Sandia National Laboratories

Solar Thermochemical Hydrogen Production on Hexagonal Perovskites $BaX_{0.25}Mn_{0.75}O_3$ (X=Ce, Nb, Pr)

Andrew I. Smith[1,a], James E. Park[1], Sean R. Bishop[1], Eric N. Coker[1], Mark A. Rodriguez[1], Andrea Ambrosini[1], H. Evan Bush[1], and Anthony H. McDaniel[2]

1 Sandia National Laboratories, Albuquerque, New Mexico USA, 87185

2 Sandia National Laboratories, Livermore, California USA, 94551

[a] Presenting and corresponding author: aismith@sandia.gov

1. Introduction

Solar thermochemical hydrogen (STCH) production is promising for generating hydrogen gas from water. While cerium oxide (CeO_2) is gaining commercial popularity, it is not optimal for STCH. Recent publications suggest that hexagonal perovskite $BaCe_{0.25}Mn_{0.75}O_3$, (BCM) is a viable water splitter, even at elevated H_2 concentrations. Examined for STCH here are three hexagonal perovskites: $BaCe_{0.25}Mn_{0.75}O_3$, (BCM), $BaNb_{0.25}Mn_{0.75}O_3$ (BNM) and $BaPr_{0.25}Mn_{0.75}O_3$ (BPM)

2. Thermodynamics

H_2O and CO_2 can be thermodynamically split (thermolysis) at temperatures > 3000 °C in a single step. The use of metal oxides, like CeO_2, allows for a two step process, thermal reduction and H_2O/CO_2 splitting, at significantly lower temperatures (1000-1700 °C), making H_2/CO production economically viable.

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \ (1; H_2O\ thermolysis)$$

$$\frac{1}{\delta}MO_x \rightarrow \frac{1}{\delta}MO_{x-\delta} + \frac{1}{2}O_2\ at\ T = \boldsymbol{T_{TR}}\ (\mathbf{2; thermal\ reduction})$$

$$\frac{1}{\delta}MO_{x-\delta} + H_2O \rightarrow \frac{1}{\delta}MO_x + H_2\ at\ T = \boldsymbol{T_{WS}}\ (\mathbf{3; H_2O\ splitting})$$

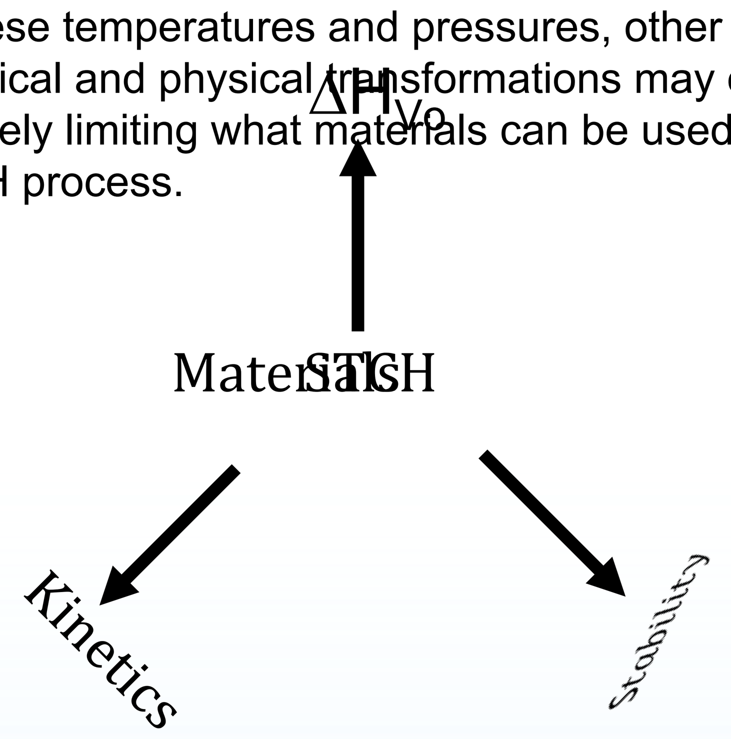
3. Materials Selection

Selecting a STCH capable MO_x is not a trivial process, to be a viable STCH material it must be stable under STCH conditions, have fast kinetics and a reasonably deep reduction potential.

STCH Conditions

- T_{TR} = 1500-1200 °C
- T_{WS} = 1000-800 °C
- pO_2 in reduction = 10^{-3} – 10^{-6} atm
- H_2O: H_2 10:1 in oxidation (higher with advanced separation)

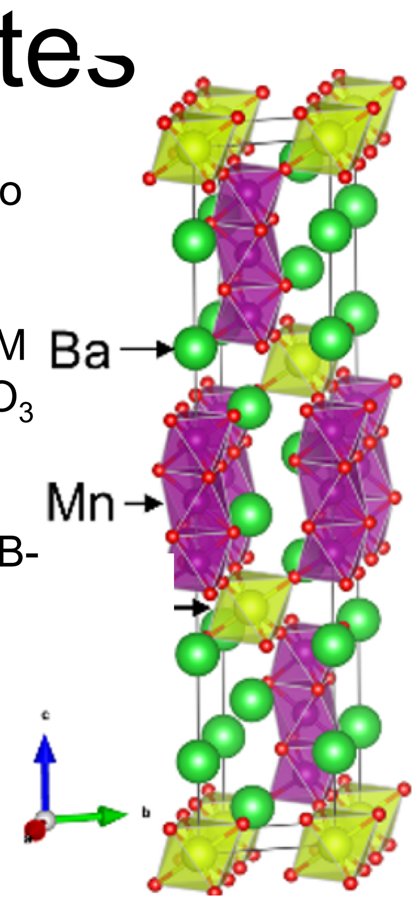
At these temperatures and pressures, other chemical and physical transformations may occur, severely limiting what materials can be used in a STCH process.



CeO_2 has excellent stability and kinetics, however its ΔH_{Vo} (oxygen vacancy formation energy) is too high, limiting its reduction at STCH conditions → investigate BCM, BNM and BPM

4. BXM Perovskites

$BaCe_{0.25}Mn_{0.75}O_3$, (BCM) a hexagonal perovskite, has recently shown the ability to split water and demonstrated improved H_2 production over CeO_2 when T_{TR} =1350 °C. We under took a STCH comparison of BCM to two isostructural materials, $BaNbMn_{0.75}O_3$ (BNM) and $BaPr_{0.25}Mn_{0.75}O_3$ (BPM). It is thought that Mn is redox active, and that modification of the Mn-O bond though the B-Site (Ce, Nb, and Pr) will result in different water splitting behavior.

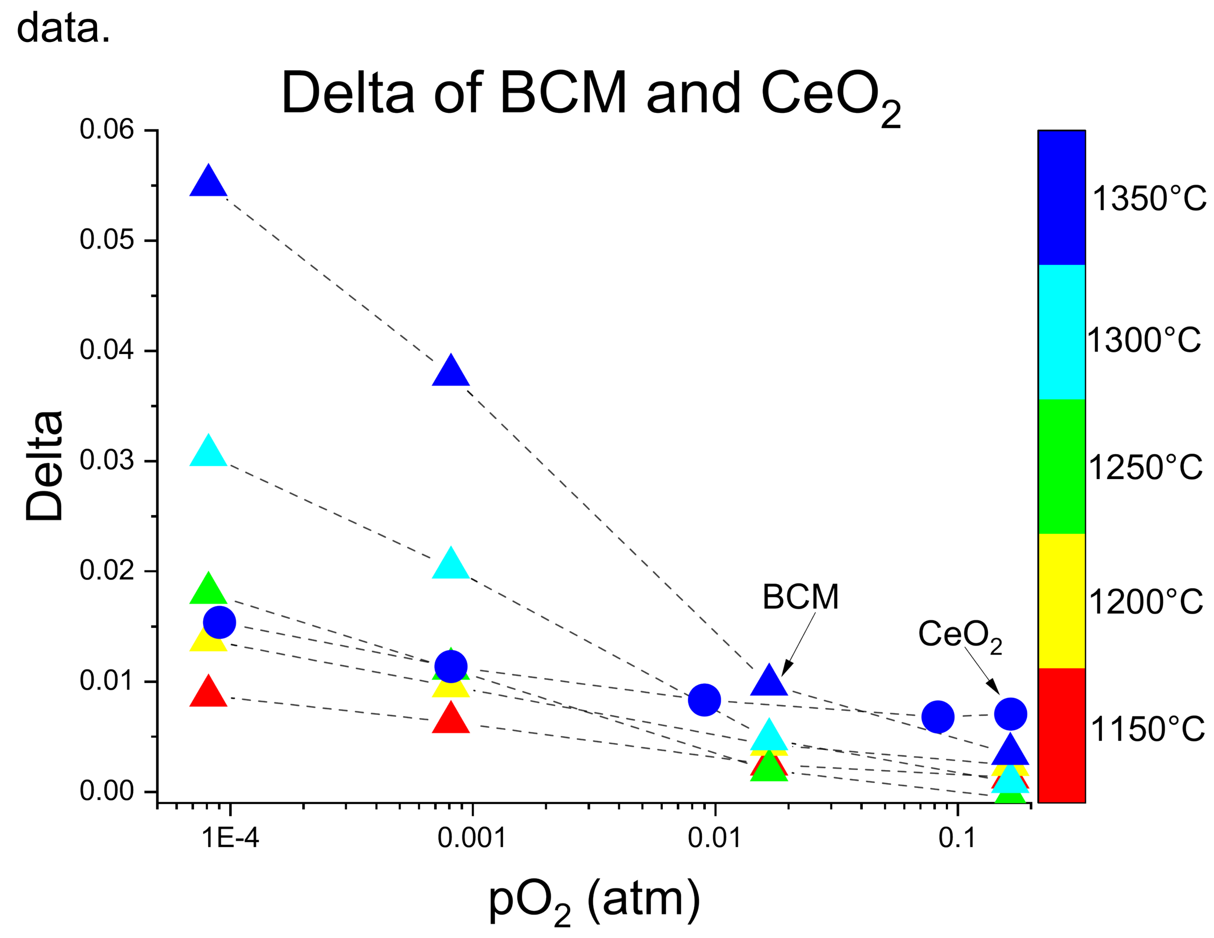


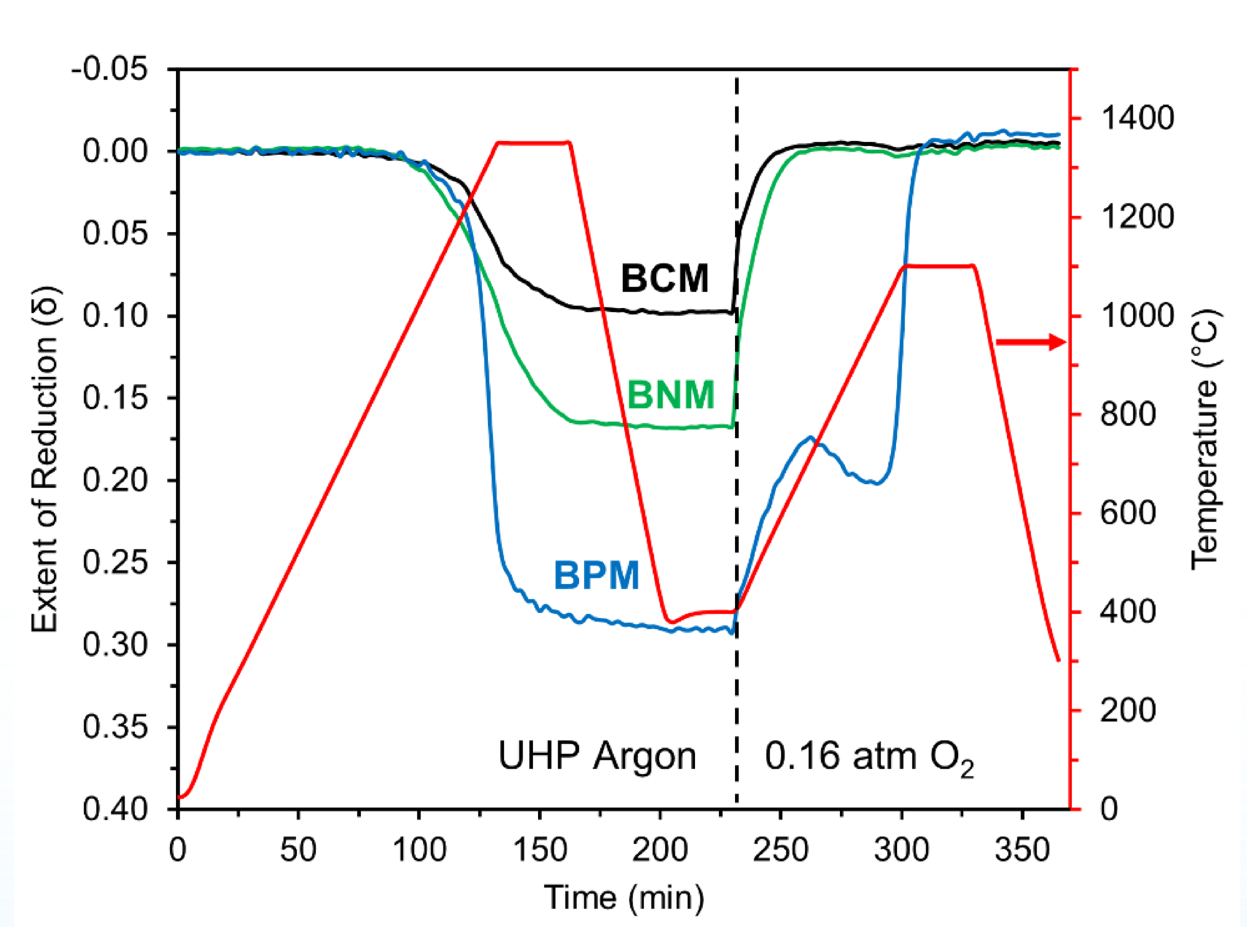
B-Site Modifications

- Pr is more redox active then Ce
- Nb significantly smaller than Ce

5. TGA

Thermogravimetric Analysis (TGA) experiments are used to screen potential STCH materials by measuring their extent of reduction (δ) at various pO_2 and temperatures. TGA of BCM shows significant reduction at T_{TR} >1300 °C and pO_2 < 10^{-3} atm. Phase instability was apparent above 1350 °C in TGA data.

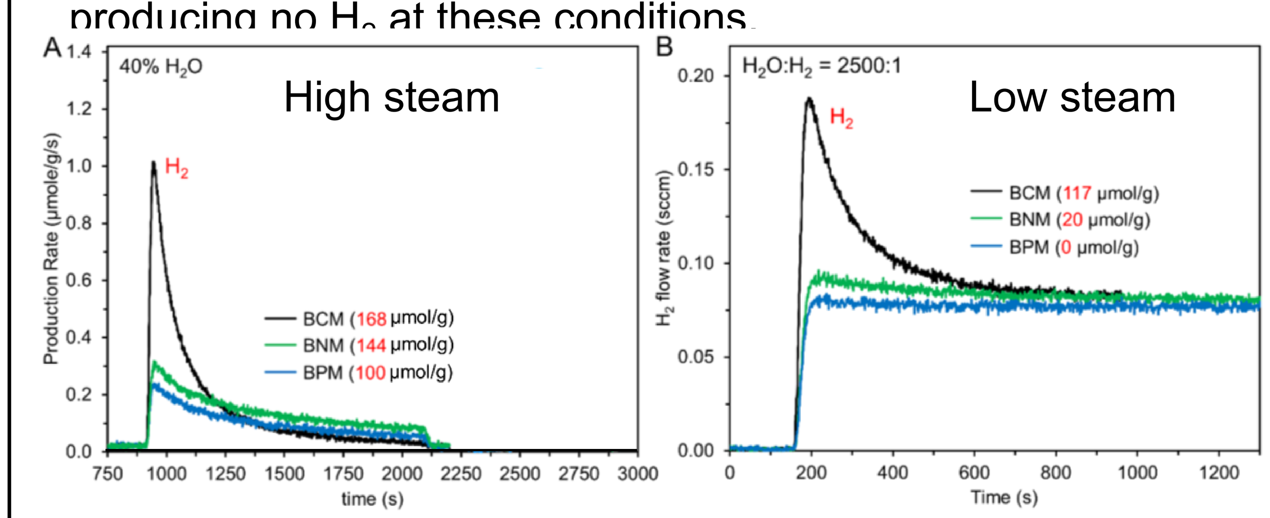




BCM, BNM and BPM showed reduction under Ar at 1350 °C (δ = 0.08-0.28) and oxidation at 1100 °C under air (δ=0), with BCM showing the smallest reduction. BPM shows the largest reduction, suggesting possible $Pr^{+3/+4}$ reduction, oxidation of BPM appears to also show the two-step oxidation of Mn^{+3} to Mn^{+4} and Pr^{+3} to Pr^{+4}.

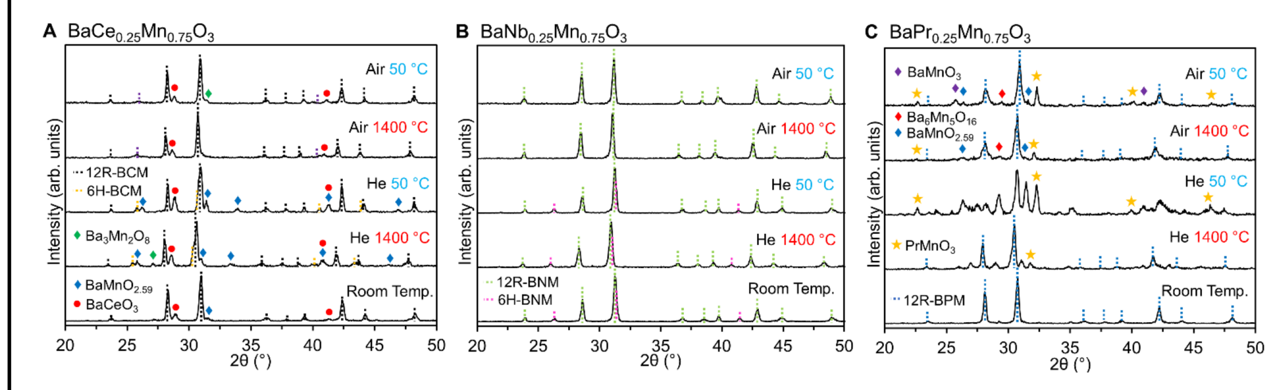
6. Water Splitting

Water splitting experiment carried out with BCM (black), BNM(green) and BPM(blue) T_{TR} =1350 °C in Ar and T_{WS} = 850 °C, showed that all three perovskites can split water at (A) 40% H_2O. These results compare favorably with CeO_2 which only produce 50 umol/g under the same conditions. At lower H_2O: H_2 ratios, (B) H_2O: H_2 = 2500:1, all three perovskites showed reduced H_2 production, with BPM producing no H_2 at these conditions.



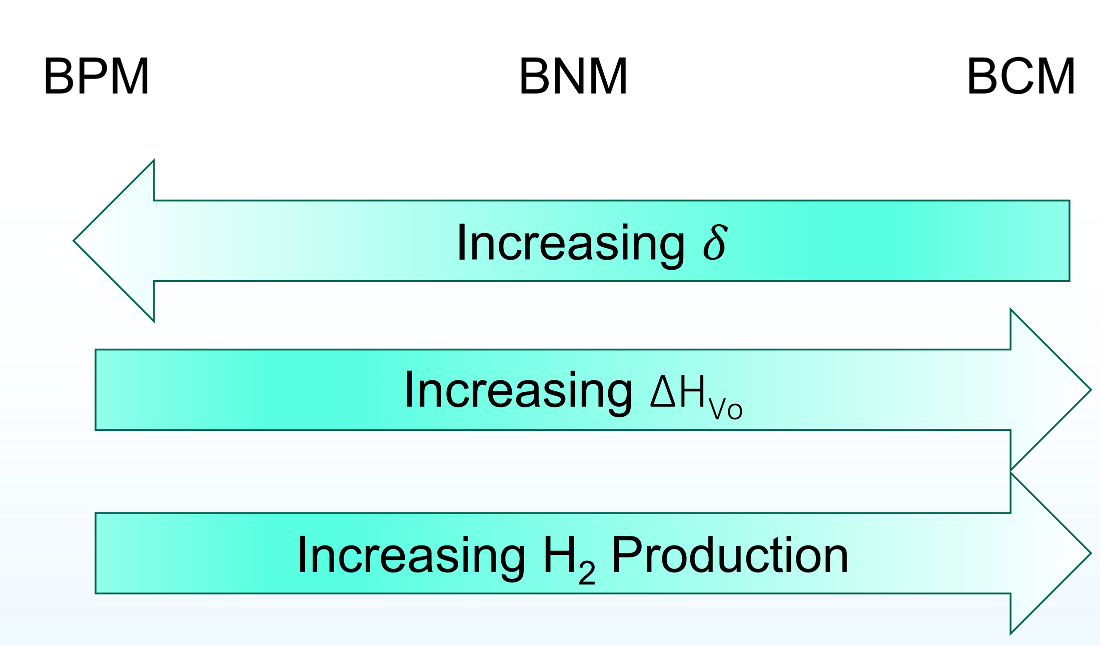
7. XRD

XRD of BCM, BNM and BPM suggests that all three BXM perovskites undergo polytype phase changes (1400 °C and Ar). Of these phase changes, BPM's is the most drastic, it transitions into its constituent oxides. These changes are not likely driven by structural differences, BCM and BPM have similar tolerance factors, but instead by the reduction of Pr^{+4} to Pr^{+3}. This $Pr^{+4/+3}$ reduction leads to phase instability and resulting in the formation of other oxides under reducing conditions.



8. Summary

The hexagonal perovskite family of BCM, BNM and BPM have all been screened as potential water splitters. Of these materials, BCM showed the greatest affinity towards water splitting, despite having the shallowest reduction potential, highlighting the importance of phase stability, and ΔH_{Vo} and the roll it plays in all steps of the STCH process.



U.S. DEPARTMENT OF ENERGY
NNSA

This work was supported by the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy (EERE), Hydrogen and Fuel Cell Technologies Office (HFTO), and specifically the HydroGEN Advanced Water Splitting Materials Consortium, established as part of the Energy Materials Network under this same office. Sandia National Laboratories is a multi-mission 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. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND No.______________

SAND No.______________

Sandia National Laboratories