



# Accelerated Discovery of Advanced RedOx Materials for STWS to Produce Renewable Hydrogen

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June 8, 2016

Project ID: PD120

NSF CBET-1433521

# Overview:

## Year 1 of 3-Year Project



### Timeline

Project Start Date: 9/1/2014

Project End Date: 8/31/2017

Percent Complete: 50%

### Budget

Total project funding: \$525,371 (NSF)

Funding received: \$178,107

Total funding remaining: \$347,264

### Technical Barriers Addressed

W. Materials and catalysts development

### Partners/Collaborators

National Renewable Energy  
Laboratory (NREL), Golden, CO

- High-performance computing facilities

Weimer Group, CU Boulder

- Active materials synthesis and testing



***Project Objective: Develop novel reactor materials capable of producing 50,000 kg H<sub>2</sub>/day at a cost < \$2/kg H<sub>2</sub> in a particle solar thermal water splitting system.***

## ***Specific Objectives:***

1. Develop a computationally accelerated and experimentally validated materials-by-design approach to discover materials with optimum STWS properties and that can be tailored for materials discovery for other technologies
2. Use our accelerated materials discovery approach to screen metal oxide materials for STWS and the reactor developed in the DOE effort and provide a rank ordered list of promising redox materials
3. Address fundamental and broad materials chemistry questions in accomplishing tasks 1 and 2.

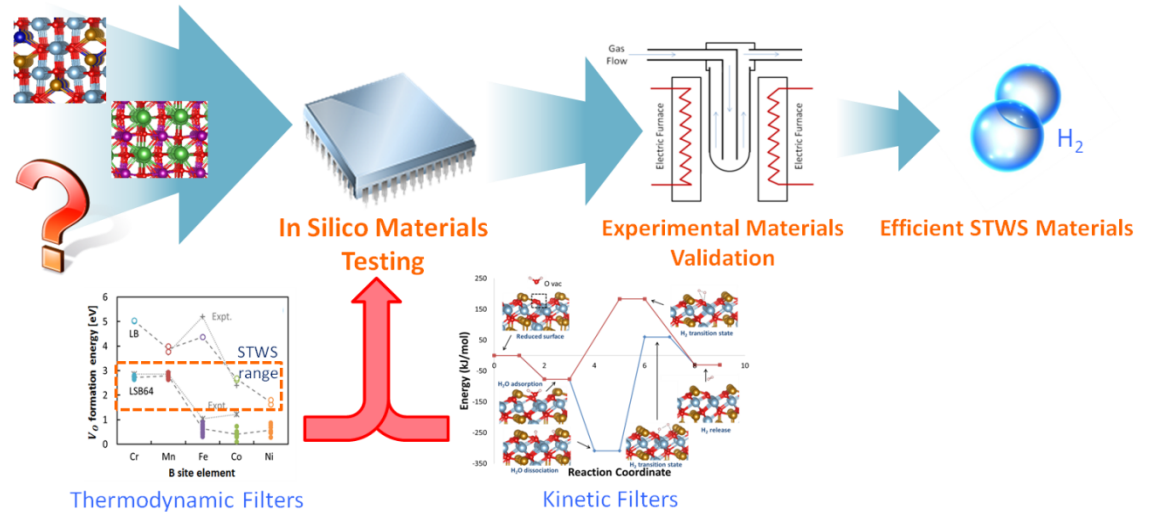
## ***This Reporting Period:***

- ✓ Applied screening approach to binary normal spinel materials (**Barrier W**)
- ✓ Investigated the effect of inversion on spinel STWS behavior (**Barrier W**)
- ✓ Tested a variety of factors to validate computational methods for predicting the H<sub>2</sub> production capacities in binary perovskites (**Barrier W**)
- ✓ Studied H<sub>2</sub> evolution and vacancy migration on doped and pure hercynite (**Barrier W**)

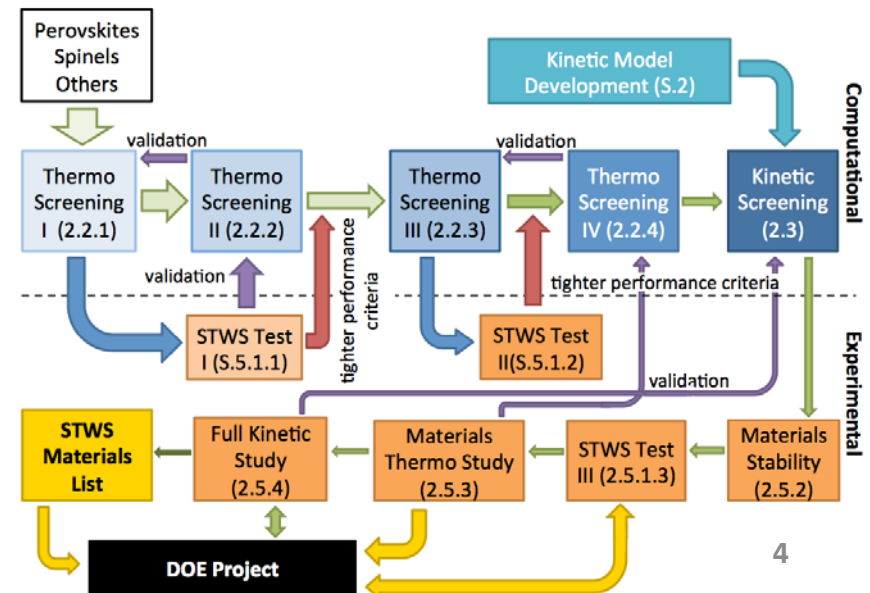
# Approach: Computational Prototyping of Oxide RedOx Materials

## Project Technical Approach

- Computational prototyping of hercynite & related materials integrating theory and experimentation
- Using both thermodynamic and kinetic filters in optimization of materials for quasi-isothermal solar water splitting



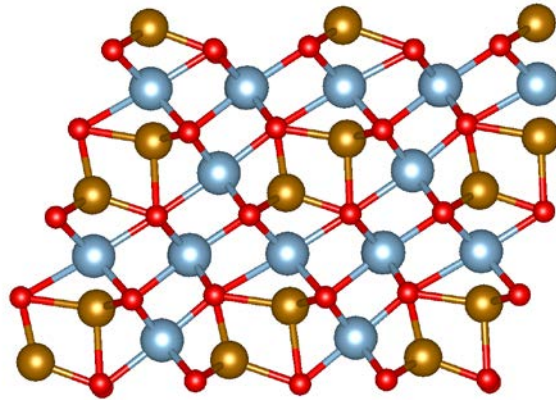
Apply fundamental materials science, chemistry and physics to develop materials design rules and discover promising materials using state-of-the-art electronic structure theory. For this objective, quantum simulations require careful, expert application due to limits of the methods, effects of spin and complexity of detailed mechanisms.





# Accomplishments and Progress: Screening Binary Spinel Materials

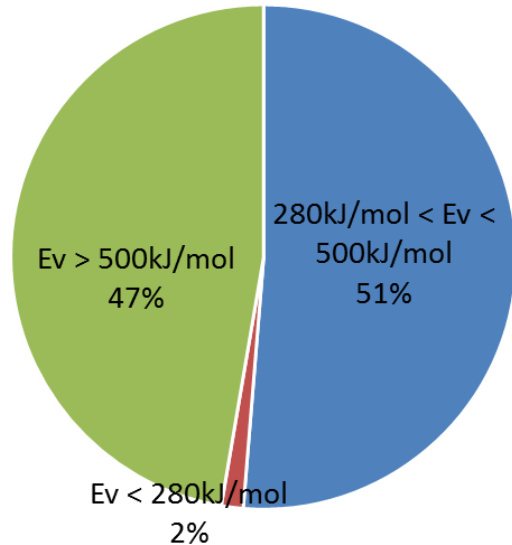
AB<sub>2</sub>O<sub>4</sub> Normal Structure



**Legend:**  
● A Atom (Fe)  
● B Atom (Al)  
● Oxygen

Elements Considered for  
Use in RedOx Materials

Binary Spinel Screening Results



- Calculated predicted E<sub>v</sub> for 955 possible binary spinels using method developed in our group by Deml *et al.*
- 16 materials have reduction enthalpies too low to drive STWS (E<sub>v</sub> < 280 kJ/mol)
- 490 materials are potentially capable of driving STWS\* (280 kJ/mol < E<sub>v</sub> < 500 kJ/mol)
- 449 materials have reduction enthalpies too high for practical use as STWS materials (E<sub>v</sub> > 500 kJ/mol)

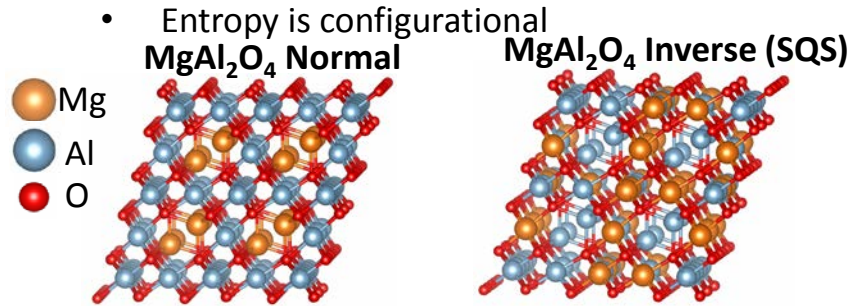
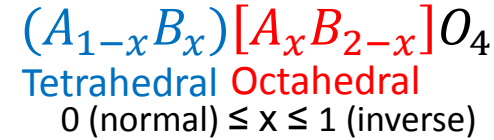
\* Materials were not analyzed for thermal stability or fabrication practicality

955 materials screened as of 3/22/2016

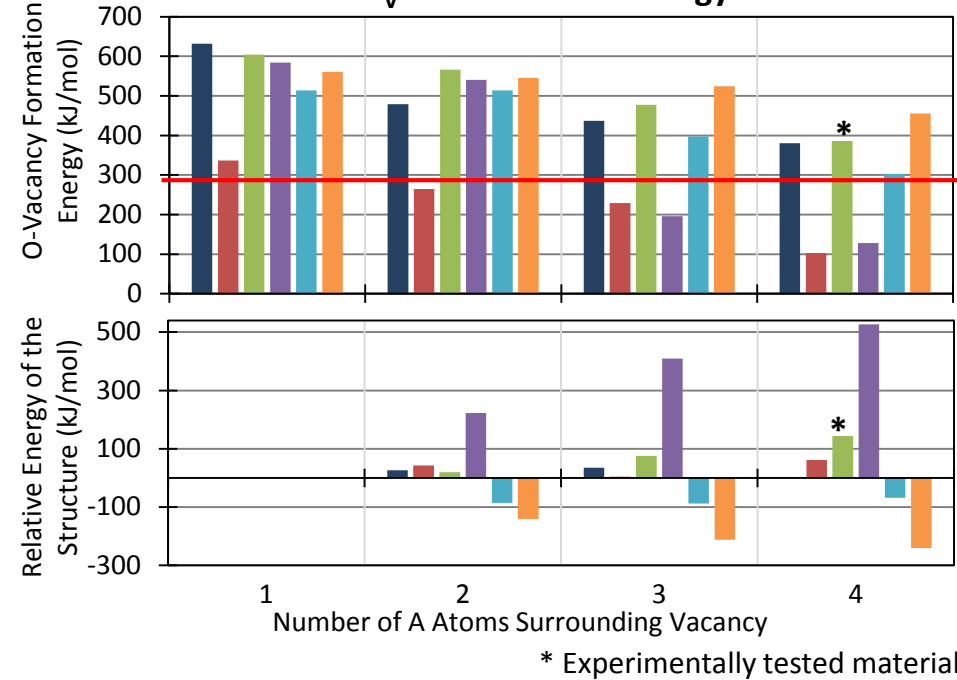
# Accomplishments and Progress: Investigating Inversion in Spinel

- A and B cations can be on either octahedral and tetrahedral sites
  - O-vacancy formation energy depends on local cation environment
- Inversion parameter (x) can be calculated as a function of temperature:  $\Delta G(x) = \Delta H(x) - T\Delta S(x)$ <sup>[1]</sup>
  - Special Quasi-random Structures (SQS) method used to generate random inverse structures

## Inversion Parameter (x)



## Impact of Cation Environment on E<sub>v</sub> and Structure Energy



## Equilibrium Inversion Parameter at 1500°C

| Compound                         | $\Delta E$ (eV) | $x_{eq}$ |
|----------------------------------|-----------------|----------|
| ZnAl <sub>2</sub> O <sub>4</sub> | 0.85            | 0.08     |
| SiMg <sub>2</sub> O <sub>4</sub> | 0.8             | 0.1      |
| GeMg <sub>2</sub> O <sub>4</sub> | 0.67            | 0.14     |
| ZnGa <sub>2</sub> O <sub>4</sub> | 0.48            | 0.24     |
| SiZn <sub>2</sub> O <sub>4</sub> | 0.39            | 0.3      |
| MgAl <sub>2</sub> O <sub>4</sub> | 0.34            | 0.34     |
| SnMg <sub>2</sub> O <sub>4</sub> | 0.23            | 0.44     |
| GeZn <sub>2</sub> O <sub>4</sub> | 0.05            | 0.62     |
| MgGa <sub>2</sub> O <sub>4</sub> | 0.03            | 0.64     |
| SnZn <sub>2</sub> O <sub>4</sub> | -0.42           | 0.95     |

Incorporation of spinel inversion allows for identification of new promising spinel materials

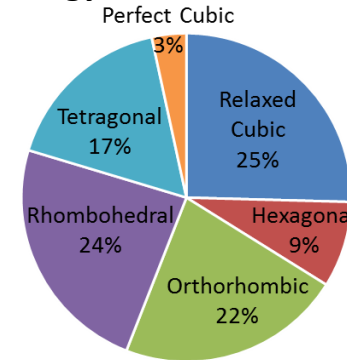
[1] A. Navrotsky and O.J. Kleppa. *J. Inorg. Nucl. Chem.* (1967), **29**.



# Accomplishments and Progress: Investigating Perovskite Structure

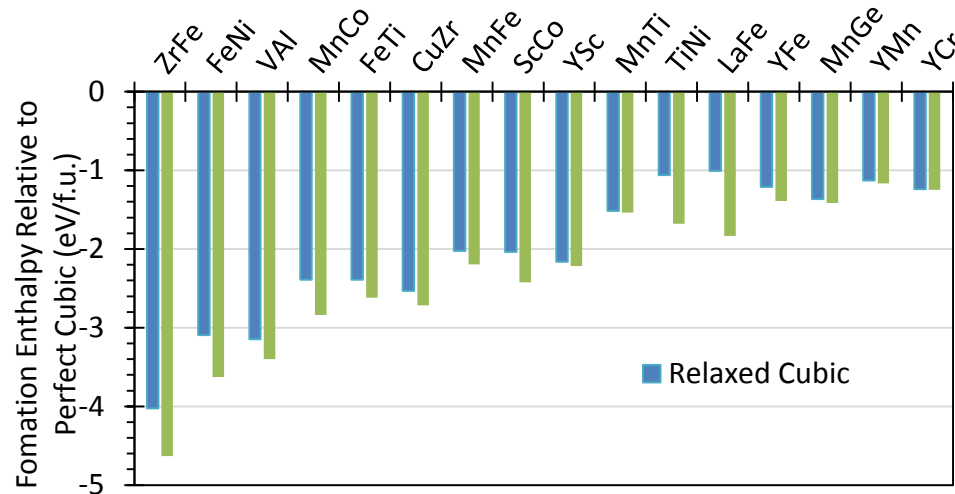
- Perovskites may adopt a variety of structures: cubic, orthorhombic, tetragonal, rhombohedral, or hexagonal
  - Previous studies typically assume a perfect cubic structure
- Deviation from the ideal cubic structure described by the Goldschmidt tolerance factor:  $t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$
- Calculated the formation enthalpy for 75 compounds in 6 different structures
- Computationally demanding phonon calculations used to compute entropy and free energy of 36 structures

## Distribution of the Lowest Energy Structure at 0K



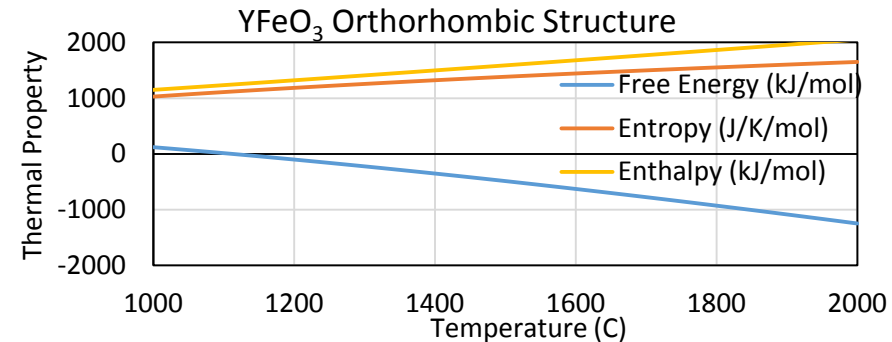
Relatively even distribution in lowest energy structure, but only a small percentage favored the perfect cubic structure

## Enthalpy of Formation Compared to Perfect Cubic



Significant differences in calculated formation enthalpy between perfect cubic structure and alternative structures

## Effects of Temperature on Perovskite Structure



Placeholder for phase transitions of YFeO<sub>3</sub>

Entropy calculations indicate that all compounds are not perfect cubic structure even at high temperatures

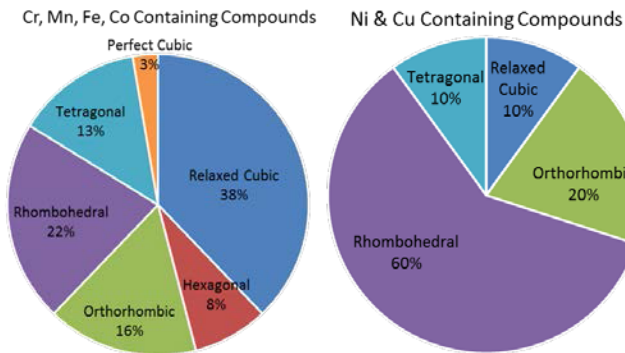
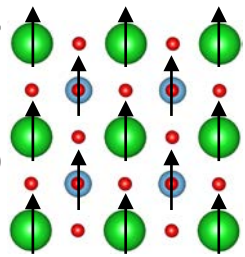


# Accomplishments and Progress: Investigating Perovskite Magnetic Ordering

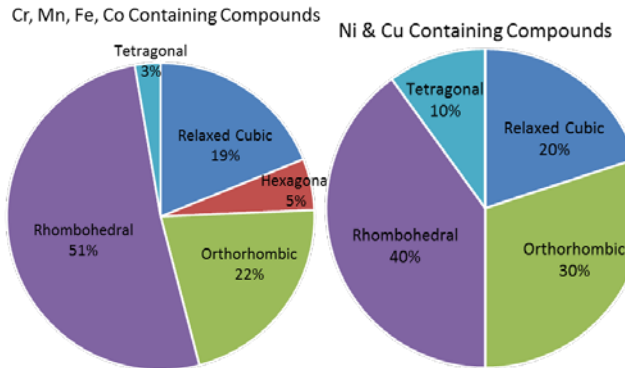
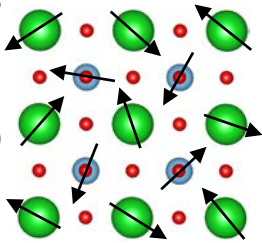
- STWS operates well above Curie or Néel temperatures → no magnetic ordering
- Model random spin states with periodic boundary model using Special Quasirandom Structures (SQS)<sup>1-2</sup>

## Effect of Spin on Distribution of Low Energy Structure

Paramagnetic Spin



Ferromagnetic Spin



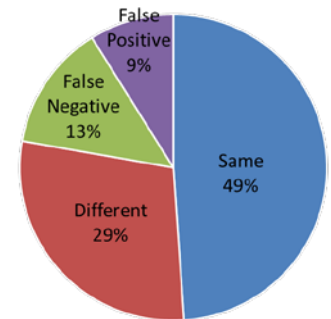
Chosen spin state has significant impact on distribution of low energy structure

## Effect of Spin on O-Vacancy Formation Energy

- O-Vacancy energy categorized for STWS ability ( $E_v < 0$ kJ/mol,  $0 < E_v < 280$ kJ/mol,  $E_v > 280$ kJ/mol, and  $E_v > 500$ kJ/mol) for different structures and spin states

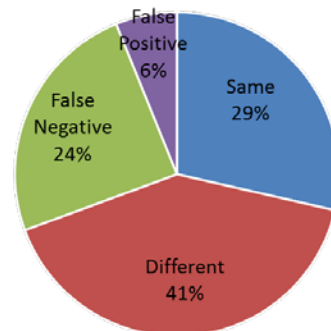
## Perfect Cubic Structure Paramagnetic vs. Ferromagnetic

>50% of materials were characterized differently for STWS ability when only changing the spin state



## Low Energy Structure Paramagnetic vs. Perfect Cubic Ferromagnetic

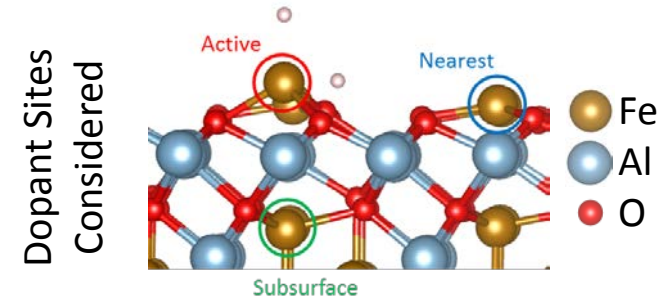
>70% of materials were characterized differently for STWS ability when changing the spin state and considering low energy structures



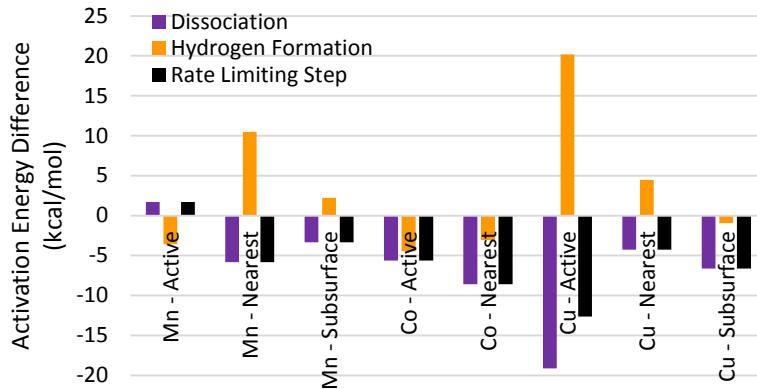


# Accomplishments and Progress – H<sub>2</sub> Evolution Reaction on Hercynite

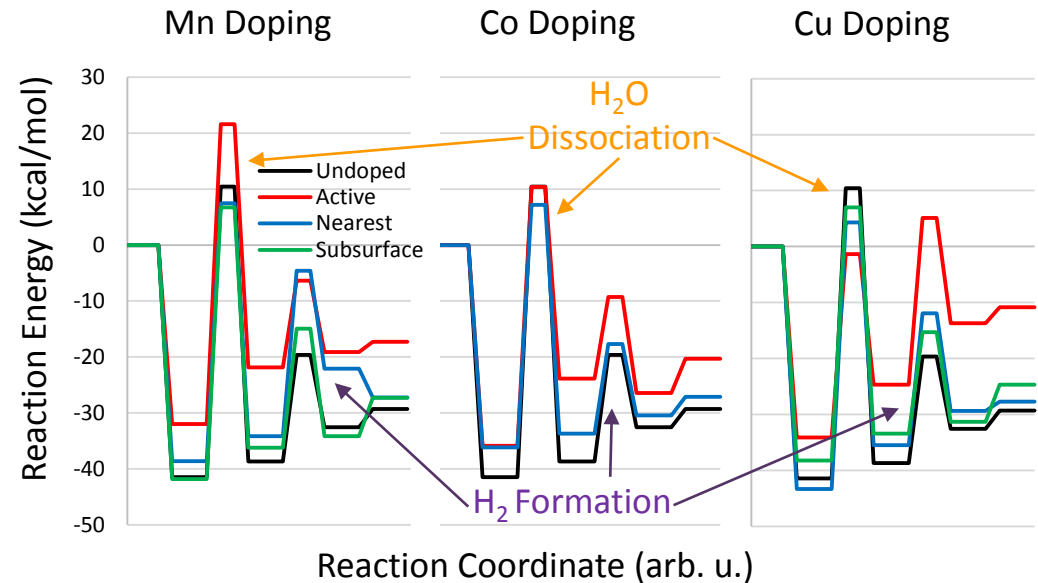
- Improved the reliability of electronic convergence
  - Error introduced by not treating non-occupied bands explicitly
  - Identical structures could have energies that differed by 15 kcal/mol.
- Performed a case study for hydrogen evolution reaction on hercynite.
  - Looked at the lowest energy pathway, involving a surface hydride, and a hydroxyl incorporating into the surface via an oxygen vacancy
  - Considered three different dopants (Co, Cu, Mn) at low concentrations



Activation Energy Difference (kcal/mol) for Various Doped Hercynites vs. Pure Hercynite



By doping we see significant, and generally beneficially, changes in the activation energies

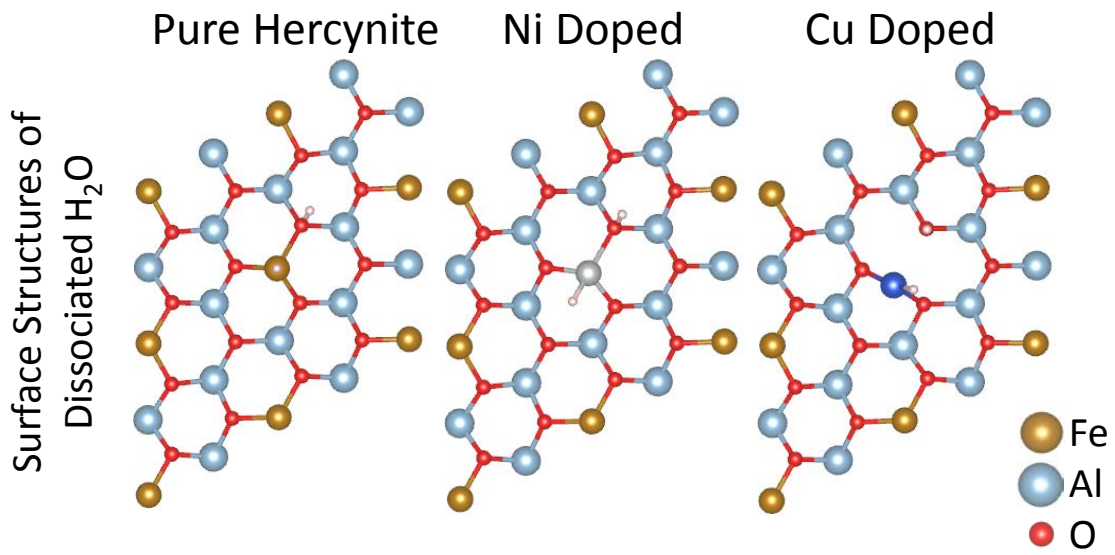


The activation energy for H<sub>2</sub> formation is closely related to the barrier of the reverse reaction (H<sub>2</sub> dissociation = 15 ± 3 kcal/mol). The water dissociation barrier does not obey a simple linear scaling relationship.

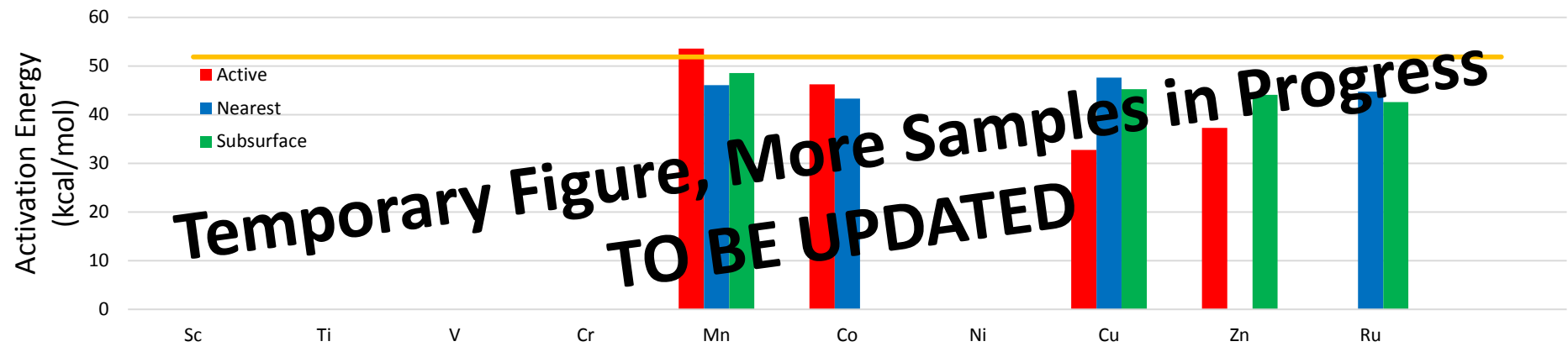
# Accomplishments and Progress – H<sub>2</sub> Evolution Reaction – Focus on H<sub>2</sub>O Dissociation



- Transition state calculations are time consuming
  - Necessary to focus study in order to gather enough data to reliably extrapolate to new structures
- Only a few structures have qualitatively different stable structures
  - Cu, and Ni
  - These have largest differences in activation barriers



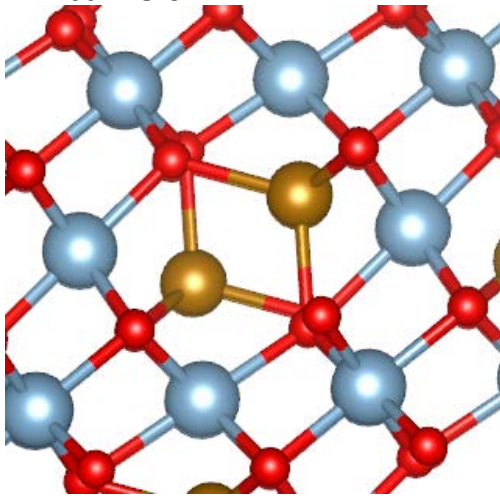
Water Dissociation Activation Energy for Doped Hercynite Materials



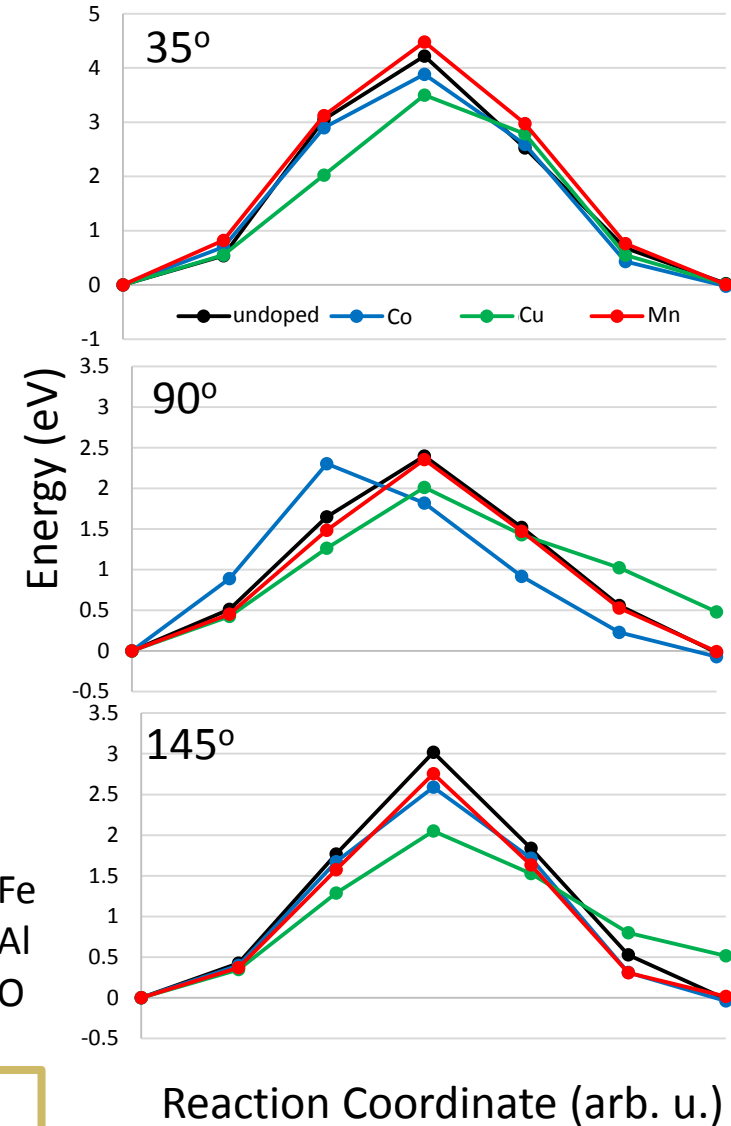
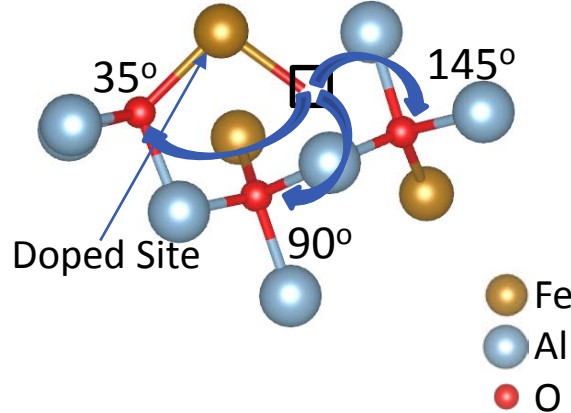
# Accomplishments and Progress – Bulk Transport in Doped Hercynite

- Bulk transport of  $O_{vac}$  must also be considered
  - Surface reaction can not proceed without surface  $O_{vac}$
- The symmetry of the spinel structure provides three possible migration directions
  - Pathways are distinguished by the angle formed from the Fe/dopant neighboring the initial  $O_{vac}$ , the initial  $O_{vac}$  itself, and final  $O_{vac}$ .
- Considering cases with dopant atom neighboring  $O_{vac}$  at low dopant and  $O_{vac}$  concentration (1/16 and 1/64 respectively)
  - Dopant concentration must be high enough to form a percolation pathway through the lattice to achieve these barriers



Hercynite Bulk Structure



Migration Pathways



Bulk transport barriers decrease as later transition elements are introduced to the lattice.

| Collaborator  | Project Roles  |
|---|--|
|  <p>NREL<br/>NATIONAL RENEWABLE ENERGY LABORATORY</p> <p>National Renewable Energy Laboratory (NREL)</p> | <p>High-performance computing facilities (Peregrine). High-throughput computing advisement</p> |
|  <p>Weimer Group, CU Boulder</p>   | <p>Active material synthesis and testing through “sister” DOE project PD114</p>                |

# Accomplishments and Progress: Responses to Previous Year Reviewer' Comments



| Reviewer Comment   | Response to Comment  |
|--|--|
| <p>Suggest maintaining heavy focus on finding redox materials with improved performance -- don't let this focus slip.</p>  | <p>Collaboration between this material discovery project and the DOE project (PD114) is ongoing for the entire course of the projects</p>  |
| <p>Reactive materials R&amp;D should include some detailed investigation of the effects of kinetics and oxygen vacancy levels on active material bond strength for better understanding of the relationship between production capacity and material durability.</p> | <p>Investigations on the detailed kinetic mechanisms of the RedOx reactions were a heavy focus this year. Descriptions of these results are provided in the accomplishment and progress section. Initial work on single oxygen vacancies allows for screening of a large number of materials; however, as the pool of candidate materials is narrowed, investigations into the effects of oxygen vacancy levels are planned.</p> |
| <p>The effort in materials development is outstanding, providing a high through-put methodology for candidate active materials identification.</p>   | <p>We are continuing to work on developing, executing, and validating models for high throughput screening of the thermodynamics and kinetics of candidate active materials.</p>   |

Note: This project is funded by NSF. No reviewer comments were provided directly for this project. Comments were taken from DOE "Sister" project PD-114



# Remaining Challenges and Barriers

- Thermodynamic Screening
  - Higher H<sub>2</sub> productivity needed for higher efficiency and lower cost
  - Spinel inversion can be critical to predicted behavior and needs to be included into high-throughput modeling
  - Doped materials have additional computational complexities that must be considered
- Kinetic Screening
  - Faster reduction and oxidation kinetics required for feasible STWS processes
  - Developing a descriptor model for kinetics requires a large set of explicit kinetic calculations
  - Materials with random structure/occupancy have large space of possible structures
- Material Testing
  - Materials must be stable over many water splitting cycles and must be compatible with reactor containment materials

***Project Objective: Develop novel reactor materials capable of producing 50,000 kg H<sub>2</sub>/day at a cost < \$2/kg H<sub>2</sub> in a particle solar thermal water splitting system.***





# Proposed Future Work

- Thermodynamic Screening
  - Incorporate cation inversion into screening methods for spinel materials
  - Complete screening of binary spinels and begin screening doped spinels
  - Utilize lessons learned from perovskite screening validation study to screen doped perovskites
- Kinetic Screening
  - Expand study to new materials to begin development of descriptor model
  - Investigate reactions on perovskite surfaces. May require implementation of a genetic algorithm due to random doping
- Material Testing
  - Test perovskites in SFR and/or TGA to provide feedback to validation study
  - Synthesize and test H<sub>2</sub> production of various spinels in SFR
  - Work with DOE project to test long-term stability of new materials

# Technology Transfer Activities

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None to date



- Approach
  - Computational prototyping of metal oxide materials integrating theory and experimentation
- Thermodynamic Screening
  - Majority of binary normal spinels screened for STWS ability
  - Promising spinel materials identified through the inclusion of inversion in screening process
  - Structure and magnetic ordering play a critical role in predicting the STWS behavior of perovskite metal oxides
- Kinetic Screening
  - Quantified reaction barriers on hercynite and doped hercynite surfaces
  - Low concentrations of Cu shows promise in enhancing surface reactions
  - Determined oxygen vacancy diffusion barriers for hercynite and doped hercynite materials
  - Bulk transport barriers decrease as later transition elements are introduced to the lattice

# Acknowledgements

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Amanda Hoskins (Univ. of Colorado Boulder)

Brian Ehrhart (Univ. of Colorado Boulder)

Aaron Holder (NREL)

National Science Foundation - CBET



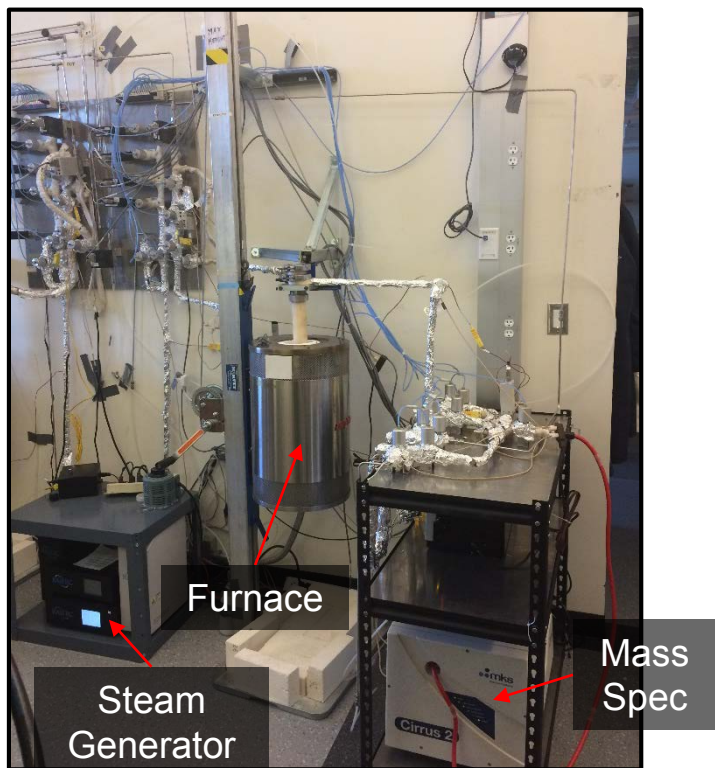
# Technical Backup Slides

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# Accomplishments and Progress – DOE “Sister” Project: Material Testing

- Synthesis of materials using a citrate gel process
  - Homogeneous product with control of stoichiometry
- Materials tested using stagnation flow reactor (SFR)
  - Quantify  $H_2$  production at different conditions
  - Can remove diffusion effects to fit kinetic models to data
- New SFR built for long-term material testing
  - Materials must be stable over many cycles

## New SFR for Long-Term Material Testing







# Publications and Presentations

## Publications

- Muhich, C. L., B. D. Ehrhart, V. A. Witte, S. L. Miller, E. N. Coker, C. B. Musgrave, A. W. Weimer. (2015). "Predicting the Solar Thermochemical Water Splitting Ability and Reaction Mechanism of Metal Oxides: A Case Study of the Hercynite Family of Water Splitting Cycles." Energy & Environmental Science **8**(12): 3687-3699.
- Muhich, C. L., B. D. Ehrhart, I. Alshankiti, B.J. Ward, C. B. Musgrave, A. W. Weimer. (2015) "A Review and Perspective of Efficient H<sub>2</sub> Generation via Solar Thermal Water Splitting." Wiley Interdisciplinary Reviews: Energy and Environment

## Presentations

- S. L. Miller, C. L. Muhich, R. Trottier, B. D. Ehrhart, A. W. Weimer, and C. B. Musgrave, "Screening of Metal Oxide Materials for Solar Thermochemical Water Splitting," in American Institute of Chemical Engineers (AIChE) Annual Meeting, Salt Lake City, UT, 2015.
- C. Muhich, K. Weston, D. Arifin, A. McDaniel, E. Coker, B. Ehrhart, V. Witte, C. Musgrave, A. Weimer. "The Mechanism of the Doped-Hercynite Cycle for Solar-thermal Water Splitting" presented at ACS Spring Meeting, March 2015 (Denver, Co)
- C. Muhich, K. Weston, B. Ehrhart, V. Witte, D. Arifin, A. McDaniel, E. Coker, C. Musgrave, A. Weimer. "The Chemistry and Thermodynamics of the Hercynite Cycle Solar-thermal Water Splitting Reaction" presented at AIChE Annual Meeting, Nov 2014 (Atlanta, Ga)
- C. Muhich, B. Ehrhart, K. Weston, I. Al-Shankiti, D. Arifin, A. McDaniel, C. Musgrave, A. Weimer. "Extracting Kinetic Information from Complex Gas-solid Reaction Data: the Kinetics of Hercynite Materials for Solar Thermal CO<sub>2</sub> Splitting" presented at AIChE Annual Meeting, Nov 2014 (Atlanta, Ga)