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# HydroGEN Seedling: Accelerated Discovery of Solar Thermochemical Hydrogen Production Materials via High-Throughput Computational and Experimental Methods

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Project End Date: September 30, 2020

## Overall Objectives

- Theoretical stability analysis of at least 8,500 “potential” compounds, based on a combination of existing data located in material databases and new density functional theory (DFT) calculations.
- Determination of oxide formation enthalpy, bandgap, and atomic electronegativity for at least 500 theoretically stable compounds, based on a combination of existing data located in material databases and new DFT calculations.
- Determination of material properties that can be used as identifiers for water-splitting performance and verification of predictive capability experimentally.
- Production of combinatorial thin-film “libraries” for at least 20 material families that have been identified by the theoretical screening as candidate materials.
- Demonstration that thin-film compositions of candidate material families can be evaluated for solar thermochemical hydrogen production (STCH) potential using simple experimental techniques.
- Identification of at least three new materials that split water under any steam-to-hydrogen ratio with a hydrogen capacity at least equal to

that of cerium oxide (ceria) under the reduction conditions of 1,350°C and oxidation temperatures of 850°–1,000°C.

- Identification of one or more new materials that split water under steam-to-hydrogen ratios lower than 10:1 and with a hydrogen capacity under the reduction conditions of 1,350°C and oxidation temperatures of 850°–1,000°C at least equal to that of ceria under the reduction conditions of 1,450°C and oxidation temperatures of 850°–1,000°C.
- Characterization of final materials including cycling, durability, thermodynamic and kinetic property investigations, and performance verification at both Colorado School of Mines and Sandia National Laboratory’s Stagnation Flow Reactor facility.

## Fiscal Year (FY) 2018 Objectives

- Theoretical stability analysis of at least 4,250 “potential” compounds, based on a combination of existing data located in material databases and new DFT calculations.
- Determination of oxide formation enthalpy, bandgap, and atomic electronegativity for at least 250 theoretically stable compounds, based on a combination of existing data located in material databases and new DFT calculations.
- Determination of material properties that can be used as identifiers for water-splitting performance and verification of predictive capability experimentally.
- Production of combinatorial thin-film “libraries” for at least 10 material families that have been identified by the theoretical screening as candidate materials.
- Demonstration that thin-film compositions of candidate material families can be evaluated for STCH potential using simple experimental techniques.
- Identification of at least one new material that splits water under any steam-to-hydrogen ratio

with a hydrogen capacity at least equal to that of ceria under the reduction conditions of 1,350°C and oxidation temperatures of 850°–1,000°C.

## Technical Barriers

This project addresses the following technical barrier from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan<sup>1</sup>:

(S) High-Temperature Robust Materials.

## Technical Targets

The objective of this project is to discover new STCH materials. Those materials are necessary to meet the following DOE 2020 STCH targets:

- Cost: \$2/kg H<sub>2</sub>
- Steam-to-hydrogen efficiency: 20%

## FY 2018 Accomplishments

- Performed high-throughput DFT screening of 400 potential compounds and detailed DFT calculations, involving charged and neutral defects, for 15 potential compounds.
- Our National Renewable Energy Laboratory theory node partners (S. Lany et al.) identified that the propensity of an oxide to form charged oxygen vacancies (as opposed to charge-neutral vacancies) is a key (and previously overlooked) metric for STCH potential.
- Produced 15 combinatorial library films across six material families
- Successfully developed a proof-of-concept protocol for rapid optical screening of combinatorial films for thermochemical activity.
- The hydrogen production of three compositions within the Ce<sub>x</sub>Sr<sub>2-x</sub>MnO<sub>4</sub> compositional family, x = 0.1, 0.2, and 0.3, exceeded the Milestone 3.2 target of 59 μmol H<sub>2</sub>/g sample (based on the performance of ceria under similar conditions) with production of 218, 247, and 166 μmol H<sub>2</sub>/g sample, respectively.

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<sup>1</sup> <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

## INTRODUCTION

Two-step metal oxide cycles for solar thermochemical hydrogen production have the potential to produce industrial-scale quantities of hydrogen. In step one, a suitable oxide is defected by driving oxygen from the lattice at high temperatures derived from concentrated solar energy. In step two, and upon exposure to steam at a lower temperature, oxygen is stripped from steam and transferred back into the oxide. This completes the cycle and results in the net production of hydrogen.

While ceria has shown itself to be the best-performing and most cycle-tolerant STCH oxide, it requires very high reduction temperatures ( $>1,500^{\circ}\text{C}$ ) to attain sufficient per-cycle hydrogen yield. This leads to severe efficiency penalties that make the 2020 target of 20% steam-to-hydrogen efficiency unattainable. Ultimately, this work looks to culminate in the discovery and characterization of new STCH materials that can produce hydrogen at quantities that will attain the 20% steam-to-hydrogen efficiency target and facilitate the production cost target of  $<\$2/\text{kg H}_2$ . This requires finding a material that reduces significantly at the target reduction temperature of  $1,350^{\circ}\text{C}$  under moderate oxygen partial pressures of 10–100 ppm and can split water while in the presence of hydrogen at a steam-to-hydrogen ratio of 10:1.

## APPROACH

Because STCH utilizes the full solar spectrum, it has the potential to achieve high theoretic efficiency. Despite its promise, however, surprisingly few candidate STCH materials have been uncovered that can compete with ceria, which remains the state of the art. Our objective is to merge combinatorial synthesis methods with combinatorial theoretical calculations to discover new potential materials for use in two-step metal oxide cycles for STCH. This project will make significant inroads to replacing ceria by obtaining outcomes along several distinct fronts: combinatorial DFT screening; combinatorial thin-film production and testing; bulk powder synthesis and characterization; and the integration of experimental results into the refinement of DFT methodologies and screening criteria. By combining these capabilities with the high-throughput nature of combinatorial synthesis and testing, our goal is to not only efficiently and methodically uncover new potential materials that can meet DOE's 2020 targets, but to better understand fundamental links between oxide structure, chemical composition, and STCH performance.

As a HydroGEN Energy Materials Network (EMN) seedling project, we are afforded the opportunity to leverage the national labs' world-class capability and expertise. This collaboration is critical to our project, with interactions occurring with three different nodes across all three of our tasking fronts. The "First Principles Materials Theory for Advanced Water Splitting Pathways" node, led by Stephan Lany, is assisting with all DFT work, and Andriy Zakutayev's "High-Throughput Experimental Thin Film Combinatorial Capabilities" node is supplying thin films and characterization for the rapid screening effort. Finally, actual water-splitting testing is being performed using Sandia's "Virtually Accessible Laser Heated Stagnation Flow Reactor for Characterizing Redox Chemistry of Materials Under Extreme Conditions" node, overseen by Anthony McDaniel.

## RESULTS

### Task 1: Computation Effort

The computational effort comprises two distinct thrust areas: (1) searching for promising transition-metal-doped perovskites among known compounds, and (2) discovery of new materials using advanced structure search modeling techniques.

In the first thrust area, a detailed protocol for determining good STCH compounds was established. The workflow consisted of evaluating the formation enthalpy followed by calculating its stability against competing phases. The temperature-pressure requirements for ideal STCH material translates to a unique oxygen chemical potential window [1] that can be used as a first descriptor in determining the suitability of a given composition. This is followed by a second descriptor that relates to charged defect formation energies

( $E_f$ ). It was recently shown by the National Renewable Energy Laboratory's Stephan Lany that an additional electronic entropy contribution is obtained when the O vacancies form in a charged  $V_O^{2+}$  state [1].

Figure 1 shows the  $E_f$  relative to the valence band maximum for charged and neutral  $V_O$  for ternaries and quaternaries. A closer inspection reveals important trends such as (1) the addition of Y, La, and Ta increases the  $E_f$ ; (2) replacing Ba with Sr increases the  $E_f$ ; and (3) Ce and V additions result in  $E_f$  that is in the desired range (2.5–3.5 eV). These trends lay out a guiding principle that is critical in *informing* the selection of elements for the structure search in the second thrust area. In addition to sampling the defects for various crystallographic positions, a detailed configurational defect sampling was performed for BaMnO<sub>3</sub> (BMO) and BaCe<sub>0.25</sub>Mn<sub>0.75</sub>O<sub>3</sub> (BCM). It was found that the oxygen  $E_f$  can be promoted if the vacancy sits near a Ce in BCM. The magnetic configuration sampling was found to have smaller impact on  $E_f$  as demonstrated by anti-parallel and parallel states of Mn neighboring the  $V_O$  in BCM.

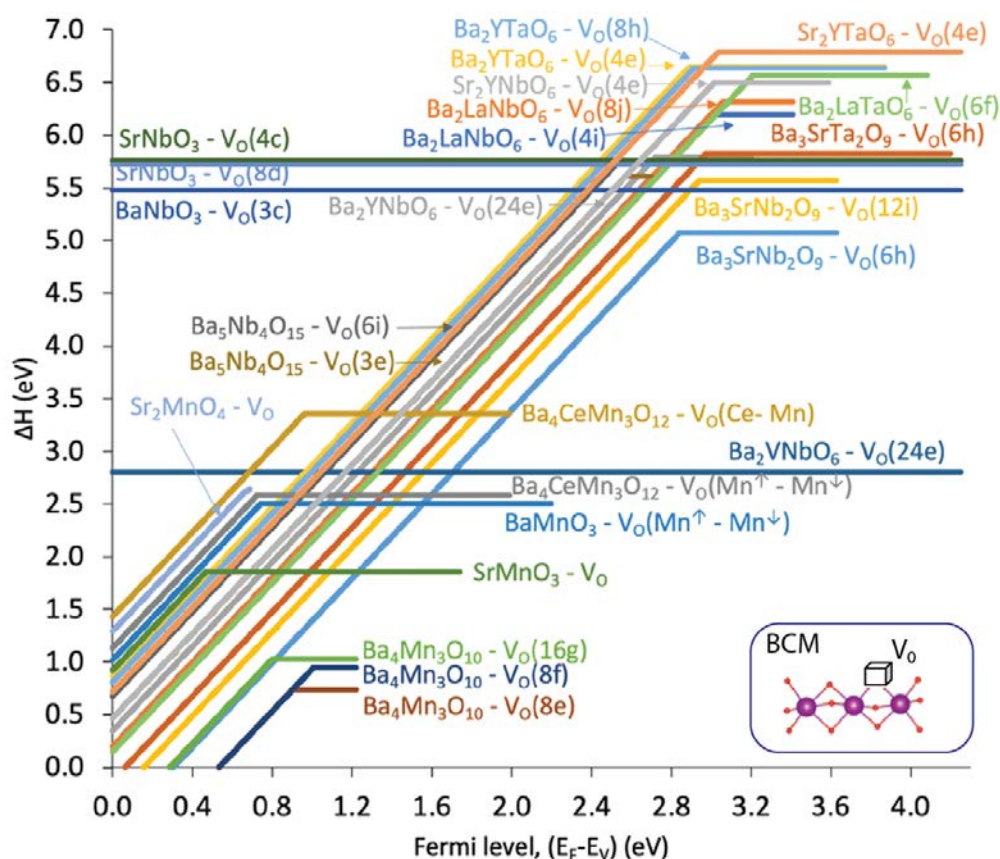


Figure 1. Calculated oxygen vacancy ( $V_O$ ), charged and neutral, formation energies for several ternaries and quaternaries studied in this work. The defect calculation involved studying various Wyckoff positions (as shown by Wyckoff labels next to compositions) and magnetic configuration specifically for BaCe<sub>0.25</sub>Mn<sub>0.75</sub>O<sub>3</sub> (inset shows  $V_O$  with different Mn neighbors that can take varying spin arrangements). Compositions in the range of 2.5–3.5 eV are of greatest interest.

The second thrust area focused on discovering novel quaternary oxides using random and prototype structure search methodologies. The cation search space constituted combinations of Ba, Sr, La, Ce, and Mn, with the constraint that the unit cell had no more than 20 atoms. This limit was placed to enable proper sampling of random structures in a realistic timeline and given computational resources. Figure 2 shows predicted oxide formation enthalpy for all possible stoichiometries where the Ce and Mn oxidation states were kept fixed at +4. A cross-validation of this approach involved searching for known composition, such as BaCeO<sub>3</sub>. The  $\Delta H_f$  of BaCeO<sub>3</sub> was found to be in close agreement to that of the known structure ( $\sim 0.03$  eV/atom). This procedure resulted in the discovery of an La containing compound, La<sub>2</sub>CeMn<sub>3</sub>O<sub>11</sub>, that has not been previously reported

in literature. The  $\Delta H_f$  of this material is slightly higher than that of BCM, suggesting that it may be well suited to STCH application. Additional calculations are in process to further understand its potential as a STCH material.

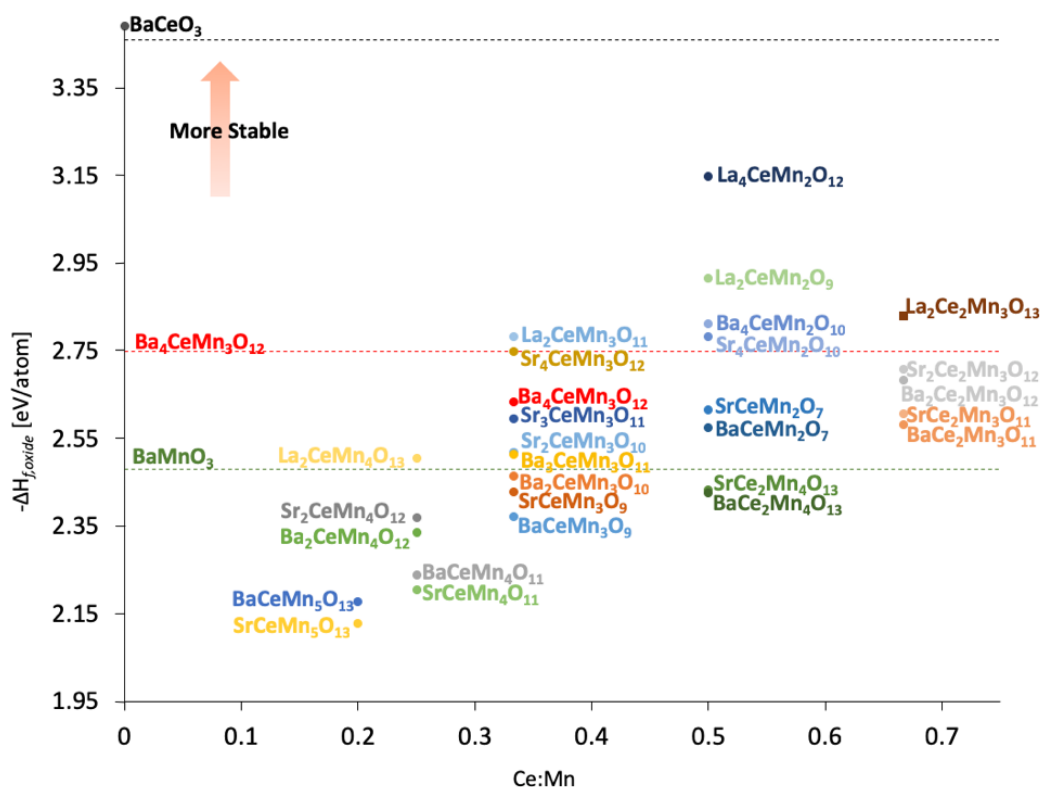


Figure 2. Predicted oxide formation enthalpy ( $\Delta H_f$ ) for quaternary compounds identified in the structure search procedure for [(Ba,Sr,La),Ce,Mn,O] chemical space. The horizontal dashed line corresponds to  $\Delta H_f$  of known compositions.  $\Delta H_f$  is a rough predictor of oxygen vacancy formation energy.

The direct tie between DFT-estimated oxygen vacancy formation energy and thermal-gravimetric-analysis-measured extent of reduction was validated across several compositional families. While previously suspected, the confirmation allows for more rapid “down-selection” of DFT-screened STCH candidates to only those that have stability and vacancy formation energies that fall within well-defined bounds. While the energy values listed in Table 1 do not all come from the same computational methodology, the general trends hold across many families and strongly correlate within a family.

Table 1. Comparison of Calculated Oxygen Vacancy Formation Energy and Experimental Extent of Reduction Results. Formation Energies Were Not All Calculated Using Same Methods.

Composition	Vo (DFT) [eV]	Extent of Reduction (Exp) [ $\delta$ ]
CSM1	1.8	0.175
CSM2	2.2	0.12
CSM3	2.7	0.075
BCM	3.0	0.175
BMO	2.5	0.45
BCO	10	0.02
CeO <sub>2</sub>	4	0.04
SLMA6464	1.5	0.20



### Task 2: Combinatorial Effort

The collaboration with the thin film combinatorial node resulted in well over 20 films being produced in the first year. Some of these were single compositions used for evaluation of the optical screening method; however, 15 films had compositional variations.

Table 2. Thin-Film Compositions Produced in Year 1

Single Composition	Combinatorial Families
WO <sub>3</sub>	BaMnO <sub>3</sub> : BaCeO <sub>3</sub>
Fe <sub>2</sub> O <sub>3</sub>	BaCe <sub>0.25</sub> Mn <sub>0.75</sub> O <sub>3</sub> : SrCeMnO <sub>3</sub>
BaCe <sub>0.25</sub> Mn <sub>0.75</sub> O <sub>3</sub>	BaCe <sub>0.25</sub> Mn <sub>0.75</sub> O <sub>3</sub> : LaSrCoMnO <sub>3</sub>
SrCeMnO <sub>3</sub>	BaCe <sub>0.25</sub> Mn <sub>0.75</sub> O <sub>3</sub> : LaSrCoO <sub>3</sub>
LaSrCoO <sub>3</sub>	BaMnO <sub>3</sub> : LaSrCoO <sub>3</sub>
BaMnO <sub>3</sub>	SrMnO <sub>3</sub> : LaSrCoO <sub>3</sub>
BaCeO <sub>3</sub>	
CeO <sub>2</sub>	

The optical-screening method showed promise in the proof-of-concept trials. Figure 3 shows images of two post-oxidized films, one BCM and the other a gradient of BCM and BMO, with the analysis overlaid. Black boxes highlight regions where there is significant color change (at this point, set to a 2% difference in any color channel [i.e., hue, saturation, or brightness]). BCM changed on both films, while the BMO, not a water splitter, did not (depending on the threshold setting). Later testing has not been as successful, and further validation is necessary to determine the long-term viability of the optical technique.

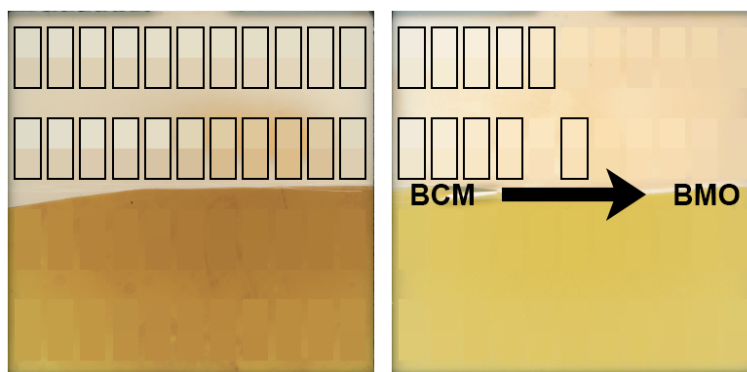
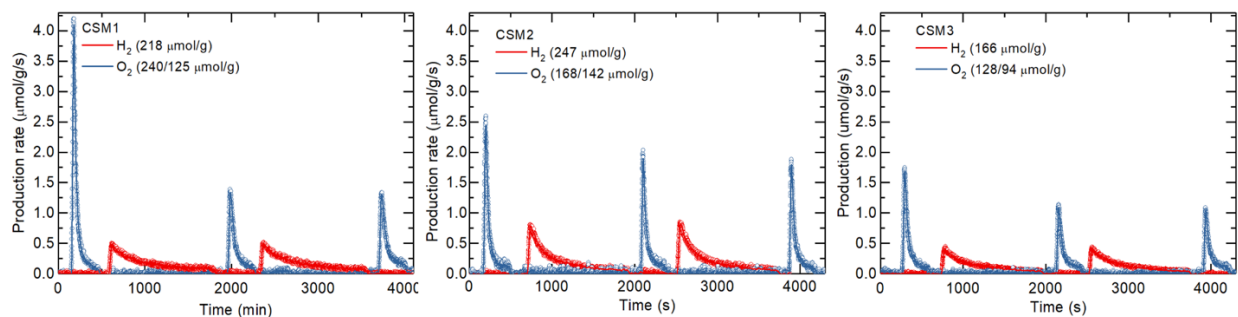


Figure 3. The reduced and then reoxidized test films, BCM on zirconia (left) and a gradient of BCM to BMO on alumina (right). Inside the overlaid rectangles is the reduced film color on top and the oxidized color on bottom. If the color change meets the threshold (currently 2%, which may be difficult to see by eye) the rectangle is highlighted with a black border. In both films, the lower half is the as-received film, while the upper half is the post-processed film (after undergoing the simulated water splitting cycle).

### Task 3: Bulk Testing

Motivated by the development of BCM and the insights from our theory effort, we expanded our search for new Ce- and Mn-containing perovskites. We replaced Ba with Sr on the A-site to permit greater structural and compositional flexibility because BCM is a line-compound material that lacks this compositional tunability. In the process, we instead encountered the unexpected formation of a layered perovskite Ce<sub>x</sub>Sr<sub>2-x</sub>MnO<sub>4</sub> (CSM), previously unreported in the literature for this compositional family. DFT calculations played a key role in the iterative process of identifying and corroborating the stability of the new phase. The hydrogen production of three compositions within the Ce<sub>x</sub>Sr<sub>2-x</sub>MnO<sub>4</sub> compositional family, x = 0.1, 0.2, and 0.3, exceeded the Milestone 3.2 target of 59 μmol H<sub>2</sub>/g sample (based on the performance of ceria under similar conditions) with production of 218, 247, and 166 μmol H<sub>2</sub>/g sample, respectively. Results from Sandia's stagnation flow reactor showing the oxygen peak, during reduction, and hydrogen peak, during oxidation, are shown in Figure 4.



**Figure 4.** Water-splitting results for two complete cycles at  $T_{RE} = 1,400^{\circ}\text{C}$  for 330 s and  $T_{OX} = 1,000^{\circ}\text{C}$  for 1,200 s. Blue lines are oxygen peaks evolved during reduction and red lines are hydrogen peaks recorded during the reoxidation (water splitting) step. The peaks were integrated to calculate the total amount of hydrogen and oxygen produced, with the results listed in the legend. For the oxygen values, the first value indicates the oxygen produced by the initial reduction and the second value corresponds to the subsequent cycles average. The hydrogen value refers to the average hydrogen production.

## CONCLUSIONS AND UPCOMING ACTIVITIES

Great progress was made in the first year of this project. The computational results not only have identified a few new compositional combinations but have helped to clarify both the target stability and defect formation energy bounds for materials screening. Furthermore, the results from our combined theory and experiment approach have helped establish how certain elements (e.g., Ba vs. Sr on the A site; Ce, Mn, V, Nb, and Y on the B-site) can be combined to favorably tune those parameters. Our development of  $\text{Ce}_x\text{Sr}_{2-x}\text{MnO}_4$  is a tangible example of the payoff from this approach, and its promising performance further motivates the search for additional perovskite-related compounds with unique and potentially valuable STCH properties.

Going forward, our efforts will follow a similar track for the next year, including the continued collaboration with all three EMN nodes. Year 2 will see further refinement of the computational effort to take advantage of the lessons learned in the first year. There will also be a reversal of roles as portions of the combinatorial film effort will be used to inform the computational work, rather than vice-versa. This information will mainly consist of stable structure/phase identification and to delineate the limits of element solubility in complex, multi-cation compositional regions of interest. These are both tasks that are difficult for DFT theory but that the combinatorial thin-film experiment process is exceptionally well equipped to handle.

The optical screening technique will also be further investigated in the first part of the year. Additional testing is necessary to unequivocally determine the feasibility of such a technique. Other characterization techniques or a revamped in situ screening process may turn out to be more viable.

Finally, an in-depth thermodynamic study of the CSM system will be performed to feed valuable experimental information back to the computational team. This work dovetails nicely with the EMN's new "super-node" work on the BCM system.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. Debora R. Barcellos, Michael Sanders, Jianhua Tong, Anthony H. McDaniel, and Ryan O'Hayre, "BaCe<sub>0.25</sub>Mn<sub>0.75</sub>O<sub>3-δ</sub>—A Promising Perovskite-Type Oxide for Solar Thermochemical Hydrogen Production," *Energy Environ. Sci.* 11 (2018): 3256–3265, DOI: 10.1039/C8EE01989D.

## REFERENCES

1. Stephan Lany, "Communication: The electronic entropy of charged defect formation and its impact on thermochemical redox cycles," *The Journal of Chemical Physics* 148, no. 7 (2018): 071101.