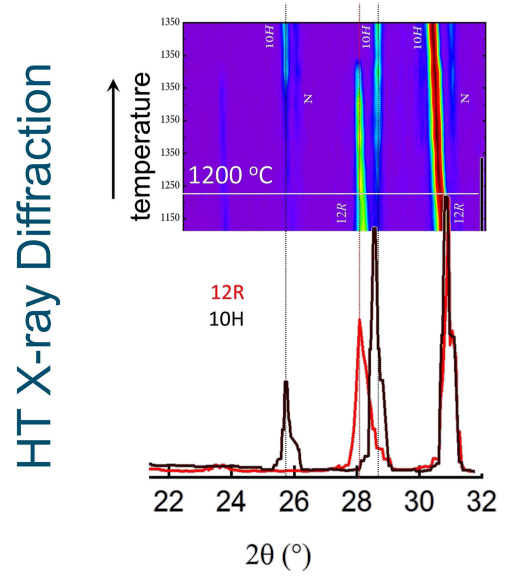




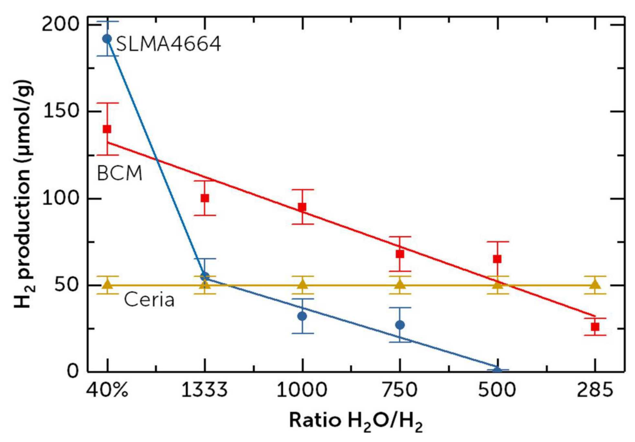
Supernode Goals

- Develop a fundamental understanding of how unique electronic structures induced by Mn-O ligand bond arrangements influence favorable water splitting material behavior.
- Use $Ba_4CeMn_3O_{12}$ (BCM) as a model compound by developing methods to synthesize pure phase polytypes in powders, pellets, and thin film forms.
- Examine perovskite electronic structures resulting from redox transitions using advanced spectroscopies.
- Decipher links between electronic configurations and favorable water splitting material behavior using atomistic theory.

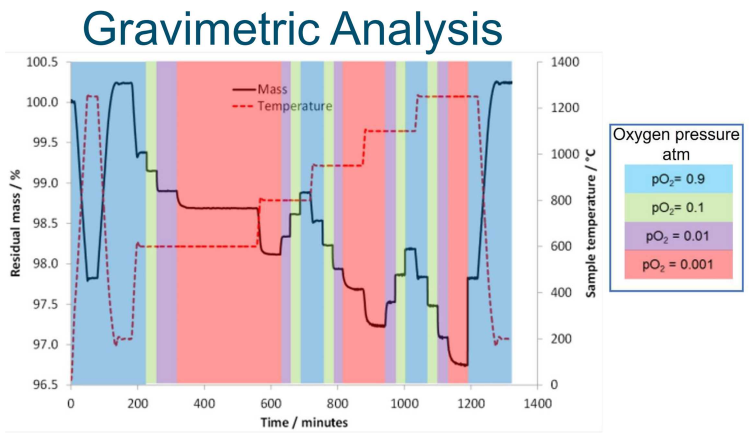
Results

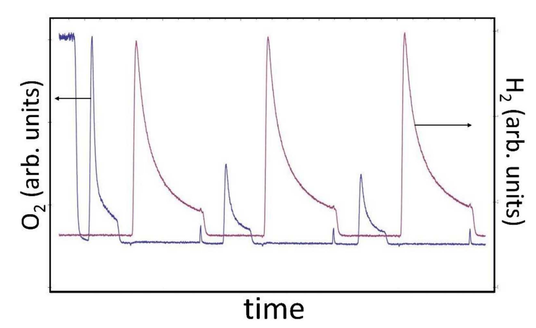


Motivation, Why BCM:
- *12R Perfectly ordered line compound*
  - *Simplifies synthesis and modeling*
- *Polymorph transitions*
  - *10H observed on reduction*
  - *Range of Mn-O ligand field effects*
- *Uncommon redox behavior*
  - *High capacity, low T reduction*
  - *Splits water @ "low" H_2O/H_2 ratio*

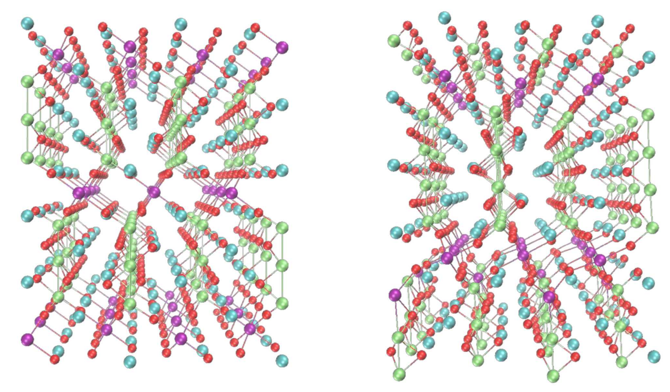


D. R. Barcellos, M. D. Sanders, J. Tong, A. H. McDaniel, R. P. O'Hayre, Energy & Environmental Science (2018), doi:10.1039/C8EE01989D.



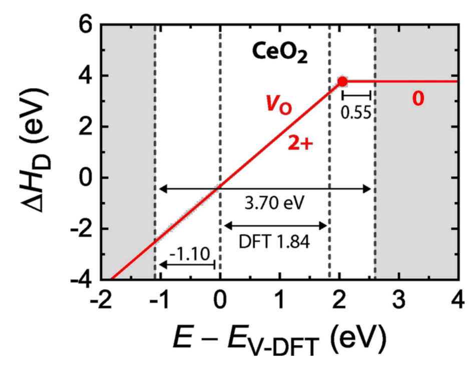


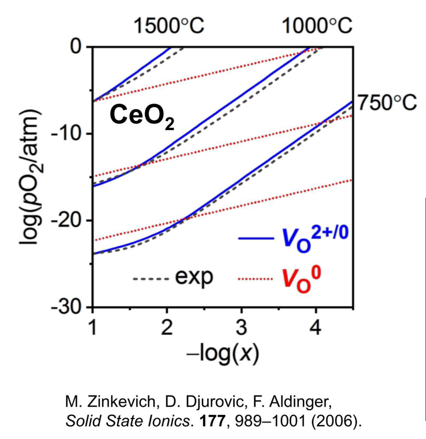
DFT Modeling Approach:
- *Build validated structure models*
- *Apply high level theory for analysis*
  - *Many body perturbation theory*
  - *XAS and EELS*
- *Model defect thermodynamics*
  - *V_o formation energy*



$$\Delta H_D = [E_{tot}^{D,q} - E_{tot}^{Host}] + q(E_{VBM} + \Delta E_F) + \sum_\alpha n_\alpha(\mu_\alpha^0 + \Delta\mu_\alpha)$$

supercell energies | electron reservoir | atomic reservoir



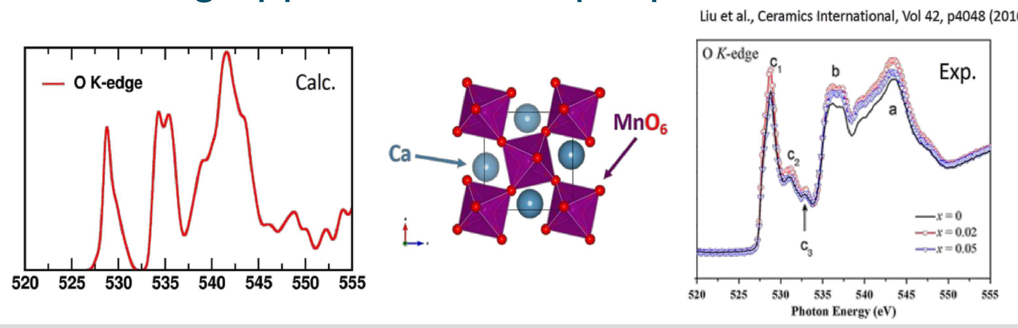


M. Zinkevich, D. Djurovic, F. Aldinger, Solid State Ionics. 177, 989–1001 (2006).

Effects Of Charged Defects:
- *V_O^{2+} defect mechanism active in CeO_2*
  - *Explains "low" H_2O/H_2 ratio water splitting*
- *Defect mechanism not likely active in BCM*

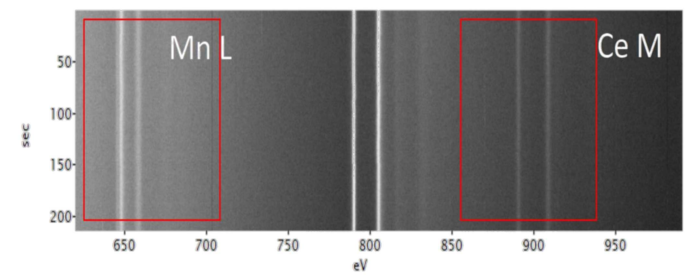
Developing XANES modelling approach on simple perovskites

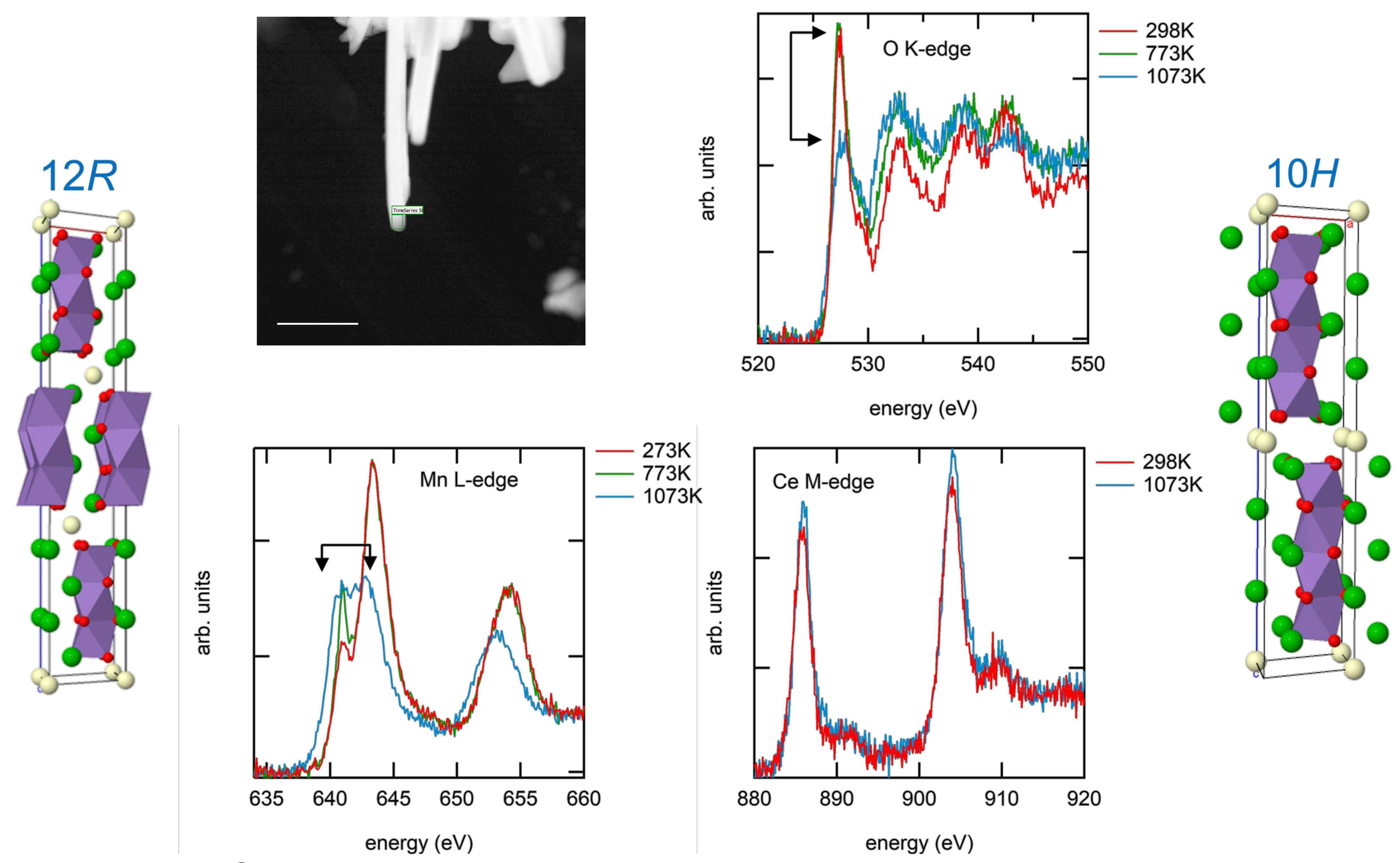
Example XANES:
- *PBE-GGA+U*
- *Spin ordering*
- *ΔSCF*
- *Full core hole FS*

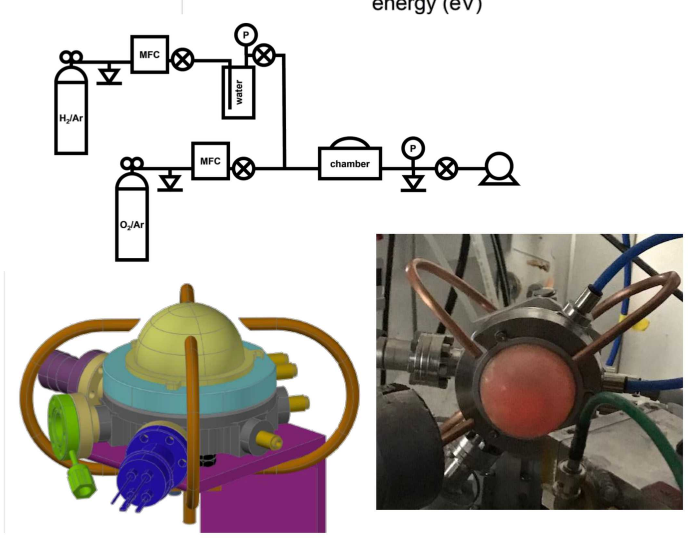


Results

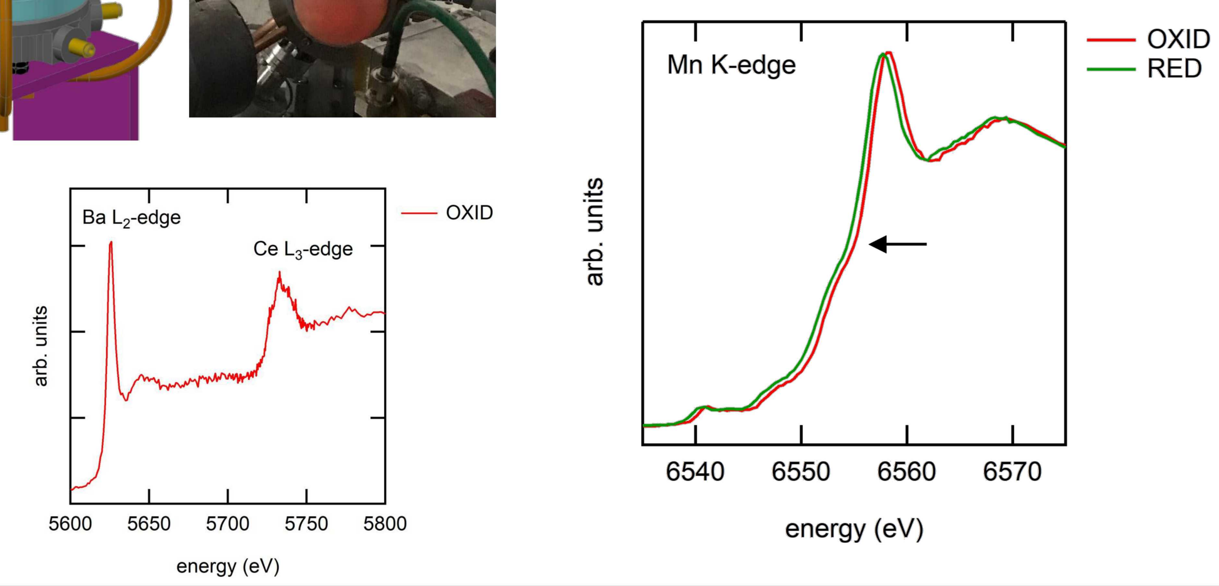
Preliminary findings:
- *Hot stage HR/STEM EELS*
  - *BCM 12R reduction in vacuum*
  - *Mn likely only redox active cation in system*







Preliminary findings:
- *Operando XAS and XRD*
  - *SLAC beamlines 2-1 and 2-2*
  - *Bulk pellets and thin films*
  - *1073K, pO_2 = 1E-04 to 1E-17*



Future Work

- Continue fundamental studies of model compounds under precisely-controlled environments.
  - Operando high-temperature X-ray scattering in both lab and synchrotron settings
  - Hot stage HR/STEM and EELS of core and valence band
- Explore mechanisms and effects involving charged defect states, pairs, and clusters on defect thermodynamics.
- Develop and exercise a DFT theory-based approach to analyzing electron diffraction, electron energy loss spectroscopy, and X-ray spectroscopy measurements.
  - Model evolution of band structures induced by oxygen defects

Acknowledgements

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