DESIGN OF MATERIALS FOR SOLAR THERMOCHEMICAL HYDROGEN PRODUCTION

By

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ABSTRACT

Hydrogen is one of the most widely produced and used commodity “chemicals” in the world. Besides its current widespread use in the petrochemicals and ammonia production industries, it also has the potential to be used as an energy carrier for future power, transportation and storage applications. However, the environmental sustainability of hydrogen for such applications can only be assured if it can be obtained from renewable sources.

Solar thermochemical hydrogen production (STCH) is a carbon-free technique that uses solar thermal heat to split water and produce hydrogen. The predicted high process efficiencies and scalability make this technique preferred for large scale hydrogen production over electrolysis or thermolysis.

The current state-of-the-art material for STCH is ceria (CeO$_2$), which produces hydrogen via a relatively straightforward two-step water splitting (WS) cycle. In the first step, carried out at a high temperature, the oxide reduces by creating oxygen vacancies and releases oxygen. In the second step, carried out at a lower temperature, the oxygen deficient oxide splits the water molecule and reoxidizes, thereby releasing hydrogen. The great challenge of using ceria is the high temperature required for the first reduction step, which is over 1600 °C. In this work I propose new materials for water splitting BaCe$_{0.25}$Mn$_{0.75}$O$_3$ and three materials of composition Ce$_a$Sr$_{2-a}$MnO$_4$ ($a = 0.1, 0.2$ and $0.3$) that meet or exceed ceria’s water splitting performance, but at significantly lower temperatures (~1350-1400 °C).

BaCe$_{0.25}$Mn$_{0.75}$O$_3$ (BCM) is shown to produce about 3X more H$_2$ than ceria at a lower reduction temperature (1350 °C) and is demonstrated to have a higher steam-to-hydrogen conversion than other promising perovskite candidates. This steam-to-hydrogen conversion concept was shown to be of extreme importance for the application of the STCH process in a realistic reactor. The thermodynamic properties of BCM were investigated to further understand the underlying reasons for its outstanding performance. This study led to the discovery of a beneficial polytype phase change that may take place during STCH cycling in this materials system and that likely contributes to its performance.
Motivated by my discovery of the BCM system, we subsequently identified a Ruddlesden-Popper phase, $\text{Ce}_a\text{Sr}_{2-a}\text{MnO}_4$ (CSM) which also showed excellent potential for STCH WS. Importantly, this phase had never before been reported in the literature. After a structure characterization study, this new materials system was demonstrated to produce 2-3X more hydrogen than ceria at the reduction temperature of 1400 °C. Both the BCM and CSM systems open up new directions for the design and optimization of redox-active STCH materials that can provide higher performance at lower temperatures than $\text{CeO}_2$, thereby underscoring remaining opportunities to further discover new materials for this important renewable energy application.
# TABLE OF CONTENTS

ABSTRACT ................................................................................................................................................. iii

LIST OF FIGURES ................................................................................................................................... viii

LIST OF TABLES ..................................................................................................................................... xvi

ACKNOWLEDGMENTS ....................................................................................................................... xviii

CHAPTER 1 INTRODUCTION .............................................................................................................. 1
  1.1 Thesis Statement ........................................................................................................... 1
  1.2 Motivation ..................................................................................................................... 1
  1.3 Thesis Organization ...................................................................................................... 3
  1.4 Acknowledgment of Contributions ............................................................................... 4
  1.5 Financial support ........................................................................................................... 6

CHAPTER 2 BACKGROUND ................................................................................................................ 7
  2.1 The role of hydrogen in society .................................................................................... 7
  2.2 Renewable water splitting techniques ........................................................................... 8
  2.3 Solar thermochemical hydrogen production ............................................................... 10
  2.4 Thermodynamics of STCH materials ......................................................................... 13
  2.5 Design criteria for water splitting materials ............................................................... 17
  2.6 Doped-ceria compounds for STCH ............................................................................ 19
  2.7 Perovskite oxides for STCH ....................................................................................... 22

CHAPTER 3 DESIGN OF NEW PEROVSKITES FOR STCH ............................................................. 29
  3.1 Screening method to identify potential STCH-active materials ................................. 29
  3.2 Perovskites synthesized in this work .......................................................................... 32

CHAPTER 4 EXPERIMENTAL METHOD FOR ASSESSING PRODUCTIVITY AND
CONVERSION IN METAL OXIDE THERMOCHEMICAL WATER AND
CARBON DIOXIDE SPLITTING WITHOUT KNOWLEDGE OF OXIDE
THERMODYNAMICS .................................................................................................... 40
4.1 Experimental methods

4.2 Acknowledgments

4.4 Supporting information

CHAPTER 5  
BaCe$_{0.25}$Mn$_{0.75}$O$_{3-δ}$ — A PROMISING PEROVSKITE-TYPE OXIDE FOR SOLAR THERMOCHEMICAL HYDROGEN PRODUCTION

5.1 Introduction

5.2 Experimental

5.3 Results and discussion

5.4 Conclusions

5.5 Acknowledgments

5.6 Co-authors contribution

5.7 Supporting information

CHAPTER 6  
PHASE IDENTIFICATION OF THE LAYERED PEROVSKITE Ce$_6$Sr$_2$MnO$_4$ AND APPLICATION FOR SOLAR THERMOCHEMICAL WATER SPLITTING

6.1 Introduction

6.2 Experimental

6.3 Results and discussion

6.4 Conclusions

6.5 Acknowledgments

6.6 Co-authors contribution

6.7 Supporting information

CHAPTER 7  
CONCLUSIONS

7.1 Future Work

APPENDIX A  
CO AND H$_2$ PRODUCTION LITERATURE REVIEW ON DOPED-CERIA AND PEROVSKITE MATERIALS

APPENDIX B  
TEMPERATURE PROGRAMMED REDUCTION RESULTS FOR PEROVSKITE FAMILIES

APPENDIX C  
WATER SPLITTING RESULTS OBTAINED FOR PEROVSKITES
APPENDIX D  INVESTIGATION OF BaCe$_{0.25}$Mn$_{0.75}$O$_3$ POLYTYPES ................................................... 152

D.1 Introduction .............................................................................................................. 152
D.2 Experimental ......................................................................................................... 154
D.3 Results and discussion ......................................................................................... 157
D.4 Conclusion ............................................................................................................ 165

REFERENCES ............................................................................................................. 176
LIST OF FIGURES

Figure 2.1: Two-step solar thermochemical water splitting cycle illustration for a generic metal oxide MOx using Kröger-Vink notation. ................................................................. 10

Figure 2.2: Change in molar Gibbs free energy with respect to temperature for H₂ oxidation, CO oxidation and ceria oxidation at different oxygen stoichiometries all in equilibrium at pO₂ = 1 bar. .......................................................................................................................... 15

Figure 2.3: CO production via thermochemical CO₂ splitting by ceria and several doped-ceria materials (Ce₀.₇₅Zr₀.₂₅O₂, Ce₀.₇₅Hf₀.₂₅O₂, Ce₀.₈₀Ti₀.₂₀O₂ and Ce₀.₈₅La₀.₁₅O₂ named CeZr25, CeHf25, CeTi20 and CeLa15 respectively) compiled from the literature [57]. Reduction temperatures used were 1400 and 1500°C and oxidation temperatures used were 700, 800, 900, 1000 and 1100 °C as indicated in the plot using 500 sccm of CO₂. 20

Figure 2.4: H₂ production via thermochemical H₂O splitting by ceria and several doped-ceria materials (Ce₀.₇₅Zr₀.₂₅O₂, Ce₀.₈₅Fe₀.₁₅O₂, Ce₀.₈₅Co₀.₁₅O₂, Ce₀.₈₅Ni₀.₁₅O₂, Ce₀.₈₅Mn₀.₁₅O₂, Ce₀.₉₀Mn₁₀O₂, Ce₀.₉₀Fe₀.₁₀O₂, Ce₀.₉₀Ni₀.₁₀O₂ and Ce₀.₉₀Cu₀.₁₀O₂, named CeZr25, CeFe15, CeCo15, CeNi15, CeMn15, CeFe10, CeNi10 and CeCu10 respectively) compiled from the literature. Reduction temperatures used were 1300, 1400, 1450 and 1500°C and oxidation temperatures used were 845, 945, 1000, 1045, and 1150 °C as indicated in the plot. .......................................................................................................................... 21

Figure 2.5: BaTiO₃ cubic perovskite crystal structure. The blue atoms are Ti cations sitting on the B-site of the perovskite forming oxygen (red atoms) octahedra. Ba sits on the A-site of the perovskite and is bonded to 12 oxygens. .......................................................................................................................... 23

Figure 2.6: CO production via thermochemical CO₂ splitting by several perovskite materials LSM (La₀.₆₅Sr₀.₃₅MnO₃ and La₀.₅₀Sr₀.₅₀MnO₃), LCM (La₀.₆₅Ca₀.₃₅MnO₃, La₀.₅₀Ca₀.₅₀MnO₃ and La₀.₃₃Ca₀.₆₆MnO₃), LSF (La₀.₇₅Sr₀.₂₅FeO₃₃), ACM (Y₀.₅₀Ca₀.₅₀MnO₃, Nd₀.₅₀Ca₀.₅₀MnO₃, Sm₀.₅₀Ca₀.₅₀MnO₃, Gd₀.₅₀Ca₀.₅₀MnO₃ and Dy₀.₅₀Ca₀.₅₀MnO₃) ASM (Y₀.₅₀Sr₀.₅₀MnO₃, Nd₀.₅₀Sr₀.₅₀MnO₃, Sm₀.₅₀Sr₀.₅₀MnO₃, Gd₀.₅₀Sr₀.₅₀MnO₃ and Dy₀.₅₀Sr₀.₅₀MnO₃), LBM (La₀.₅₀Ba₀.₅₀MnO₃), LSMA (La₀.₅₀Sr₀.₅₀Mn₀.₇₅Al₀.₀₅O₃ and La₀.₅₀Sr₀.₅₀Mn₀.₇₅Al₀.₀₅O₃) LMMg (La₀.₅₀Sr₀.₅₀Mn₀.₈₅Mg₀.₁₇O₃) and LScrCo (La₀.₆₅Sr₀.₄₀Cr₀.₈₀Co₀.₂₀O₁) compiled from the literature. More details on Table A.3. .... 26

Figure 2.7: H₂ production via thermochemical H₂O splitting by several perovskite materials LAM (La₀.₅₀Sr₀.₅₀MnO₃ and La₀.₅₀Ca₀.₅₀MnO₃), SLMA (Sr₀.₄₀La₀.₀₆Mn₀.₆₀Al₀.₄₅O₃, Sr₀.₆₀La₀.₄₀Mn₀.₆₀Al₀.₄₀O₃ and Sr₀.₄₀La₀.₆₀Mn₀.₄₀Al₀.₆₀O₃), CTF (CaTio.₇₅Fe₀.₂₅O₃), LSCO (LaSrCoO₄) and ASCA’ (Ba₀.₅₀Sr₀.₅₀Co₀.₈₀Fe₀.₂₀O₃ and La₀.₆₅Sr₀.₄₀Cr₀.₈₀Co₀.₂₀O₁) compiled from the literature. More details on Table A.4. .... 27

Figure 3.1: Temperature Programmed Reduction screening method to evaluate redox capacity of materials for STCH. Samples of the SLMA family are shown to exhibit different extent of reduction and reoxidation behaviors. The reduction step was carried at 1350 °C in UHP N₂ for 1 h and synthetic air was introduced just before the sample was cooled down to room temperature. .......................................................................................................................... 31
Figure 3.2: Temperature Programmed Reduction screening experiment performed at 1350 °C in UHP N₂ followed by introduction of synthetic air for 5 min to allow for reoxidation. Samples tested were selected as the most representative in their families (SrFe₈₀Nb₂₀ = SrFe₀.₈₀Nb₀.₂₀O₃, Sr₈₀La₂₀Mn₆₀Ce₄₀ = Sr₀.₈₀La₀.₂₀Mn₀.₆₀Ce₀.₄₀O₃, LaMn₅₀V₅₀ = LaMn₀.₅₀V₀.₅₀O₃, CaMn₅₀Ce₅₀ = CaMn₀.₅₀Ce₀.₅₀O₃, CeFe = CeFeO₃, CeMn = CeMnO₃ and CaZr₅₀Mn₅₀ = CaZr₀.₅₀Mn₀.₅₀O₃). Ceria was added for comparison............................................. 36

Figure 3.3: Temperature Programmed Reduction screening experiment performed at 1200 °C in UHP N₂ followed by introduction of synthetic air for 5 min to allow for reoxidation. Samples tested were selected as the most representative in their families (SrZr₅₀Fe₂₀ = SrZr₀.₅₀Fe₀.₅₀O₃, CaZr₅₀Fe₅₀ = CaZr₀.₅₀Fe₀.₅₀O₃, CaSn = CaSnO₃). ........ 38

Figure 3.4: Temperature Programmed Reduction screening experiment performed at 1350 °C in UHP N₂ followed the oxidation step at 1000 °C in synthetic air. Samples tested are the most promising for WS. (Ce₀₂Sr₁₈Mn = Ce₀.₂₀Sr₁.₈₀MnO₄, Sr₆₀Ce₄₀Mn = Sr₀.₆₀Ce₀.₄₀MnO₃, BaCe₂₅Mn₇₅ = BaCe₀.₂₅Mn₀.₇₅O₃). Ceria and SLMA6464 are added as the two limits for WS................................................................. 39

Figure 4.1: a) Experimental H₂ Production at various H₂O:H₂. Dashed lines are WS with 40 vol. % water. LSMA was reduced for 330 s and oxidized for 1200 s, whereas CZ05 and ceria were reduced for 240 s and oxidized for 480 s. b) Residual oxygen non-stoichiometry remaining after reoxidation (1 − δO/δR). ................................................................. 44

Figure 4.2: Simulated closed-reactor thermochemical cycles of CeO₂ (blue lines), CZ05 (red lines) and LSMA (green lines). The thick solid lines represent the equilibrium pO₂ as a function of oxygen stoichiometry x at 850 °C (upper lines) and 1350 °C (lower lines). The dashed lines represent the evolution of pO₂ and δ during a stable reduction half-cycle in a closed reactor with excess inert gas (β = 10³) and the corresponding stable oxidation-with-water half-cycle with a) excess water (γ = 10³) and b) limiting water (γ = 1)................................................................................................................................. 47

Figure 4.3: a) Thermodynamic property maps showing favorability regions for water-splitting at T₀ₓ = 850 °C and variable H₂O:H₂ (water splitting is favorable for dots above the gray lines). Each dot represents a different oxygen content, which increases to the left in intervals of 0.02 from 0.001 – 0.35. White symbols show the final oxygen non-stoichiometry for the reduction conditions used for experiments in Figure 4.1. b) Oxidation temperature dependence of RRR for ceria, CZ05 and LSMA. ........................................ 49

Figure 5.1: Summary of phases present in five of the target compositions................................................. 62

Figure 5.2: High Temperature XRD done on a 12R-BaCe₀.₂₅Mn₀.₇₅O₁₋δ sample, heating from room temperature to 1350 °C in He flow. At 1150 °C the 12R phase starts to convert to 10H phase and by 1350 °C the onset of a new H polytype phase (N) is also apparent. ... 64

Figure 5.3: Temperature Programmed Reduction experiment evaluates the extent of reduction (formation of oxygen vacancies or δ) and reversibility of samples BCO, ceria, SLMA 4664, BC25M75, SLMA6464 and BMO. Reduction at 1350 °C for 1 h and Oxidation in air at 1000 °C................................................................. 65
Figure 5.4: Average H\textsubscript{2} productivity over 3 cycles (\textmu mol H\textsubscript{2}/g sample) for BMO, BC25M75, BC50M50, BC75M25, BCO, and ceria (included as a reference). Superimposed on this data is the relative phase fraction of the hypothesized active water-splitting phase (12\textit{R}-BaCe\textsubscript{0.25}Mn\textsubscript{0.75}O\textsubscript{3-\textdelta}) in each sample. H\textsubscript{2} productivity closely correlates with the percentage of 12\textit{R}-BaCe\textsubscript{0.25}Mn\textsubscript{0.75}O\textsubscript{3-\textdelta} present in each sample. ........................................ 67

Figure 5.5: Water splitting experiment at T\textsubscript{RE} 1350 °C for 330 s and T\textsubscript{OX} 850 °C with 40 vol\% H\textsubscript{2}O for 1200 s. Ceria was oxidized for 300 s. O\textsubscript{2} peaks (blue) and H\textsubscript{2} peaks (red) record the amount of oxygen and hydrogen evolved per gram of sample as a function of time. Integrated totals for the first three peaks are listed in the legend. ........................... 69

Figure 5.6: Mass normalized H\textsubscript{2} production rate as a function of time (scattered dots) measured during WS at T\textsubscript{RE} 1350 °C and T\textsubscript{OX} (a) 850 °C and (b) 1000 °C at 40 vol. % steam, and best fit (solid lines) derived from the solid-state kinetic model assuming second-order reaction. More details described in the SI. .............................................................. 72

Figure 5.7: Total H\textsubscript{2} produced per cycle by BCM (square), SLMA4664 (circle) and ceria (triangle) at T\textsubscript{RE} of 1350 °C with 40 vol. % steam and various oxidation temperatures. Reduction heating rate is 10 °C/s, with a reduction time of 330 s and a reoxidation time of 1200 s. .............................................................. 73

Figure 5.8: “High conversion” water splitting performed at various steam to hydrogen mixture ratios for all three materials: BCM (square), SLMA4664 (circle), and ceria (triangle) at T\textsubscript{RE} 1350 °C and T\textsubscript{OX} 850 °C. .............................................................. 75

Figure 5.9: Stability experiment done in the BCM sample. The fifty hydrogen peaks are shown in (a) and the integrated amounts of O\textsubscript{2} and H\textsubscript{2} obtained in each cycle are plotted in (b). Reduction was done at T\textsubscript{RE} 1350 °C for 210 s and oxidation with 40 vol. % steam was carried out at T\textsubscript{OX} 850 °C for 10 min. The data was collected over three days of experiment. ....................................................... 77

Figure 5.10: X-ray diffraction comparison between the samples BaCe\textsubscript{x}Mn\textsubscript{1-x}O\textsubscript{3}, where x = 0, 0.05, 0.15, 0.25, 0.50, 0.75, and 1................................................................. 81

Figure 5.11: X-ray diffraction results for BC25M75 sample as calcined and after the first TPR cycle (reduction at 1350 °C and re-oxidation at 1000 °C) shows the increase of the 12\textit{R} structure and decrease of the 10\textit{H} structure............................................................... 83

Figure 5.12: Temperature Programmed Reduction experiment evaluates the extent of reduction (formation of oxygen vacancies or \textdelta) and reversibility of samples BCO, ceria, SLMA, BC75M25, BC50M50, BC25M75, BC15M85, BC05M95 and BMO. Reduction at 1350 °C for 1 h in UHP N\textsubscript{2} and Oxidation in air at 1000 °C. ........................................... 85

Figure 5.13: BCM three consecutive reduction and oxidation cycles at 1350 °C in UHP N\textsubscript{2} for 4 h and 1000 °C for 30 min in air respectively. The experiment indicates that after the first redox cycle BCM two polytypes were all converted to the main phase 12\textit{R}. ........... 86

Figure 5.14: Total H\textsubscript{2} produced per cycle by BCM (red), SLMA (blue) and Ceria (yellow) at a) T\textsubscript{RE} of 1250 °C and b) T\textsubscript{RE} of 1400 °C with 40% steam and various oxidation temperatures. Reduction heating rate is 10 °C/s, with a reduction time of 330 s and a reoxidation time of 1200 s. ............................................................................. 89
Figure 5.15: 10H sample tested on 5 simulated WS cycles carried out in a TGA. The sample was heated at 10 °C/min to $T_{OX}$ 850 °C in UHP N$_2$. The reduction step was done by heating the sample at 99 °C/min to $T_{RE}$ 1350 °C and held for 330s. The sample was then cooled to $T_{OX}$ at 99 °C/min and 16 sccm of synthetic air (21% O$_2$ balanced in N$_2$) mixed with 100 sccm of UHP N$_2$ was flowed for 10 min. The oxidizing flow was turned off and 100 sccm of UHP N$_2$ purged the chamber for another 10 min preparing the sample for the subsequent reduction cycle. ................................................ 94

Figure 5.16: XRD done on 10H samples before and after WS simulated runs done in TGA. The as prepared sample indicates the presence of 10H phase, whereas the sample after the TGA WS simulated run indicates that the 10H phase was converted to 12R phase....... 95

Figure 6.1: Illustration of the Ce$_{a}$Sr$_{2-a}$MnO$_4$ Ruddlesden-Popper layered perovskite crystal structure. Purple octahedra are MnO$_6$ and green/yellow atoms denote the A-site positions which are randomly shared between Sr and Ce atoms. ..................................... 99

Figure 6.2: Powder X-ray diffraction using synchrotron radiation ($\lambda = 0.412628$ Å) on (a) Ce$_{0.1}$Sr$_{1.9}$MnO$_4$ (CSM1), (b) Ce$_{0.2}$Sr$_{1.8}$MnO$_4$ (CSM2), and (c) Ce$_{0.3}$Sr$_{1.7}$MnO$_4$ (CSM3). Observed (dark), calculated (light grey), difference plot (bottom) and expected phase peaks (vertical marks). ........................................................................... 107

Figure 6.3: Indexed SADPs (left) and CBED patterns (right) of the three main zone axes of the Ce$_{0.1}$Sr$_{1.9}$MnO$_4$ layered perovskite: a) [001], b) [100], and c) [110]. The yellow lines represent the mirror symmetries present in each CBED pattern and they confirm the I4/mmm space group. The diffraction patterns are not necessarily at the same scale. ... 111

Figure 6.4: Simulated and experimental images of the two shortest projections of the layered perovskite under two different defocus conditions. The projections of the unit cells on the same orientations are displayed for comparison. ......................................................... 113

Figure 6.5: Water splitting results for two complete cycles at $T_{RE} = 1400$ °C for 330 s and at $T_{OX} = 1000$ °C for 1200 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, with the second value corresponding to the subsequent cycles average. The hydrogen value refers to the average hydrogen production.......................................................... 115

Figure 6.6: XRD of samples SMO, SCM3070, SCM5050, SCM7030 and SCO. ............................. 119

Figure 6.7: Active phase plot. Comparison between SCM5050 and SCM7030 hydrogen production and amount of water splitting active phases present in each sample. WS experiment was performed at reduction temperature of 1400 °C in Ar and oxidation temperature of 1000 °C with 50 vol% H2O for 1000 s. Ceria was tested at the same temperature conditions. ................................................................................................... 121

Figure 6.8: Additional TEM characterization results of the CSM samples. (a) SADP of [100] zone axis of the layered perovskite in the CSM 2 sample. (b) SADP of [001] zone axis of the layered perovskite in the CSM 3 sample and (c) EDS map with bright field –
scanning transmission electron microscopy image of CSM 1 sample showing its single-phase character.......................................................... 122

Figure 6.9: Temperature Programmed Reduction performed on CSM1, CSM2 and CSM3. BCM (BaCe0.25Mn0.75O3) and ceria (CeO2) are added for comparison. In this experiment, we measured extent of reduction as a function of temperature. Reduction was done at T_{RE} 1350 °C for 1 h in nitrogen followed by oxidation at T_{OX} 1000 °C for 1 h in air ......................................................................................................................................... 125

Figure B.1: Temperature programmed reduction results for CaZr, Mn_{1-x}Oy family. Reduction was carried in a TGA at 1350 °C for 1 h in UHP N2 flow. Oxidation was carried for 5 min in synthetic air flow. Samples tested were CaZr50Mn50 = CaZr0.50Mn0.50O3, CaZr40Mn60 = CaZr0.40Mn0.60O3, CaZr30Mn70 = CaZr0.30Mn0.70O3, CaZr20Mn80 = CaZr0.20Mn0.80O3 and CaZr10Mn90 = CaZr0.10Mn0.90O3. ........................................................................................................ 138

Figure B.2: Temperature programmed reduction results for CaZr, Fe_{1-y}Oy family. Reduction was carried in a TGA at 1200 °C for 1 h in UHP N2 flow. Oxidation was carried for 5 min in synthetic air flow. Samples tested were CaZr50Fe50 = CaZr0.50Fe0.50O3, CaZr40Fe60 = CaZr0.40Fe0.60O3, CaZr30Fe70 = CaZr0.30Fe0.70O3, CaZr20Fe80 = CaZr0.20Fe0.80O3 and CaZr10Fe90 = CaZr0.10Fe0.90O3. Signal to noise ratio is very small, leading to noisy data. Most of these samples melted during TPR. ......................... 139

Figure B.3: Temperature programmed reduction results for CaTi, Nb_{1-y}Oy family. Reduction was carried in a TGA at 1350 °C for 1 h in UHP N2 flow. Oxidation was carried for 5 min in synthetic air flow. Samples tested were CaTi80Nb20 = CaTi0.80Nb0.20O3, CaTi90Nb10 = CaTi0.90Nb0.10O3, CaTi85Nb15 = CaTi0.85Nb0.15O3. Signal to noise ratio is very small, leading to noisy data. ................................................................................. 140

Figure B.4: Temperature programmed reduction results for AMn_{0.5}Oy family as well as related compositions such as CeFe = CeFeO3 and CaCe50Mn50 = CaCe0.50Mn0.50O3, Reduction was carried in a TGA at 1350 °C for 1 h in UHP N2 flow. Oxidation was carried for 5 min in synthetic air flow. Other samples tested were YMn = YMnO3, CeMn = CeMnO3, CaMn = CaMnO3. ........................................................................................................ 141

Figure B.5: Temperature programmed reduction results for ASn_{1-y}Oy family as well as related compositions such as CaSn = CaSnO3, SrSn = SrSnO3, and BaSn = BaSnO3, Reduction was carried in a TGA at 1200 °C for 1 h in UHP N2 flow. Oxidation was carried for 5 min in synthetic air flow. .................................................................................... 142

Figure B.6: Temperature programmed reduction results for SrZr, Mn_{1-x}Oy family as well as related compositions such as SrZr10Mn90 = SrZr0.10Mn0.90O3, SrZr20Mn80 = SrZr0.20Mn0.80O3, and SrZr30Mn70 = SrZr0.30Mn0.70O3. Reduction was carried in a TGA at 1350 °C for 1 h in UHP N2 flow. Oxidation was carried for 5 min in synthetic air flow. .................................................................................... 143

Figure B.7: Temperature programmed reduction results for SrZr, Fe_{1-y}Oy family as well as related compositions such as SrZr10Fe90 = SrZr0.10Fe0.90O3, SrZr20Fe80 = SrZr0.20Fe0.80O3, and SrZr30Fe70 = SrZr0.30Fe0.70O3. SrZr40Fe60 = SrZr0.40Fe0.60O3, and SrZr50Fe50 = SrZr0.50Fe0.50O3. Reduction was carried in a TGA at 1200 °C for 1 h in UHP N2 flow. Oxidation was carried for 5 min in synthetic air flow. .................................................................................... 144
Figure D.1: Crystal structure BaCe$_{0.25}$Mn$_{0.75}$O$_3$ (BCM) 12R and 10H polytypes. .......................... 153

Figure D.2: High temperature XRD done on 12R-BaCe$_{0.25}$Mn$_{0.75}$O$_3$. The powder samples was deposited onto an YSZ 110 single crystal plate and was heated to 1350 °C under He atmosphere. After an isotherm of 1.5 h, the sample was cooled to 1150 °C and oxidized in synthetic air flow for 1 h. 12R phase converts to 10H phase as well as a new polytype phase upon reduction. Symbols represent the highlighted 12R (★), 10H (◇) and H (□) polytype phase peaks. ................................................................. 158

Figure D.3: High temperature XRD done on 12R-BaCe$_{0.25}$Mn$_{0.75}$O$_3$. The powder samples was deposited onto an YSZ 110 single crystal plate and was heated to 1350 °C under synthetic air flow atmosphere. After an isotherm of 1.5 h, the sample was cooled to 1150 °C followed by a dwell of 1 h. 12R phase decreases in intensity giving place to 10H phase and a small amount of the H polytype phase. Symbols represent the highlighted 12R (★), 10H (◇) and H (□) polytype phase peaks. ................................. 159

Figure D.4: High temperature XRD done on 12R-BaCe$_{0.25}$Mn$_{0.75}$O$_3$. The powder sample was deposited onto an YSZ 110 single crystal plate and was heated to 1150 °C under...
synthetic air flow atmosphere. After an isotherm of 1.5 h, the sample was cooled to 1050 °C followed by a dwell of 1 h. 12R phase starts to convert to 10H phase and upon oxidation it slowly converts back to 12R. A small amount of H polytype phase is present at the end of the experiment. Symbols represent the highlighted 12R (★), 10H (◇) and H (□) polytype phase peaks.

Figure D.5: Differential Scanning Calorimetry performed on BaCe₀.₂₅Mn₀.₇₅O₃. The sample was heated from 1000 °C to 1250 °C under flowing UHP N₂ at various heating rates 10, 20 and 40 °C/min. The endothermic peak indicates the heat capacity required for the phase change from 12R to 10H phase. The data and plot presented here was a contribution from Dr. Eric Coker.

Figure D.6: Simulated five WS cycles on 10H (blue) and H (black) polytype. Reduction was carried out in 100 sccm UHP N₂ flow at T_{RE} 1350 °C for 5 min and oxidation carried out in 100 sccm N₂ and 16 sccm (21 % O₂ balanced with N₂) flow at T_{OX} 850 °C for 20 min.

Figure D.7: Temperature programmed reduction performed on BaCe₀.₂₅Mn₀.₇₅O₃ 12R, 10H and H polytypes. Reduction was carried out under flowing N₂ for 1 h at 1350 °C and oxidation was carried out in flowing synthetic air for 1 h at 1000 °C.

Figure D.8: High temperature X-ray Diffraction on BaCe₀.₂₅Mn₀.₇₅O₃, Experiment 1. The sample starts at room temperature at He flow and is heated to 1350 °C with a dwell of 1.5 h. The sample is then cooled to 1150 °C and synthetic air is introduced (21% O₂ balanced with N₂). After a dwell of 1 h the sample is cooled down to room temperature. This experiment starts with a 12R phase and at the reduction step, the sample suffers a phase change to 10H and H polytype.

Figure D.9: High temperature X-ray Diffraction on BaCe₀.₂₅Mn₀.₇₅O₃, Experiment 2. The sample starts at room temperature in air flow and is heated to 1350 °C with a dwell of 1.5 h. The sample is then cooled to 1150 °C. After a dwell of 1 h the sample is cooled down to room temperature. This experiment starts with a 12R phase and a partial phase change occurs forming 10H and H polytype.

Figure D.10: High temperature X-ray Diffraction on BaCe₀.₂₅Mn₀.₇₅O₃, Experiment 3. The sample starts at room temperature in air flow and is heated to 1150 °C with a dwell of 1.5 h. The sample is then cooled to 1000 °C. After a dwell of 1 h the sample is cooled down to room temperature. A small amount of 10H phase starts to appear at the end of the reduction step as well as the H polytype.

Figure D.11: XRD on starting samples and after the cycle WS simulated cycles performed on TGA. a) 10H phase sample converted to 12R phase and b) H polytype sample converted to 12R phase.

Figure D.12: XRD performed on BaCe₀.₂₅Mn₀.₇₅O₃ 10H and H polytype samples after TPR run. The 10H sample converted its majority to 12R phase having a small amount of 10H phase still present. The H sample converted partially to 10H.

Figure D.13: Differential Scanning Calorimetry performed on BaCe₀.₂₅Mn₀.₇₅O₃. The samples were loaded into an alumina crucible and heated to the oxidation temperature 1050 °C under UHP N₂ flow. The sample were further heated from the oxidation.
temperature to the reduction temperature 1250 °C at three different heating rates rates 10, 20 and 40 °C/min. After a dwell of 10 min, the temperature was dropped at same ramp rates to the oxidation temperature under synthetic air flow. The phase change from $12R$ to $10H$ phase was identified during heating.
Table 3.1: List of compounds synthesized in this work according to computational prediction and chemical intuition. A and B correspond to generic cations occupying the A and B-sites respectively. ................................................................. 33

Table 5.1: Oxygen vacancy formation energies and oxygen-cation bond dissociation energies for the two family end-member compounds (BaMnO$_3$ and BaCeO$_3$). See supplemental information for details on the calculation of $E_v$ based on Deml’s model. .......................... 58

Table 5.2: Summary of the oxidation reaction rate constants using the second-order kinetics model F2 for BCM and Ceria at $T_{OX}$ 850 °C and 1000 °C. .............................................. 71

Table 5.3: Reported calculated values used to approximate the oxygen vacancy formation energy.................................................................................................................. 80

Table 5.4: Crystal structures determined from Rietveld Refinement for each of the 5 samples studied .......................................................................................................................... 82

Table 5.5: Extent of reduction and onset temperature at $\delta = 0.025$. Data obtained from TPR experiment where $T_{RE}$ 1350 °C at 10 °C/min and held for 4 h and $T_{OX}$ 1000 °C. ......... 84

Table 5.6: Non-exhaustive list of promising STCH materials reported in the literature for comparison of performance. ........................................................................................................ 87

Table 5.7: Hydrogen production (µmol/g of sample) at $T_{OX}$ (750 °C, 850 °C and 1000 °C) and $T_{RE}$ (1250 °C, 1350 °C) with 40 vol. % steam ......................................................................................... 88

Table 5.8: Fitted parameters for the reactor calculated from four blank runs that used 2 sccm and 4 sccm trace amount of H$_2$ (5 % H$_2$ balanced in Ar) mixed in the 40 vol. % steam flow ........................................................................................................ 91

Table 5.9: Rate constants calculated for BCM using the four different mixing models at 850 °C and 1000 °C. ..................................................................................................................... 91

Table 5.10: Rate constants calculated for ceria using the four different mixing models at 850 °C and 1000 °C. ..................................................................................................................... 93

Table 6.1: DFT calculations of stability, decomposition reactions and oxygen vacancy formation energy of SrCe$_b$Mn$_{1-b}$O$_3$ ($b = 0, 0.25, 0.5, 0.75, 1$). .................................................. 105

Table 6.2: DFT stability and oxygen vacancy formation energy calculations on CSM1, CSM2 and CSM3. ...................................................................................................................... 106

Table 6.3: Final structural parameters for Ce$_{0.1}$Sr$_{1.9}$MnO$_4$, Ce$_{0.2}$Sr$_{1.8}$MnO$_4$ and Ce$_{0.3}$Sr$_{1.7}$MnO$_4$. .... 109

Table 6.4: Rietveld refinement of the samples SMO, SCM3070, SCM5050, SCM7030 and SCO................................................................................................................................. 120
Table 6.5: Preliminary water splitting summary. WS was performed at \( T_{\text{RE}} \) 1400 °C for 330 s and at \( T_{\text{OX}} \) 1000 °C for 1000 s in 50 vol.% steam balanced with argon. ........................................... 121

Table 6.6: Atomic composition obtained from EDS measurements on samples CSM1, CSM2 and CSM3. ........................................................................................................................................ 124

Table A.1: Fluorite oxide materials CO production via thermochemical CO\(_2\) splitting compiled from Jiang et al. [57]. ..................................................................................................................... 129

Table A.2: Fluorite oxide materials H\(_2\) production via thermochemical H\(_2\)O splitting compiled from the literature. .......................................................................................................................... 131

Table A.3: Perovskite oxide materials suggested for CO production via thermochemical CO\(_2\) splitting extracted from the literature. ...................................................................................................... 134

Table A.4: Perovskite oxide materials suggested for H\(_2\) production via thermochemical H\(_2\)O splitting extracted from the literature. ........................................................................................................... 136

Table C.1: Water splitting experiment performed in SFR, under 40 vol. % steam. Reduction time was 300 s and oxidation time was 20 min. ................................................................. 151
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The first person I would like to thank is my advisor, Prof. Ryan O’Hayre, for allowing me the opportunity to work on a theme related to renewable energy, something I am very passionate about. I am very grateful for all his advice, support, motivation and for sending me to Sandia National Laboratories Livermore and New Mexico to conduct exciting experiments for my thesis!

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CHAPTER 1
INTRODUCTION

This chapter presents the statement of my doctorate thesis and describes the motivation for my work in terms of its impact to society and contribution to the scientific community. A brief description of each chapter guides the reader through this work before a final acknowledgment to the main contributions to this work.

1.1 Thesis Statement

The main objective of this thesis is to discover new materials that can be applied to Solar Thermochemical Hydrogen production. This work was done by understanding the main requirements of the Solar Thermochemical Hydrogen Production (STCH) process specifically in terms of materials stability and tolerance for nonstoichiometry, thermodynamics, temperature requirements, and fuel input limitations to inform the design of new perovskite oxide materials that have improved performance over the state-of-the-art, cerium oxide.

1.2 Motivation

In the drive to develop alternative energy sources, hydrogen has been proposed as an attractive energy storage medium because it can be efficiently converted to electricity in fuel cells and because it can be obtained via carbon-neutral processes such as water splitting. Among other applications, H₂ also plays an important role in the ammonia synthesis for production of fertilizers. Among the several solar water splitting techniques available, Solar Thermochemical Hydrogen production (STCH) is advantageous when
large-scale H₂ production is considered, because of the potential for energetically high efficiency processes and scalability.

The water splitting process via STCH requires a reactive intermediary to lower the required temperature of water thermolysis to a more tangible and accessible temperature that can be achieved in concentrated solar towers. This “intermediary” material is usually a metal oxide that, through redox reaction steps, may split water at temperatures as low as 1300-1600 °C. The two-step STCH process, by using non-volatile materials, is advantageous over processes that require more steps, because of its lower complexity. During the higher temperature reduction step, the metal oxide is reduced, thereby increasing its oxygen nonstoichiometry. During the subsequent lower temperature water splitting step, the metal oxide re-oxidizes in the presence of steam, producing H₂.

Ceria (CeO₂) is the state-of-the-art material for STCH because of its fast redox reaction kinetics, chemical stability and high fuel selectivity. However, the largest disadvantage of ceria is the high temperature required for reduction. Over the past decade, scientists have been on the search for materials that can achieve a higher water splitting performance than ceria.

The search has bifurcated between two main classes of materials; the doped-ceria compounds and the perovskite oxides. Many doped-ceria compounds have been proposed, however the addition of a dopant has so far always negatively impacted performance due to either decreased redox reaction kinetics or decreased H₂ production capacity. Several perovskites, on the other hand, have been shown to achieve larger H₂ production capacity at much lower temperature ranges than ceria (800-1400 °C). However, they also suffer from redox kinetic limitations and require increased amounts of steam, which impacts the H₂ production conversion reaction and the overall process efficiency.

In this thesis, I focus on the design of new perovskite and perovskite-related oxide materials to increase the H₂ production capacity compared to ceria, using lower reduction temperatures and less steam. This is achieved by analyzing each materials’ oxygen redox performance under chosen temperature and oxygen partial pressure conditions. The redox performance is directly related to the thermodynamic
properties of the material’s redox capacity and these can be indirectly compared among several potential perovskites.

1.3 Thesis Organization

In chapter 2, I present the background information necessary to understand hydrogen’s current role in the society and its production demands for the future. I describe the most important renewable hydrogen production techniques and then explain STCH and its attractiveness relative to other techniques. I then detail the key metrics for water splitting materials and briefly describe the history of other suggested STCH materials over the past few decades.

Chapter 3 discusses the early part of my work, where through computational guidance and chemical intuition I started designing new perovskite materials for STCH. In this work, among the hundred materials I synthesized, I identified two potential new perovskites for STCH by using a screening method to rapidly (but indirectly) evaluate each material’s driving force for water splitting (WS).

Chapter 4 provides a study that delineates the importance of the steam-to-hydrogen conversion concept and proposes a key metric for making the real application possible. I demonstrate why conversion must be considered when designing new water splitting materials and how conversion limitations may be measured experimentally rather than being inferred from extensive thermodynamic studies.

The first identified STCH-active perovskite, \( \text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3 \) (BCM), is discussed in Chapter 5. BCM’s water splitting performance is shown in terms of hydrogen productivity, reoxidation reaction kinetics, cycle-stability and finally steam-to-hydrogen conversion limitations. BCM is the first perovskite demonstrated to split water at higher conversion ratios.

Another identified STCH-active perovskite-related oxide is described in Chapter 6. This layered perovskite is a non-conventional structure for STCH materials, the Ruddlesden-Popper phase \( \text{Ce}_a\text{Sr}_{2-a}\text{MnO}_4 \) (\( a = 0.1, 0.2 \) and 0.3) which has never been reported in the literature before. Structure characterization and
water splitting performance are discussed. DFT calculations are used to evaluate the structure stability and oxygen vacancy formation energies in this system, which corroborate the potential of this material for STCH.

BCM’s thermodynamic properties are studied in Chapter 7 to further explore its promising WS performance potential. I show oxygen nonstoichiometric results obtained at different temperature and oxygen partial pressure conditions and extract estimates of the enthalpy and entropy of oxygen vacancy formation energy. High-temperature characterization experiments indicate that BCM’s outstanding performance might lie in the polytypic phase changes that it likely experiences during redox cycling.

I finalize this thesis with the main conclusions and future work outlined in Chapter 8. I introduce a potentially interesting third water splitting material, a CSM sister-structure, Sr0.6Ce0.4MnO3 and suggest a complete WS performance assessment on this new material. Additionally, I lay out additional characterization studies that could be done to manipulate the different BCM polytypes for potential WS cycle operation under a phase change regime, with the aim to further increase its H2 production performance.

1.4 Acknowledgment of Contributions

This work started as a project with funding from Sandia National Laboratories and the Department of Energy, which has formed a consortium of research groups dedicated to different aspects of the STCH technology such as materials design, solar reactor’s design and economic viability. Many collaborations arose from this starting-project.

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CHAPTER 2
BACKGROUND

This chapter introduces the STCH concept and its advantage over other H₂ production techniques, describe the relevant work that has been done in this field and the main approaches for design of water splitting materials.

2.1 The role of hydrogen in society

Over the past few decades, scientists have been studying alternative sources of energy in order to decrease humanity’s reliance on fossil fuels, the main culprit in global carbon dioxide emissions. In 2010, global emissions reached 30.6 Gt and emissions are projected to increase a further 70% by 2050 due to increases in energy demand [1].

Hydrogen, in a role not as an energy source, but rather as an energy storage medium, has been proposed as a substitute for fossil fuels because of its versatility and energy density. As an example of hydrogen’s energy density, the energy obtained from 1 kg of hydrogen is equivalent to the energy obtained from 1 gallon of gasoline/E10 (about 2.9 kg), nearly a threefold increase in energy per weight (with the important caveat that weight-efficient hydrogen gas storage is still challenging) [2]. World hydrogen demand, as reported in 2010, is about 43Mt [3]. This enormous demand is driven by use in many sectors of industry, including chemical production, oil refining, metal processing, and to a lesser extent, transportation and aerospace. 53% [3] of all hydrogen produced today is designated to the synthesis of ammonia via the Haber-Bosch process, mainly for fertilizer production. The second largest use for hydrogen, about 20%, is in oil refining processes and 7% is designated to methanol production, which is crucial to the synthesis of other olefins and hydrocarbon-based products. A key challenge posed by hydrogen’s current and future
demand is that 95% of the global hydrogen production is currently accomplished via steam methane reforming, coal gasification, and/or cracking of hydrocarbons, all of which are CO$_2$-intensive processes [4].

Additional pressure on finding new “clean” sources of hydrogen comes from the burgeoning demand for alternative fuels for transportation and electricity generation. To achieve the target CO$_2$ emission cutdown of 80% by 2050, Europe must decarbonize 95% of its passenger car fleet (small and medium size as well as SUVs) by replacing it with hydrogen fuel cell cars and/or electric cars [3].

2.2 Renewable water splitting techniques

In order to accommodate the expected growth in the hydrogen economy and to consider hydrogen as a viable alternative energy solution [5], it has to be obtained from a truly renewable source. With that in mind, solar energy can be leveraged to produce hydrogen via solar water splitting (WS). This process not only produces hydrogen from renewable sources, but also addresses one of the challenges of solar energy: the mismatch between production and demand cycles. By converting solar energy to hydrogen, excess solar energy can be stored for later use. One of the simplest techniques proposed for large-scale water splitting using solar energy is solar thermolysis, which involves the direct use of solar heat to split water. However, this has proven to be an expensive and energy demanding way to produce hydrogen, requiring temperatures above 2450 °C to be feasible [6]. Not only are there few options for refractory reactor materials to withstand these temperatures, but direct thermolysis also requires continuous separation of H$_2$ and O$_2$ at temperature, which demands even more energy and expensive separation techniques.

Alternative technologies are being explored to provide a more practical route to solar hydrogen. Solar water electrolysis is one alternative. In solar electrolysis, an electrical current generated by solar irradiance and delivered to an electrochemical cell leads to the separate production of independent H$_2$ and O$_2$ molecules on the cathode and anode electrodes respectively. The inefficiencies associated with this technique lie in the conversion of solar energy to electricity. Photovoltaic panels [7] that can provide
efficiencies in the order of 10 to 20% [8], [9], limit the maximum efficiency of this technique to about 16% [10]. Other methods for converting solar energy to electricity can increase the efficiency by taking advantage of the full spectrum of solar energy, such as harnessing steam or other working fluid turbines in solar plants, which may achieve conversion efficiencies from 30 to 60% [11], [12] increasing the overall solar electrolysis efficiency into the range of 16 to 32%. Photoelectrolysis [13] may also be considered. This approach combines the photovoltaic step and the electrolysis step into a single process. However, the process requires a potential difference of at least 1.23V (realistically >2 V) to allow for WS, so the electrolyte must have a band gap in this range. Unfortunately photoelectrolysis is not yet a viable commercial option because of intrinsic problems associated with electrochemical corrosion of the electrodes [14]. The same challenges have hampered photochemical [15] processes that, to one extent or another, mimic photosynthesis. Additionally, efficiency relies on catalysts and preparation of the sensitizer, not to mention apparatus complexity [16].

Among the several alternative water splitting techniques [17], the thermochemical water splitting approach offers several compelling advantages. One significant advantage of this approach is its simplicity; it doesn’t require expensive catalysts, membranes, or electrodes to produce hydrogen. The thermochemical technique instead depends mostly on temperature swings. The required heat for the process can come from a number of sources, including sunlight and/or waste heat from other thermal processes. For instance, gas-cooled nuclear reactors can be a source of heat for thermochemical WS [18], where heat generated by fission nuclear reactions (or in the future, fusion reactions) can be used in various thermochemical process cycles to decompose water into hydrogen and oxygen. The main drawback to using nuclear reactors is that temperatures tend to be limited to 1200 K. Above this temperature, thermal energy from additional sources would be required to be coupled to the nuclear source. This represents a considerable engineering challenge, as well as leading to lower overall efficiency.
2.3 Solar thermochemical hydrogen production

This thesis focuses on another proposed thermochemical WS pathway known as Solar Thermochemical Hydrogen (STCH) production. This technique is a carbon-neutral way to produce hydrogen using mainly concentrated solar thermal energy and water (some electricity is required to power support systems and general plant activities). Realistically, water solar electrolysis and STCH are the only two techniques that have the potential to be applied to the production of hydrogen at large scale. STCH has been predicted to achieve larger energy-to-fuel conversion efficiencies and has the potential to lower production costs enough to compete with conventional fossil-fuel processes [19], [20]. Figure 2.1 illustrates the two-step WS process [20]–[22].

![Diagram of the two-step solar thermochemical water splitting cycle illustration for a generic metal oxide MO\textsubscript{x} using Kröger-Vink notation](image)

Figure 2.1: Two-step solar thermochemical water splitting cycle illustration for a generic metal oxide MO\textsubscript{x} using Kröger-Vink notation
The cycle begins with a metal oxide that, when exposed to high temperatures, i.e. reduction
temperature \( T_{\text{RE}} \), and/or decreased oxygen partial pressure, is reduced, forming oxygen vacancies and
evolving oxygen gas as described by equation 2.1, where \( \delta_1 \) is the extent of reduction.

\[
\text{MO}_x \leftrightarrow \text{MO}_{x-\delta_1} + \frac{\delta_1}{2} \text{O}_2(g)
\]

After being reduced, the metal oxide is separated from the evolved oxygen and cooled to a lower
temperature, i.e. oxidation temperature \( T_{\text{OX}} \), that favors reoxidation. In this situation, when steam is
introduced, the material reoxidizes by splitting water and producing hydrogen. Equation 2.2 describes the
oxidation step, where the amount of steam added is \( y \) and the amount of hydrogen produced is \( \delta_2 \).

\[
\text{MO}_{x-\delta_1} + y\text{H}_2\text{O}(g) \rightarrow \text{MO}_{x-\delta_1+\delta_2} + \delta_2\text{H}_2(g) + (y - \delta_2)\text{H}_2\text{O}(g)
\]

A similar process has been developed that uses \( \text{CO}_2 \) as the oxidant, producing \( \text{CO} \) rather than
hydrogen. Coupling the two processes to produce carbon-neutral synthesis gas is also feasible [23]; however
this thesis focuses solely on water splitting.

Volatile cycles were initially discussed for STCH application, where \( \text{ZnO/Zn} \) [19], [24] and
\( \text{SnO}_2/\text{SnO} \) [25] were studied due to the potential for large amounts of hydrogen production per cycle.
However the challenge with these cycles is that they involve solid to gas phase transitions which requires
quenching of the reduced gas phase to allow for \( \text{O}_2 \) separation before recombination. Extremely high
temperatures are required for decomposition of \( \text{ZnO} \) into \( \text{Zn} \) and \( \frac{1}{2} \text{O}_2 \) (\( \sim 2000 \) °C) or to decompose \( \text{SnO}_2 \)
into \( \text{SnO} \) and \( \frac{1}{2} \text{O}_2 \) (\( \sim 1600 \) °C). The gas phase separation process, whether by quenching or other methods,
as well as the challenge of transport the oxidized solid material back to the reduction chamber, led the
researchers to move away from these cycles.

As an alternative to the volatile cycles, iron oxide was proposed as one of the first two-step, all-solid
STCH stoichiometric materials systems [21]. Iron oxide has a large theoretical hydrogen capacity [26], is
earth abundant, and is easy to synthesize. However, extremely high temperatures (2500 K) are required to
reduce \( \text{Fe}_3\text{O}_4 \) to \( \text{FeO} \), which results in melting of the sample, causing sample volatilization and cycle
irreversibility. Lower temperatures (about 1500 K) can be used in conjunction with low oxygen partial
pressures (< $10^{-11}$). However, the drawback of this lower temperature process is that it requires higher reactor complexity because of the higher vacuum capacity required for this system to work. Nonetheless, sintering problems were still experienced and implicated in the deactivation of the material after just a few cycles. Several approaches were investigated to mitigate these sintering problems, including having the iron particles supported on monolithic zirconia [27] or yttrium stabilized zirconia (YSZ) [28]–[30]. However, the problem with this practice is that it introduces an inactive material to the system, which decreases the overall hydrogen production gravimetric efficiency as well as the thermal efficiency of the reactor.

Mixed metal-ferrites (MFe$_2$O$_4$, where M is alkaline earth metal or transition metal such as Mg, Mn, Co, Ni, Zn) [17], [31], [32] were later considered for STCH because of their potential to decrease the reduction temperature of the iron redox cation and therefore eliminate melting and sintering problem while also potentially increasing the extent of reduction. However, only a few of these ferrite materials (Ni and Co mixed metal oxides) were shown to be successful [33], [34], and because they still required reduction temperatures near their melting points, they needed to be supported by inert substrate materials such as YSZ or alumina, leading to the same problems as for the previous supported iron oxide-based cycles. They also suffered from extremely slow oxidation kinetics [35].

CeO$_2$ (ceria) was proposed by Otsuka et al. [36] and later demonstrated by Abanades and Flamant [37] to be a promising WS material by reducing from CeO$_2$ to Ce$_2$O$_3$ at temperatures about 2000 °C and re-oxidizing in the presence of water at 600 °C. Nevertheless these temperatures caused reactor mechanical resistance problems as well as evaporation and sintering of ceria.

It was not until 2009 that ceria was revisited and shown by Chueh et al. [23] to be a promising material for STCH [38], [39] because it does not necessarily require full stoichiometric decomposition to be redox active. Instead, the accommodation of partial oxygen nonstoichiometry, i.e., from CeO$_2$ to CeO$_{2-\delta}$, allows for significant reduction at much lower temperatures. Ceria was shown to produce 379 µmol/g of H$_2$ if reduced at 1500 °C and oxidized at 800 °C and have a 1.4 times increase in H$_2$ production with a 100 °C increase in reduction temperature [38]. Ceria has fast reduction and oxidation kinetics, mostly
due to facile $O^{2-}$ transport through the structure, so that the oxidation reaction is limited only by surface processes. Therefore, increasing the surface area or adding catalyst on the surface can increase the oxidation rate as demonstrated by Furler et al. [40] and Chueh et al. [38]. Moreover, ceria is relatively available and easy to synthesize and has been shown to be very stable for more than 500 water splitting cycles during a single experiment. Ceria’s thermodynamics are so favorable for reoxidation that it can successfully be used for the production of syngas [23].

The major drawback of ceria is the extremely high reduction temperatures required to achieve meaningful oxygen nonstoichiometry. At 1500 °C ceria can achieve a $\delta_1$ of 0.06 and at 1600 °C it can achieve 0.09 [38]. Achieving these nonstoichiometries at such elevated temperatures comes at the cost of sintering problems which greatly affect the oxidation kinetics because of the aforementioned surface reaction limitation. Moreover, at these temperatures there are reactor reradiation losses, which substantially decrease the process efficiency. These temperature limitations have forced researchers to resume the search for better and more practical WS materials.

2.4 Thermodynamics of STCH materials

The approach to discovering of new materials for STCH starts by understanding the thermodynamics of the oxidation reaction. Consider the water formation (or hydrogen oxidation) reaction:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(g)} \quad (2.3)$$

This may be compared against the reduced metal oxide reoxidation reaction, written as:

$$\frac{1}{\delta_2}MO_{x-\delta_1} + \frac{1}{2}O_2 \rightarrow \frac{1}{\delta_2}MO_{x-\delta_1+\delta_2} \quad (2.4)$$

To obtain the metal oxide reoxidation reaction in steam, one may sum the two equations and obtain:

$$\frac{1}{\delta_2}MO_{x-\delta_1} + H_2O_{(g)} \rightarrow \frac{1}{\delta_2}MO_{x-\delta_1+\delta_2} + H_2 \quad (2.5)$$

The same can also be done for the change in Gibbs free energies:
\[ \Delta g_{\text{ox,H}_2\text{O}} = \Delta g_{\text{ox}} + \Delta g_{\text{H}_2\text{O}} \]  

(2.6)

where \( \Delta g_{\text{ox,H}_2\text{O}} \) is the change in Gibbs free energy of the metal oxide’s oxidation reaction with steam, \( \Delta g_{\text{ox}} \) is related to the metal oxide’s oxidation reaction with oxygen and \( \Delta g_{\text{H}_2\text{O}} \) is related to the water dissociation reaction.

The change in Gibbs free energy of the hydrogen oxidation reaction can be compared to the change in Gibbs free energy of the metal oxide reoxidation reaction. This comparison indicates whether a material can split water and the temperature limitations associated with this process. In general, an evaluation of the potential for fuel production from a candidate metal oxide material depends on the relative position of each reaction’s \( \Delta g \) curve. Material curves that are lower than the fuel oxidation curves indicate favorability for fuel production.

Figure 2.1 was reproduced with extracted information from Chueh et al. [38] and shows the change in Gibbs free energy as a function of temperature for ceria, which is in agreement with Takacs et al. [41] reported work.

This figure also shows three partial molar Gibbs free energy curves with respect to temperature for ceria at the stoichiometries of \((\delta = 0.01, 0.05 \text{ and } 0.1)\). Lower \( \Delta g \) represents a more favorable reaction than higher \( \Delta g \) at a particular temperature. For instance, temperatures below 1100 K favor reoxidation of nonstoichiometric ceria in steam and \( \text{CO}_2 \), i.e. favors fuel production. This is because the \( \Delta g_{\text{ox}} \) (driving force for ceria reoxidation) has a smaller value (is more negative) than either \( \Delta g_{\text{H}_2\text{O}} \) and \( \Delta g_{\text{CO}_2} \) (hydrogen and carbon monoxide oxidation reaction). The intersection between \( \Delta g_{\text{ox}} \) of ceria reoxidation and \( \Delta g_{\text{H}_2\text{O}} \) hydrogen reoxidation curves indicate the upper limit for ceria’s reoxidation temperature at a given particular starting stoichiometry.
Figure 2.2: Change in molar Gibbs free energy with respect of temperature for H₂ oxidation, CO oxidation and ceria oxidation at different oxygen stoichiometries all in equilibrium at pO₂ = 1 bar.

As this figure demonstrates, a material’s $\Delta g$ of oxidation reaction varies with extent of oxygen nonstoichiometry. The larger the oxygen nonstoichiometry (larger $\delta$), the more negative $\Delta g$ becomes. This is because oxygen stoichiometry is highly dependent on the temperature. In this sense, larger oxygen nonstoichiometries provide a larger driving force for fuel production and as a consequence they favor fuel production at higher temperatures. This can be demonstrated by ceria as CeO$_{1.99}$ favors oxidation at temperature below 1100 K whereas CeO$_{1.90}$ favors oxidation below a much more elevated temperature of 1400 K.

One may notice that water splitting and CO$_2$ splitting show similar changes in molar Gibbs free with nearly equal favorability between 1150-1200 K. In this range, water splitting materials may also be
used for CO₂ splitting, if other aspects such as reaction kinetics, chemical stability and CO poisoning are not limiting. However at temperatures far from this range, the driving forces for oxidation in steam versus CO₂ vary, indicating that different fuel production performances will be likely.

This quick analysis is helpful for finding potential materials for STCH, but only if oxygen nonstoichiometry thermodynamic data for the materials of interest are available in the literature. For previously identified compounds, this analysis may also further assist in optimizing the temperature conditions for a material’s application in the STCH. Furthermore, one may predict the theoretical yield of hydrogen at a chosen condition and even estimate the cycle efficiency [38], [41]–[44].

The challenge, however, is that in most cases, thermodynamic data is not available and it must be obtained from time-consuming experimentation and calculation so that efficiencies and cycle optimizations can be made. More often than not, to obtain the necessary thermodynamic properties, researchers turn to Thermal Gravimetric Analysis (TGA), which measures mass change as a function of time, temperature, and oxygen partial pressure. During TGA analysis, the material of interest is heated at known temperatures and oxygen partial pressures, and the equilibrium oxygen nonstoichiometry level is recorded by measuring changes in mass.

If assuming an infinitesimal oxygen stoichiometry change (δ₂ is infinitesimally small), the material’s oxidation reaction may be written as [43]:

\[
\frac{1}{\delta_1 - \delta_2} \text{MO}_{x-\delta_1-\delta_2} + \frac{1}{2} \text{O}_2(g) \leftrightarrow \frac{1}{\delta_1 - \delta_2} \text{MO}_{x-\delta_1} \quad (2.7)
\]

The oxidation reaction partial molar Gibbs free energy for each nonstoichiometry may be written as:

\[
\Delta \bar{g}_0^\circ(\delta, T) = -\frac{1}{2} RT \ln \left( \frac{p_{O_2}}{p^o} \right) \quad (2.8)
\]

From a Ahrrenius-type plot, where the pO₂ versus temperature (data sets collected experimentally) are plotted for a given δ, one may obtain the molar partial enthalpies and entropies of the redox reaction. This process is further discussed and applied in Chapter 7.
The thermodynamic experimental data can be used to predict the material’s defect model by either assuming the defect reactions and fitting to the experimental data or by using Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) [45]. This computational method uses all the experimental thermodynamic data available in databases and calculates the best fit for the thermodynamic properties such as the Gibbs free energy of formation and extrapolates this data to more useful temperature and pO$_2$ ranges [46], [47].

2.5 Design criteria for water splitting materials

The last two decades have seen significant advancement in the search for potential STCH materials, however it has been only recently that researchers have begun to fully investigate the constraints of economical viability [48] for this technology. With the major goal of scaling up [49] this application to large concentrated solar towers for the production of industrial amounts of H$_2$ to serve nearby ammonia production facilities, oil refineries, steel mills, or fuel cell electricity plants, success is incumbent on defining the design criteria that drive further developments toward feasibility.

Key metrics such as numerical parameter ranges for water splitting materials are not easily defined because they depend on reactor parameters. This design loop is difficult to close because reactor design and requirements are not fully developed due to the need for water splitting materials parameters and limitations details. Researchers in the field depend on the iteration between material’s and reactor’s design to define key metric requirements for efficiency, temperatures, system pressure, production capacity and production cost ranges.

Even though there are not specific target metrics, general design criteria can be defined based on what is known about the state-of-the-art material limitations and the key parameters that most significantly impact efficiencies and productivity. The primary parameters, and perhaps the most important, are the process temperatures, $T_{OX}$ and $T_{RE}$. The advantage of using a higher $\Delta T_{\text{REDOX}}$ ($T_{RE}-T_{OX}$) is an increase in
theoretical thermodynamic efficiency [50]. As demonstrated by Ermanoski et al. [51] when calculating the reactor heat-to-H₂ efficiency, by making basic assumptions about the reactor and the material’s thermodynamics one may conclude that the efficiency is directly related to the process temperature range.

Ermanoski’s study indicates that at the normal range of pressures (1 to 1kPa) the lower the temperature the greater the potential efficiency. However, large temperature swings require complex heat recovery systems and reactor mechanical integrity to withstand many thermal cycles a day for years. Furthermore, re-radiation losses at the reduction reactor increase with increasing $T_{RE}$, which also drastically affects the general process efficiency. As a result, it has been proposed that $T_{RE}$ should not exceed 1400 °C, which limits the use of many current STCH materials, including ceria [53].

The future of STCH lies now on the design of materials that follow the requirements Miller et al. [50] have compiled. Loss of active material by vaporization is a large concern, as the metal oxide must be able to withstand thousands of high-temperature cycles. Not only do the ferrite materials suffer vaporization losses, as was previously discussed, but even ceria can suffer vaporization losses at $T_{RE}$ above 1650 °C. These losses lead to larger reactor maintenance costs and active material replacement costs as well as losses in process efficiency. Sample contamination and reaction with the reactor chamber is another concern.

The morphology of the WS material also plays a role in the process viability. If materials are oxidation reaction surface limited and need to be supported or require a high surface area microstructure compared to the fully dense bulk particles, the morphology might suffer in such harsh environments. High temperatures trigger grain growth and sintering, and can also lead to surface segregation or other undesirable chemical or structural changes. Although there are ways to mitigate these problems, it is important to keep in mind that these factors may be crucial in choosing a viable STCH material.

The material’s thermodynamics must be suitable for WS, but in addition, the reaction kinetics should be relatively fast to allow for many cycles a day and a high process efficiency. Even though there are ways to improve kinetics such as the use of catalysts, purging flows, having a higher ratio of reactants to products, increase of surface area, etc., it is important to be attentive to kinetic issues, because some of
the methods for mitigating poor kinetics might not be applicable to some compositions or to specific operating conditions.

A last issue to be considered is the ratio of input steam to hydrogen generated. This ratio of reactant to product, which is called reaction conversion, greatly impacts the efficiency of the process. Materials that cannot achieve high conversion are likely to be impractical not only economically but also energetically [54]. The ideal target of $\text{H}_2\text{O}:\text{H}_2$ should be below 10:1, according to McDaniel et al. [53] and Ermanoski et al. [55], [56]. Conversion will be thoroughly addressed in Chapter 4, where I demonstrate how a material’s performance and steam-to-hydrogen conversion ratio are related and why it is important to take this concept into account.

With all these key metrics [50] in mind, including a candidate material’s earth abundance, minimal toxicity and low cost, the research community’s goal is to find a material that can “beat” ceria.

### 2.6 Doped-ceria compounds for STCH

Two principal routes have been taken by researchers in the search for materials that could have a larger fuel production than ceria; 1) improving upon ceria by doping it and 2) discovery of STCH-active perovskite oxides. Many researchers attribute the fluorite structure to ceria’s beneficial thermodynamic properties, and therefore attempt to stay within that structure for further development. It has been suggested that doping ceria could decrease the extreme reduction temperatures needed for pure ceria. Moreover, there is the possibility that the reduction capacity could also increase and, therefore, hydrogen production might also improve. Dopants studied include alkaline earth metals like Mg, as well as 3-d transition metals (e.g., Cu, Fe, Ni, Mn, Al, Cr, Co, Ti, Zr and Hf), among others [42], [57]–[63], [64].

Figure 2. summarizes reported CO$_2$ splitting results for several doped-ceria materials. Tables A.1 and A.2 in the Appendix details the information presented below.
Figure 2.3: CO production via thermochemical CO₂ splitting by ceria and several doped-ceria materials (Ce₀.₇₅Zr₀.₂₅O₂, Ce₀.₇₅Hf₀.₂₅O₂, Ce₀.₈₀Ti₀.₂₀O₂ and Ce₀.₈₅La₀.₁₅O₂ named CeZr25, CeHf25, CeTi20 and CeLa15 respectively) compiled from the literature [57]. Reduction temperatures used were 1400 and 1500 °C and oxidation temperatures used were 700, 800, 900, 1000 and 1100 °C as indicated in the plot using 500 sccm of CO₂.

The CO production results vary considerably depending on the test conditions. The thermochemical cycle is highly dependent on process temperatures and the duration of the reduction and reoxidation steps. Similar behavior can be seen in the H₂O splitting thermochemical experiments shown in Figure 2.4 and Table A.2.
Figure 2.4: H₂ production via thermochemical H₂O splitting by ceria and several doped-ceria materials (Ce₀.₇₅Zr₀.₂₅O₂, Ce₀.₈₅Fe₀.₁₅O₂, Ce₀.₈₅Co₀.₁₅O₂, Ce₀.₈₅Ni₀.₁₅O₂, Ce₀.₈₅Mn₀.₁₅O₂, Ce₀.₉₀Mn₀.₁₀O₂, Ce₀.₉₀Fe₀.₁₀O₂, Ce₀.₉₀Ni₀.₁₀O₂, Ce₀.₉₀Cu₀.₁₀O₂, named CeZr25, CeFe15, CeCo15, CeNi15, CeMn15, CeMn10, CeFe10, CeNi10 and CeCu10 respectively) compiled from the literature. Reduction temperatures used were 1300, 1400, 1450 and 1500 °C and oxidation temperatures used were 845, 945, 1000, 1045, and 1150 °C as indicated in the plot.

CO₂ experiments are more common than those done with steam, primarily because of the complexity in using a condensable gas. The reactor must be equipped with heated gas lines so that the steam does not condense and alter the results. Steam generation, especially at large concentrations, is also challenging, often requiring a steam generator. Flow controls for steam are also much more complicated
and less accurate than non-condensible gas equivalents. CO\textsubscript{2} and H\textsubscript{2}O splitting have similar redox thermodynamics as shown in

Figure 2.2, with H\textsubscript{2}O requiring a slightly higher dG due to the stronger H-O bond compared to the C-O bond. Therefore, in this community it is very common to infer a material’s performance for water splitting from the analysis of the CO\textsubscript{2} splitting results. Other differences in behavior are usually related to kinetics, since the kinetic mechanisms between CO\textsubscript{2} and H\textsubscript{2}O splitting might differ as shown by McDaniel et al. [65], [66].

Although most of these doped-ceria materials have been shown to improve fuel (H\textsubscript{2} or CO) productivity, they present lower fuel efficiency [42]. Moreover, most of the doped-ceria materials incur sintering problem, particularly for the Ni, Fe and Co-doped compounds [67], or a dramatic decrease in oxygen vacancy formation energy, leading to complete deactivation of several of these materials for WS, as occurs for the case of doped compounds containing Ni, Cu, Cr, and Al [59]. Other dopants such as Zr [41], [64], [68]–[71] and Hf [64] have been shown to increase the WS capacity, as reported by Le Gal et al. [70], [71], however at the cost of significantly slower oxidation reaction kinetics.

These mixed results lead some researchers to abandon the fluorite structure and begin looking at alternative structures, particular the perovskite structure, for new STCH candidates.

### 2.7 Perovskite oxides for STCH

Perovskite oxides have been studied and applied to numerous applications, including solid-oxide fuel cells (SOFC) [72], chemical looping [73], colossal magnetoresistors [74], multiferroics [75], oxygen separation membranes [76], STCH [20], and a variety of other applications that require oxygen mobility and/or high oxygen vacancy concentration. Specifically for STCH, the greatest advantage of perovskites over fluorites is their capacity to accommodate larger oxygen nonstoichiometries without destabilizing the structure. This can theoretically lead to increases in hydrogen production.
Perovskite oxides are generally described with the formula $\text{ABO}_3$, where A and B are cations; the A-site is XII-coordinated to oxygen anions and the B-site is VI-coordinated to oxygen anions forming the crystal structure shown in Figure 2. There are multiple combinations of cations possible, with different valency requirements. The two most common configurations typically pair a transition metal on the B-site with either an earth alkaline cation on the A-site, in the case of $\text{A}^{2+}\text{B}^{4+}\text{O}_3^{2-}$ perovskites, or a lanthanide on the A-site, in the case of $\text{A}^{3+}\text{B}^{3+}\text{O}_3^{2-}$ perovskites.

![Figure 2.5: BaTiO$_3$ cubic perovskite crystal structure. The blue atoms are Ti cations sitting on the B-site of the perovskite forming oxygen (red atoms) octahedra. Ba sits on the A-site of the perovskite and is bonded to 12 oxygens.](image)

While Figure 2.5 shows an example of a cubic perovskite, perovskites may also assume different symmetries, such as orthorhombic, tetragonal, or rhombohedral. This flexibility is the second advantage of the perovskites over fluorites, because they may accommodate many different compositions by assuming different symmetries, which may, in-turn, impact the material’s redox capacity.
Besides their tolerance for oxygen nonstoichiometry, the perovskite structure can accommodate various site-substitutions and defects. For example, perovskites used in SOFC cathodes may have four different cations sharing the B-site such as in BaCo$_{0.4}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$O$_3$ [77]. The A-site can also accommodate different substitutions such as shown by Shao et al. [78] in Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$ for oxygen permeation membranes. The site substitution is an important advantage of the perovskites, because by substitution-doping of the structure, one may tune the redox capacity of a material.

Deml et al. [79], [80] have demonstrated that the capacity for WS in two-step STCH materials partially depends on the enthalpy of thermal reduction of the material, as well as the redox capacity (i.e., reversible oxygen nonstoichiometry). Furthermore, the enthalpy of reduction is intimately related to the energy of formation of oxygen vacancies ($E_v$). Therefore, through compositional tuning one may tune the $E_v$ to fall into the right range for STCH.

One of the first successful perovskite families for STCH was introduced by Scheffe et al. [54], La$_{1-x}$Sr$_x$MnO$_3$ (LSM) with $x = 0.30$, 0.35 and 0.40. In Scheffe’s study, it was predicted that LSM would produce 3 times more hydrogen than ceria at a $pO_2 = 10^{-5}$, $T_{RE} = 1327$ °C and at low oxidation temperatures ($T_{OX} = 800$ °C). It was later shown that increases in $x$ ($0 < x < 0.5$) increase the hydrogen production, but also hinder the reaction kinetics [44], dictating that a middle range would be optimal for WS.

McDaniel et al. [66] suggested the partial substitution of the Mn for Al to stabilize the structure and force the transition metal Mn$^{4+}$ to a reduced valence state, Mn$^{3+}$. The resulting Sr$_x$La$_{1-x}$Mn$_y$Al$_{1-y}$O$_3$ (SLMA) perovskite family resulted in one of the most promising perovskites discovered so far for STCH. McDaniel demonstrated that SLMA4664 ($x = 0.4$ and $y = 0.6$) can produce 9 times more hydrogen than ceria under the equivalent conditions of $T_{RE} 1350$ °C and $T_{OX} 1000$ °C, with 40 vol.% steam.

Although LSM and SLMA are promising for water splitting because of their increased oxygen capacity and lower required reduction temperatures, they also possessed a reduced thermodynamic driving force for WS compared to ceria and therefore suffered from incomplete reoxidation. The lower favorability for WS can be compensated by using large amounts of steam. However, this dramatically decreases the
steam-to-hydrogen conversion ratio, likely making practical application in a realistic reactor impossible as pointed out by several researchers [43], [54], [81], [82].

Deml et al. [80] investigated the thermodynamic favorability for WS in relation to the composition among the SLMA family members by calculating the $E_v$ as a function of composition. Her work demonstrated that $E_v$ decreases with increasing Sr content, making the perovskite easier to thermally reduce, but therefore also making the perovskite less favorable to reoxidize in steam. This was in agreement with Yang’s [44] discovery that increases in Sr amount above $x = 0.4$ decreased fuel yield.

The work of Deml et al. [80], [83] as well as others such as Emery et al. [84]–[86] suggested an easier path for predicting promising WS materials. Deml and Emery have demonstrated through DFT computational work that materials with $E_v$ in the range of 2.5 to 5 eV should be thermodynamically suitable for WS. This is because of the tradeoff between reduction capacity and the thermodynamic driving force for water splitting. Materials with $E_v$ less than 2.5 eV will be very easy to thermally reduce, but will not possess sufficient thermodynamic driving force to split water. As $E_v$ increases above 2.5 eV, the thermodynamic driving force for WS increases (this is beneficial) but the ability to thermally reduce decreases (this is undesirable). For $E_v > 5$ eV, impractically high thermal reduction temperatures are required to give a reasonable hydrogen productivity.

Additional perovskite variants, most of them derived from LSM, have subsequently been demonstrated to give increased fuel (H$_2$ and CO) production over ceria. These perovskites include La$_{1-x}$A$_x$Fe$_y$B$_{1-y}$O$_3$ (A= Sr, Ce ; B= Co and Mn) [87], La$_{0.6}$Sr$_{0.4}$Cr$_{0.8}$Co$_{0.2}$O$_3$ [88], La$_{1-x}$A$_x$MnO$_3$ (A = Ca, Sr) [82], [89], [90], Ln$_{1-x}$A$_x$MnO$_3$ (Ln = Nd, Sm, Gd, Dy; A = Sr, Ca) [91], La$_{1-x}$Sr$_x$Mn$_{1-y}$B$_y$O$_3$ (B= Al and Mg) [92], A$_{1-x}$Sr$_x$BO$_3$ (A= La, Ba; B = Mn, Co and Fe) [93], and La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_4$ [93]. Figure 2.6 and Figure 2.7 show the fuel production performance reported in the literature for several of these materials. More details can be found on tables A.3 and A.4.
Figure 2.6: CO production via thermochemical CO\textsubscript{2} splitting by several perovskite materials LSM (La\textsubscript{0.65}Sr\textsubscript{0.35}MnO\textsubscript{3} and La\textsubscript{0.50}Sr\textsubscript{0.50}MnO\textsubscript{3}), LCM (La\textsubscript{0.65}Ca\textsubscript{0.35}MnO\textsubscript{3}, La\textsubscript{0.50}Ca\textsubscript{0.50}MnO\textsubscript{3} and La\textsubscript{0.35}Ca\textsubscript{0.65}MnO\textsubscript{3}), LSF (La\textsubscript{0.70}Sr\textsubscript{0.30}FeO\textsubscript{3}), ACM (Y\textsubscript{0.50}Ca\textsubscript{0.50}MnO\textsubscript{3}, Nd\textsubscript{0.50}Ca\textsubscript{0.50}MnO\textsubscript{3}, Sm\textsubscript{0.30}Ca\textsubscript{0.50}MnO\textsubscript{3}, Gd\textsubscript{0.50}Ca\textsubscript{0.50}MnO\textsubscript{3} and Dy\textsubscript{0.50}Ca\textsubscript{0.50}MnO\textsubscript{3}), ASM (Y\textsubscript{0.50}Sr\textsubscript{0.50}MnO\textsubscript{3}, Nd\textsubscript{0.50}Sr\textsubscript{0.50}MnO\textsubscript{3}, Sm\textsubscript{0.50}Sr\textsubscript{0.50}MnO\textsubscript{3}, Gd\textsubscript{0.50}Sr\textsubscript{0.50}MnO\textsubscript{3} and Dy\textsubscript{0.50}Sr\textsubscript{0.50}MnO\textsubscript{3}), LBM (La\textsubscript{0.50}Ba\textsubscript{0.50}MnO\textsubscript{3}), LSMA (La\textsubscript{0.50}Sr\textsubscript{0.50}Mn\textsubscript{0.75}Al\textsubscript{0.25}O\textsubscript{3} and La\textsubscript{0.50}Sr\textsubscript{0.50}Mn\textsubscript{0.60}Al\textsubscript{0.40}O\textsubscript{3}), LSMMg (La\textsubscript{0.50}Sr\textsubscript{0.50}Mn\textsubscript{0.83}Mg\textsubscript{0.17}O\textsubscript{3}) and LSCrCo (La\textsubscript{0.60}Sr\textsubscript{0.40}Cr\textsubscript{0.80}Co\textsubscript{0.20}O\textsubscript{3}) compiled from the literature. More details on Table A.3.
Figure 2.7: H₂ production via thermochemical H₂O splitting by several perovskite materials LAM (La₀.₅₀Sr₀.₅₀MnO₃ and La₀.₅₀Ca₀.₅₀MnO₃), SLMA (Sr₀.₄₀La₀.₆₀Mn₀.₄₀Al₀.₄₀O₃, Sr₀.₆₀La₀.₄₀Mn₀.₆₀Al₀.₄₀O₃ and Sr₀.₄₀La₀.₆₀Mn₀.₄₀Al₀.₄₀O₃), CTF (CaTi₀.₇₀Fe₀.₃₀O₃), LSCO (LaSrCoO₄) and ASCA’ (Ba₀.₅₀Sr₀.₅₀Co₀.₄₀Fe₀.₂₀O₃ and La₀.₆₀Sr₀.₄₀Cr₀.₄₀Co₀.₂₀O₃) compiled from the literature. More details on Table A.4.
Once again, WS results for the perovskite oxides are more scarce compared to CO₂ splitting results due to the complexity associated with steam experiments. Two aspects shared by both CO₂ and H₂O experiment conditions are the long reduction and oxidation steps, and the large concentration of steam and carbon dioxide used. This highlights the fact that these materials suffer from kinetic and fuel conversion limitations as was previously discussed for LSM.

Even considering these limitations, however, the promising drop in reduction temperatures coupled with the increased fuel yield compared to ceria under the same conditions, suggests that the unfavorable oxidation thermodynamics associated with the candidate perovskite-based STCH materials is not an insurmountable problem. The vast, and still largely unexplored compositional space for perovskites and the performance tunability enabled by this structure suggest that the search for new perovskite-based STCH candidates should continue.
CHAPTER 3
DESIGN OF NEW PEROVSKITES FOR STCH

With such a large compositional space to explore, two challenges immediately present themselves; how to select optimal combinations of A and B-site cations that may produce new promising STCH candidates and how to quickly screen those new compounds. Directly testing every compound for WS is an onerous task, so I began my search for new STCH materials by developing a method to rapidly test the simple redox capacity of materials first, followed by more rigorous testing only on the most promising candidates. Once a screening protocol was in place, informed by chemical intuition and Density Functional Theory (DFT) calculations, a multitude of potential compounds were synthesized and screened.

3.1 Screening method to identify potential STCH-active materials

I developed a rapid screening method to identify potential STCH-active materials based on Temperature Programmed Reduction (TPR). The TPR protocol is informed by reported thermodynamic and computational studies and knowledge of the experimental conditions of interest. This procedure is not designed to directly define the thermodynamic properties of the materials tested; such measurements are time-consuming and require careful analysis based on a knowledge of the active defect mechanisms governing the material’s redox behavior (a fact that will be illustrated more directly later when the thermodynamics of one STCH candidate are investigated in Chapter 7). Instead, TPR is meant to be used as a rapid and direct way to screen materials by comparing their reduction onset, extent of reduction and reoxidation capacity against known WS materials under standardized conditions. The short duration of this test allows for a handful of samples to easily be tested in a single day, and while the materials typically do not reach equilibrium, the times are similar to those of many proposed WS cycles.
In our lab, the screening experiment is performed on a Setaram SetSys Evolution in Thermal Gravimetric Analyser (TGA) mode. A powder sample in the range of 50 to 100 mg of material is loaded into an alumina or Pt crucible. The sample is first heated to 500 °C at 10 °C/min in a flow of 100 sccm of synthetic air (21 % O₂ balanced in N₂) to evaporate any adsorbed or surface tightly bound water as well as to burnout any organic contaminants. The sample is then cooled to room temperature at the same ramp rate and the TGA chamber is vacuum purged and backfilled with UHP N₂. A flowrate of 100 sccm of UHP N₂ is set and the sample is heated at 10 °C/min to \( T_{\text{RE}} \), either 1200°C or 1350 °C. The reduction step is carried out for 1 h. At this point two different test variants can be used. In the first variant, synthetic air is introduced at the high temperature for 5 min before cooling the sample down to room temperature. The second variant adds another temperature step, cooling the sample to \( T_{\text{OX}} = 1000 \) °C at 10 °C/min followed by flowing synthetic air to drive oxidation for 1 h. The sample is then cooled to room temperature. The mass change is recorded as a function of temperature and time and an oxygen sensor is connected to the exhaust of the TGA system to confirm that the mass change is due to oxygen and not volatilization of the sample or another unwanted reaction. Experiments using inert materials are performed to correct for buoyancy effects and flowrate changes.

Figure 3.1 shows TPR results from the \( \text{Sr}_{x}\text{La}_{1-x}\text{Mn}_y\text{Al}_{1-y}\text{O}_3 \) (SLMA) family (details of the materials compositions are found in Table 3.2.1). The redox behavior can be compared to computations, as well as WS performance for some compositions, to validate the predictive strength of the TPR protocol. As calculated by Deml et al. [80], materials in the SLMA family demonstrate distinct redox behavior (extent of reduction and reoxidation capacity) due to differences in \( E_v \) caused by variation in composition. Increasing Sr content in the sample decreases \( E_v \), thereby increasing the extent of reduction, \( i.e., \) the material becomes “easier to reduce.” This increase in favorability for reduction means that less energy has to be used to break the oxygen-cation bonds, however the tradeoff is that it also lowers the favorability for reoxidation in steam, \( i.e., \) the material is “harder to reoxidize.” This decrease in water splitting favorability can be directly correlated to the H₂ production performance shown by McDaniel et al. [66].
Sr_{0.60}La_{0.40}Mn_{0.60}Al_{0.40}O_3 produces 10% less H\textsubscript{2} (277 µmol/g) when compared to Sr_{0.40}La_{0.60}Mn_{0.60}Al_{0.40}O_3 (307 µmol/g) at \(T_{\text{RE}}=1350\) °C and \(T_{\text{OX}}=1000\) °C using 40 vol. % steam.

Figure 3.1: Temperature Programmed Reduction screening method to evaluate redox capacity of materials for STCH. Samples of the SLMA family are shown to exhibit different extent of reduction and reoxidation behaviors. The reduction step was carried at 1350 °C in UHP N\textsubscript{2} for 1 h and synthetic air was introduced just before the sample was cooled down to room temperature.

Compositional variation in the transition metal content, Mn in this case, also affects \(E_v\). As calculated by Deml, the samples SLMA6464, SLMA4646 and SLMA4664 have \(E_v\)'s that increase from 1.4 to 2.2 and 2.6 eV respectively. These calculation results are consistent with the TPR results which show
that the extent of reduction in the three samples decreases in the same order ($\delta = 0.19, 0.11$ and 0.09 respectively).

The TPR method is used throughout this thesis work as a simple and quick comparative method to screen materials for STCH potential. However, this test alone cannot definitively determine if a composition will split water. This is because the energy required to break the O-H bond in the $\text{H}_2\text{O}$ molecule during WS is larger than the energy required to break the O-O bond in the $\text{O}_2$ molecule during TPR, thus some materials that can reoxidize in air may not reoxidize in steam (i.e., the TPR method can generate “false positives”). This means that the reoxidation capacity in air might be different in steam. However, it is possible to use the extent of reduction and reduction onset temperature found by TPR to infer the likelihood of WS. Materials that reduce too easily, as illustrated by onset temperatures below 900 °C, or show large (and non-reversible) extents of reduction generally cannot split water, whereas materials that are “hard” to reduce may have suitable $E_v$ to split water. Based on this premise, we have determined to focus primarily on materials that have reduction behavior that falls between that of ceria and SLMA.

### 3.2 Perovskites synthesized in this work

Emery et al. [84], [86] have conducted extensive computational work using high-throughput DFT to predict stability and $E_v$ for undoped (“end-member”) simple perovskite compositions spanning nearly the entire periodic table. From the 5,329 compositions they surveyed, they found 383 stable simple $\text{ABO}_3$ perovskites and 139 materials that could potentially split water. These materials were calculated to be thermodynamically stable and have an oxygen vacancy formation energy between 2.5 eV and 5 eV. From this study, about one hundred compounds were selected based on chemical intuition and commercial feasibility (e.g., non-radioactive, non-toxic, relatively earth abundant, etc.) and bulk powders were synthesized.
Initially, my strategy was to focus on $A^{2+}B^{4+}O_3$ perovskites, since the higher valence of the B-site should allow for increased oxygen non-stoichiometry when compared to the $B^{3+}$ perovskites. The A-site would necessarily contain elements of the group II-A of the periodic table such as Ca, Sr and Ba, while the B-site should contain a number of 4+ transition metals (Ti, V, Mn, Fe, Co, Mo, and Nb), which are necessary to compensate for the charge accumulated when oxygen vacancies are created during reduction. Elements such as Al and Zr were added as a potential way to increase the oxygen vacancy formation energy ($E_v$), because of their fixed oxidation states. La and Ce were used because of their interesting f-orbital chemistry and the subsequent potential to further modulate $E_v$. A list of the compositions synthesized is given in Table 3.

Table 3.1: List of compounds synthesized in this work according to computational prediction and chemical intuition. A and B correspond to generic cations occupying the A and B-sites respectively.

<table>
<thead>
<tr>
<th>Compound family</th>
<th>x</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CaZr_yB_{1-y}O_3$</td>
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<td></td>
</tr>
<tr>
<td>$CaZr_yMn_{1-y}O_3$</td>
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<tr>
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<td>$CaTi_{0.60}Mn_{0.2}Fe_{0.2}O_3$</td>
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<td></td>
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<tr>
<td>$CaCe_yMn_{1-y}O_3$</td>
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</tr>
<tr>
<td>$CeFeO_3$</td>
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<td>$CeMnO_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$YMnO_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound family</td>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>-----</td>
<td>-----------------</td>
</tr>
<tr>
<td>ASnO₃</td>
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<td>CaSnO₃</td>
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<tr>
<td>SrSnO₃</td>
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<tr>
<td>BaSnO₃</td>
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<td>SrB₃Nb₁₋₂O₃</td>
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<tr>
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<td>AB₃V₁₋₂O₃</td>
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<td>La₄Sr₂₃MoO₄</td>
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<tr>
<td>Sr₃La₁₋₃Mn₁₋₃Al₁₋₃O₃</td>
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<tr>
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<td>0.4, 0.6</td>
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<tr>
<td>Sr₃La₁₋₃Mn₁₋₃Al₁₋₃O₃</td>
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<td>0.5</td>
</tr>
<tr>
<td>Sr₃La₁₋₃Mn₁₋₃Al₁₋₃O₃</td>
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<td>0.5</td>
</tr>
<tr>
<td>Sr₃La₁₋₃Mn₁₋₃Al₁₋₃O₃</td>
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<td>0.4, 0.5</td>
</tr>
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<td>Sr₀₄La₀₈₆Mn₉₆₄Nb₁₋₄₅O₃</td>
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Table 3.1 continued

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<th>x</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$<em>{0.6}$La$</em>{0.4}$Mn$<em>{0.6}$Al$</em>{0.4}$O$_3$</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaCe$<em>y$Mn$</em>{1-y}$O$_3$</td>
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<td></td>
</tr>
<tr>
<td>BaCe$<em>{0.25}$Mn$</em>{0.75}$O$_3$</td>
<td>0.05, 0.15, 0.25, 0.5, 0.75, 1</td>
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<tr>
<td>BaCe$<em>{0.25}$Mn$</em>{0.75}$Al$_{0.05}$O$_3$</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>0, 0.3, 0.5, 0.7, 1</td>
<td></td>
</tr>
<tr>
<td>SrCe$_{1-x}$Mn$_x$O$_3$</td>
<td>0.1, 0.2, 0.3, 0.4, 0.5, 0.9</td>
<td></td>
</tr>
<tr>
<td>Sr$<em>x$Ce$</em>{1-x}$MnO$_3$</td>
<td>0.1, 0.2, 0.3, 1, 1.9</td>
<td></td>
</tr>
</tbody>
</table>

Once calcined, XRD was performed on all the samples to evaluate the structure formation. Samples that formed small amounts of secondary phases were still tested, however, large amounts of secondary phases disencouraged further testing. Compositions that formed the desired phase were then screened using TPR. Figure 3.2 shows the results of single representative members of each compositional family for comparison of redox behavior.

The TPR results indicate that some of these oxides reduce too easily, such as CeFe and CeMn, and therefore are probably not suitable for STCH. CaMn$_{50}$Ce$_{50}$, suffered significant mass loss during sample pre-treatment (burnout at 500 °C in air), illustrated by the fact that the curve begins below zero (although this does not necessarily indicate that the sample was reduced).
Figure 3.2: Temperature Programmed Reduction screening experiment performed at 1350 °C in UHP N₂ followed by introduction of synthetic air for 5 min to allow for reoxidation. Samples tested were selected as the most representative in their families (SrFe₈₀Nb₂₀ = SrFe₉₀.₈₀Nb₀.₂₀O₃, Sr₈₀La₂₀Mn₆₀Ce₄₀ = Sr₀.₈₀La₀.₂₀Mn₀.₆₀Ce₀.₄₀O₃, LaMn₅₀V₅₀ = LaMn₀.₅₀V₀.₅₀O₃, CaMn₅₀Ce₅₀ = CaMn₀.₅₀Ce₀.₅₀O₃, CeFe = CeFeO₃, CeMn = CeMnO₃ and CaZr₅₀Mn₅₀ = CaZr₀.₅₀Mn₀.₅₀O₃). Ceria was added for comparison.

A subsequent mass loss occurred during heating at about the same temperature (500 °C in UHP N₂) before its final loss starting around 1200 °C. After reduction at 1350 °C it did not completely recover its mass after reoxidation. This sample likely suffered partial decomposition (investigation of this sample’s XRD results showed the presence of several secondary phase) making it uninteresting for further study.

LaMn₅₀V₅₀ and CaZr₅₀Mn₅₀ were shown to be composed of several secondary phases as well, and their reduction onset temperature was very low (about 650 °C).
As mentioned earlier, this is usually another indication of unfavourability for steam reoxidation and therefore both families were also disregarded for WS testing. SrFe80Nb20 and Sr80La20Mn60Ce40 fall in the predicted reduction range for WS. And although both materials also were scored low on at least one other metric (the SFN had a very low reduction onset temperature and SLMC did not completely reoxidize), the $\text{H}_2$ production capability was tested and they were shown to be thermochemically active. However, their low $\text{H}_2$ production and slow kinetics discouraged further investigation.

A few compositions were tested at lower $T_{\text{RE}}$ (1200 °C), as shown in Figure 3.3, because we encountered melting and/or severe sintering issues for these materials at higher temperatures. While it is unlikely that a material that undergoes significant reduction at such low temperatures would be suitable for STCH, we deemed it important to still evaluate these materials for purposes of model and prediction validation.

SrZr50Fe50 had an onset reduction temperature too low to be suitable for WS and exhibited problems with sintering, even at the lower testing temperature. CaZr50Fe50 also experienced sintering problems due to the iron composition and the CaSn sample was shown to have a low extent of reduction. As expected, all three formulations were uninteresting for WS, but they did assist in furthering our understanding of the effects of certain cation combinations and allowed us verify predicted trends in $E_v$ values.

After evaluating the structure, phase purity and redox behavior of over one hundred samples (additional TPR results for each family of materials are compiled in Appendix B), three compositions were revealed to be highly promising for WS and therefore were selected for further detailed investigation.
Figure 3.3: Temperature Programmed Reduction screening experiment performed at 1200 °C in UHP N₂ followed by introduction of synthetic air for 5 min to allow for reoxidation. Samples tested were selected as the most representative in their families (SrZr₅₀Fe₂₀ = SrZr₀.₅₀Fe₀.₅₀O₃, CaZr₅₀Fe₅₀ = CaZr₀.₅₀Fe₀.₅₀O₃, CaSn = CaSnO₃).

All three materials had extents of reduction lying within the proposed WS range (i.e., between SLMA6464 and ceria). All three also showed a larger extent of reduction than ceria, which indicates the potential for improved H₂ production compared to ceria. At the same time, all three materials had extents of reduction that were less than SLMA6464, suggesting a higher favorability for reoxidation in steam.
Figure 3.4: Temperature Programmed Reduction screening experiment performed at 1350 °C in UHP N₂ followed the oxidation step at 1000 °C in synthetic air. Samples tested are the most promising for WS. (Ce₀.₂₀Sr₁.₈₀MnO₄, Sr₆₀Ce₄₀MnO₃, BaCe₂₅Mn₇₅ = BaCe₀.₂₅Mn₀.₇₅O₃). Ceria and SLMA6464 are added as the two limits for WS.

The onset reduction temperatures fall in a reasonable temperature window (above 800 °C), also pointing towards suitability for WS. Not all could successfully achieve full reoxidation, however further TPR cycles showed full recoverability after the initial cycle. BaCe₀.₂₅Mn₀.₇₅O₃ water splitting performance was shown to be very promising and it will be discussed in more detail in the following chapters (Chapters 5 and 7). Ce₀.₂₀Sr₁.₈₀MnO₄ was shown to be a Ruddlesden-Popper phase with a composition never before reported in the literature. This sample was carefully characterized and also showed interesting WS behavior (reported in Chapter 6). Finally, in Chapter 8, the recently identified Sr₀.₆₀Ce₀.₄₀MnO₃ is suggested for future work as another potential candidate for STCH.
CHAPTER 4

EXPERIMENTAL METHOD FOR ASSESSING PRODUCTIVITY AND CONVERSION IN METAL OXIDE THERMOCHEMICAL WATER AND CARBON DIOXIDE SPLITTING WITHOUT KNOWLEDGE OF OXIDE THERMODYNAMICS

This letter has been prepared for submission to *Journal of Physical Chemistry Letters*.

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Two-step solar thermochemical hydrogen (STCH) production [20] using phase-change and/or nonstoichiometric redox oxides is receiving recent scientific and technological attention as a promising solar-to-fuel conversion technology.

The cycle begins with a metal oxide that, when exposed to high temperatures and/or decreased oxygen partial pressure, releases oxygen gas

\[
\text{MO}_{x_1} \rightarrow \text{MO}_{x_2} + \frac{\delta_R}{2} \text{O}_2(g), x_1 > x_2
\]  

(4.1)

where, the extent of reduction is given as \(\delta_R = x_1 - x_2\). After the thermal reduction, the metal oxide is separated from the evolved oxygen and subjected to lower temperatures that favor re-oxidation. When steam is introduced, the material re-oxidizes by partially splitting water, thereby producing hydrogen.
\[ \text{MO}_{x_2} + \gamma \text{H}_2\text{O}_{(g)} \rightarrow \text{MO}_{x_3} + \delta_0 \text{H}_2\text{O}_{(g)} + [\gamma - \delta_0] \text{H}_2\text{O}_{(g)} \]  

(4.2)

where the oxygen content stoichiometry at the end of the thermal reduction half-cycle is given by \( x_2 \), the extent of reoxidation at the end of the water splitting (WS) half-cycle is given by \( x_3 \) and the amount of steam introduced is given by \( \gamma \). The extent of reoxidation is \( \delta_0 = x_3 - x_2 \), and since in some cases reoxidation is not complete, \( x_3 \leq x_1 \). If the heat needed for the reduction and steam production processes is derived from renewable thermal energy, e.g., generated by concentrated solar facilities, the process can provide a near carbon-free source of industrial quantities of hydrogen. Similar process have been developed that use \( \text{CO}_2 \) as the oxidant, producing \( \text{CO} \) rather than hydrogen; combining the two processes provides a route to carbon-neutral synthesis gas. While this letter focuses on the water splitting cycle, the ensuing discussion has equal applicability to \( \text{CO}_2 \) splitting as well.

Ceria (\( \text{CeO}_2 \)) is the current state-of-the-art material for STCH [94], primarily due to its stability, fast kinetics, and distinctively favorable chemical potential of oxygen. However, it requires high temperatures to reach reduction levels that are large enough to produce meaningful hydrogen yields. Thus, a major effort in advancing STCH is the search for new materials that can exceed the benchmark performance of ceria while simultaneously meeting other reactor-driven requirements. Key metrics include: low reduction temperature (\( T_{RE} < 1400 \, ^\circ\text{C} \)) in order to limit reradiation losses and simplify reactor design [50], high \( \text{H}_2 \) yield per-cycle, and the chemical and mechanical stability to withstand tens of thousands of cycles [26]. Some of these requirements are conflicting. For instance, decreasing \( T_{RE} \) requires improved reduction thermodynamics; however, this inversely affects the thermodynamic driving force for water splitting, potentially lowering \( \text{H}_2 \) yield.

The challenging materials constraints associated with the STCH process have therefore resulted in a very broad search for candidate materials to replace ceria [50], [95]. With a few notable exceptions [38], [41], [47], [51], [55], [68], [96], steam-to-hydrogen conversion ratio is rarely considered as a figure of merit in STCH materials screening, being expressed as:
However, the solar-to-fuel efficiency is strongly dependent on water conversion (moles of hydrogen obtained per mole of steam introduced) because the heat that goes into boiling water and heating the steam (or heating CO\textsubscript{2}) is not fully recuperated [51]. A survey of the literature shows that, given the flow rate of steam, mass of reactive material, amount of hydrogen generated, and the reaction time, steam-to-hydrogen conversion averaged over the WS half-cycle in lab-scale experiments is typically much less than 0.1% [26], [51]. However, issues can arise when extending operation to higher conversions; the high concentrations of hydrogen product greatly reduce the local oxygen partial pressure, increasing the probability that the reverse-reaction will occur, removing additional oxygen from the oxide material and consuming some of the hydrogen product.

Therefore in this letter, we demonstrate the importance of screening materials for performance under multiple conversion conditions, i.e., determining their reverse reaction resistance (RRR), and introduce an experimental method that evaluates a potential STCH material’s fuel productivity without \textit{a priori} knowledge of material thermodynamics. This adds rigour to the evaluation of prospective water splitting materials because it places the material’s performance within the context of large-scale commercial viability.

Typically, evaluation of a STCH material reported in the literature is carried out in a continuous gas-flow reactor or thermogravimetric analyzer (TGA) using a static amount of oxide. In these experiments, conversion as defined in Equation 4.3 can be calculated at each instantaneous point along the reoxidation curve, but not controlled as an experimental parameter. Conversely in our testing protocol we propose to measure the material’s RRR by introducing controlled amounts of hydrogen to the input steam during the WS reaction.
Thermodynamically, this fixes the initial \( p_{O_2} \) (or equivalently, the \( p_{H_2} : p_{H_2O} \) ratio, simplified to \( H_2O:H_2 \) going forward) throughout the WS half-cycle, regardless of the amount of hydrogen generated in the cycle. By varying the \( H_2O:H_2 \) in the inlet stream during WS, we can evaluate the material’s \( H_2 \) yield and potential thermodynamic limitations. Our RRR testing protocol is reactor agnostic and can be performed using any continuous-flow apparatus.

For this study, experiments were performed using Sandia’s Stagnation Flow Reactor [65]. To evaluate the impact of conversion condition on WS behavior, we chose to test ceria as well as two alternative STCH candidates at various \( H_2O:H_2 \) and under pure steam conditions. As the current state-of-the-art material for STCH, ceria [38] is known to have a high performance even under reducing conditions (i.e., high concentration of hydrogen) during WS. It therefore serves as a baseline in this study. To provide a point of comparison vs. ceria, we also selected \( \text{Ce}_{0.95}\text{Zr}_{0.05}\text{O}_2 \) (CZ05) [41], [58], [64], [68], as it has recently been shown to enable increased reduction capacity than ceria (and hence potentially improved STCH performance).

In addition, we selected \( \text{La}_{0.60}\text{Sr}_{0.40}\text{Mn}_{0.60}\text{Al}_{0.40}\text{O}_3 \) [66] (LSMA) as a representative of the emerging class of perovskite-based STCH materials [65], [88], [97]. LSMA exhibits an extremely large \( H_2 \) production capacity and can be employed at lower reduction and re-oxidation temperatures than ceria, which makes it a potentially interesting candidate for STCH applications. The three materials were first tested in the absence of hydrogen (40 vol. % steam balanced by argon) with the WS step proceeding at an oxidation temperature \( T_{OX} = 850 \, ^\circ\text{C} \) for 480 s (ceria and CZ05) or 1200s (LSMA due to its slower oxidation kinetics). The reduction step occurred at \( T_{RE} = 1350 \, ^\circ\text{C} \) for 240 s (ceria and CZ05) or 330 s (LSMA).

RRR was tested at decreasing decades of \( H_2O:H_2 \) (1000:1, 100:1, 10:1 and 2:1). The results are shown in Figure 4.1.a.
Figure 4.1: a) Experimental H$_2$ Production at various H$_2$O:H$_2$. Dashed lines are WS with 40 vol. % water. LSMA was reduced for 330 s and oxidized for 1200 s, whereas CZ05 and ceria were reduced for 240 s and oxidized for 480 s. b) Residual oxygen non-stoichiometry remaining after reoxidation ($1 - \delta_O/\delta_R$).

Although ceria has lower hydrogen production capacity than LSMA under the original test conditions, this H$_2$ production capacity is maintained during the RRR study. In contrast, LSMA quickly deactivates even at a H$_2$O:H$_2$ ratio of 1000:1. More surprisingly, however, we found that CZ05 fails to
reproducibly split water under the same steam-to-hydrogen conditions. We attribute the failure of CZ05 to two main reasons: first, the CZ05 WS reaction appears to be kinetically limited at the temperature tested; second, the reduction temperature was not high enough to drive meaningful reduction in CZ05. Because of these issues, CZ05 and ceria were re-tested at higher \( T_{\text{RE}} \) (1500 °C), while \( T_{\text{OX}} \) was maintained at 850 °C. Reduction and oxidation times were maintained at 240 s and 480 s, respectively. At \( T_{\text{RE}} = 1500 \) °C, CZ05 demonstrates meaningful and repeatable WS behavior, although the H\(_2\) yield of ceria is larger. We note that this is contrary to initial expectations as CZ05 was predicted to have a higher H\(_2\) yield than ceria based on its higher reduction capacity. Takacs et al. [41] have pointed out the importance of also considering oxidation thermodynamics when predicting fuel productivity. The experiments show that not only are the oxidation thermodynamics less favorable at lower H\(_2\)O:H\(_2\), but that CZ05 has much slower reduction and oxidation kinetics when compared to ceria, and thus shows a lower H\(_2\) production capacity during the limited-duration STCH cycles examined in this study. This conclusion is reinforced by the fact that CZ05 retains 29% of \( \delta_R \) even after oxidation at 40 vol. % steam (i.e., \( \delta_0 = 0.71\delta_R \)). Figure 1b plots the residual oxygen nonstoichiometry created during reduction that remains after WS and confirms that the decrease in H\(_2\) yield correlates directly with the increasingly incomplete reoxidation of both materials at lower H\(_2\)O:H\(_2\). Overall, the amount of H\(_2\) produced by CZ05 and ceria follow a similar trend with decreasing H\(_2\)O:H\(_2\). At the lowest H\(_2\)O:H\(_2\) of 2:1, CZ05 suffers a 51% decrease in productivity, while ceria experiences a 30% decrease in productivity.

Although LSMA produces more H\(_2\) than ceria under 40 vol. % steam (i.e., in the complete absence of hydrogen), it fails to split water meaningfully at most of the alternative H\(_2\)O:H\(_2\) tested (losing 75% of the initial hydrogen production at 1000:1 and producing no measurable hydrogen thereafter). The deactivation of LSMA under RRR conditions is due to the decreased thermodynamic favorability for steam dissociation at the H\(_2\)O:H\(_2\) conditions tested. We illustrate the relationship between thermodynamic favorability, fuel production, and conversion in fed-batch and continuous reactors in Figure 4.2.a-b. Material-specific STCH cycles were simulated by over-laying calculated [47] and experimental [46], [81] \( P_{O_2} \)-vs-delta data on top
of isothermal curves of $p_{O_2}$ in the gas phase for a “closed” or fed-batch reactor. During reduction, the $p_{O_2}$ and oxygen content evolve along the high-temperature reaction-specific isotherm in the direction of the arrow according to the following mass-balance equation

$$x = x_1 - \frac{2\beta}{1 - \frac{p_{O_2}(\delta)}{p_{O_2}^{-1}}}$$

(4.4)

where the parameter $\beta$ is the molar ratio of inert gas to metal oxide and was held constant at $10^3$ for all simulations. The point at which the reduction isotherm crosses the material-specific isotherm represents the $p_{O_2}$ and oxygen content at which the gas and solid phases are in equilibrium and thus the thermodynamic endpoint for the reduction reaction. The WS reaction is described according to the equation

$$x = x_2 + \gamma \left( \frac{1}{p_{O_2}^{-1}} \right)^{1/2} - \frac{2}{1 - \frac{p_{O_2}^{-1}}{p_{O_2}^{-1}}}$$

(4.5)

where $K_{eq}$ is the equilibrium constant for dissociating one mole of water at $T_{OX}$. Further details of these simulations can be found in the SI.

To see the impact of the amount of steam, we simulated excess and stoichiometric steam-to-oxide ratios ($\gamma = 10^3$ and 1). For the same $T_{RE}$ and $T_{OX}$, changing the amount of steam substantially influences the fuel productivity and conversion ($\xi$). Specifically, for LSMA, decreasing steam amount causes predicted $H_2$ productivity to decrease from 427 to 19 $\mu$mol/g. For ceria, on the other hand, $H_2$ productivity is 102 $\mu$mol/g and is largely unaffected by the changing steam amount. This is due to the difference in thermodynamics between the two oxides. In Figure 2a- b, for ceria, the low temperature curve is steeply sloped and takes on values of small oxygen deficiency even at low $p_{O_2}$, which means that ceria can be oxidized even in a reducing environment at $T_{OX}$. This is not the case for the perovskite, for which the isotherm at $T_{OX}$ is shallowly slaped at low $p_{O_2}$ and largely parallel to the isotherm at $T_{RE}$. This reflects the tendancy for $H_2$ to further reduce the oxide, rather than for $H_2O$ to oxidize the oxide.
Figure 4.2: Simulated closed-reactor thermochemical cycles of CeO$_2$ (blue lines), CZ05 (red lines) and LSMA (green lines). The thick solid lines represent the equilibrium $p_{O_2}$ as a function of oxygen stoichiometry $x$ at 850 °C (upper lines) and 1350 °C (lower lines). The dashed lines represent the evolution of $p_{O_2}$ and $\delta$ during a stable reduction half-cycle in a closed reactor with excess inert gas ($\beta = 10^3$) and the corresponding stable oxidation-with-water half-cycle with a) excess water ($\gamma = 10^3$) and b) limiting water ($\gamma = 1$).
The thermodynamic deactivation behavior of LSMA relative to ceria and CZ05 is a direct result of each material’s partial molar entropy and enthalpy of reduction. Using an analysis first presented by Meredig et al. [98], one can build a screening map showing which metal oxides are thermodynamically suited for two-step water-splitting at a range of H₂O:H₂ conditions.

Figure 4.3.a shows a parametric plot of the thermodynamic parameters \( h_{MOx}(x) \) and \( s_{MOx}(x) \) of reduction for ceria [46], CZ05 [41], [99], [100], and LSMA [101] (calculation details can be found in the SI). The gray lines represent equilibrium for water-splitting at 850 °C and varied H₂O:H₂.

Materials above each water-splitting line spontaneously uptake oxygen in the presence of steam and hydrogen (WS favorable). Furthermore, as a material oxidizes (following the delta curves to the right and \( \delta_R \rightarrow \delta_0 \)), it becomes more difficult for oxidation to continue, requiring larger H₂O:H₂ ratios. Ultimately, it is the position of the final point on the curve at near stoichiometry (\( \delta = 0.001 \)) that dictates whether a material can completely reoxidize in steam. All the materials included in

Figure 4.3.a can undergo WS at 850 °C in pure steam. However, adding just 10 ppm H₂ to steam causes several of the oxygen-content symbols for LSMA to lie below the H₂O:H₂ of 10000:1 contour, indicating that there is some “residual” oxygen-nonstoichiometry that cannot be accessed in such a two-step cycle. Thus, LSMA that has very low enthalpy, will exhibit less hydrogen productivity when conversion is required to be at least 0.001% and all water splitting is thermodynamically unfavorable at H₂O:H₂ below ~200 even for deep reduction of the oxide. Ceria, on the other hand, will experience no change in hydrogen productivity unless the amount of hydrogen mixed with steam is very high. CZ05, which lies between the two materials, begins to deactivate when H₂O:H₂ < 100. Of the three materials in this study, only CeO₂ can produce large quantities of hydrogen when H₂O:H₂ is required to be 1.
Figure 4.3: a) Thermodynamic property maps showing favorability regions for water-splitting at $T_{\text{OX}} = 850$ °C and variable $\text{H}_2\text{O}:\text{H}_2$ (water splitting is favorable for dots above the gray lines). Each dot represents a different oxygen content, which increases to the left in intervals of 0.02 from 0.001 – 0.35. White symbols show the final oxygen non-stoichiometry for the reduction conditions used for experiments in Figure 4.1. b) Oxidation temperature dependence of RRR for ceria, CZ05 and LSMA.
The curves in Figure 3b are derived from the same thermodynamic data as Figure 4.3.a, but instead demonstrate how oxidation temperature also affects RRR. Any combination of H₂O:H₂ and temperature below a given line will drive further oxidation (WS) for that oxide, while any combination of H₂O:H₂ and temperature above the line will instead lead to reduction of the oxide. For all oxides considered here, decreasing $T_{OX}$ increases the favorability for lower H₂O:H₂; however, lower $T_{OX}$ also negatively impacts the reaction kinetics, leading to longer cycles and decreased H₂ production rates. It should be noted that, interestingly, LSMA has very little oxidation temperature dependence, which could perhaps be exploited by less traditional STCH cycle parameters.

The thermodynamic deactivation behavior of LSMA relative to ceria is not apparent in traditional WS experiments as the rate of steam supply greatly exceeds (by $10^6$X or more) the H₂ being produced. The key conclusion is that LSMA needs an extremely large steam excess to drive water splitting, which drops the reactor’s efficiency due to the heat losses associated with steam production and recycling. This suggests that LSMA is not likely to be a practical STCH material without new reactor design approaches. Analyses such as those provided by Figure 4.2 and Figure 4.3 are a necessary portion of the material evaluation process when suitable thermodynamic data is available (of course, it should again be noted that these analyses consider only the thermodynamic favorability for WS, and therefore disregard kinetic limitations). However, thermodynamic investigations of new materials can be a time and resource consuming process that can take away from the screening of new candidates. Alternately, the proposed RRR testing protocol provides a crucial way to evaluate the potential of candidate STCH materials while considering realistic reactor conditions and bypassing the need for thermodynamic investigation.
4.1 Experimental methods

The WS experiment was performed in a Stagnation Flow Reactor at Sandia National Laboratories as described elsewhere [65], [102], [103]. The sample is loaded at a zirconia boat. A tubular furnace heats the material at the desired \( T_{OX} \). A laser heats the sample to the \( T_{RE} \) at the controlled rate of 10 °C/s. A Mass Spectrometer and an oxygen sensor measure the amount of \( O_2 \) released during reduction. The material is cooled down at a controlled rate to the \( T_{OX} \) by controlling the laser power. Steam, or, in the case of the RRR experiment, a mixture of steam and hydrogen, is introduced into the reactor initiating the reoxidation (WS) reaction. The amount of hydrogen produced is inferred by the amount of \( O_2 \) released during the subsequent reduction, because of the Mass Spectrometer difficulties of differentiating the \( H_2 \) produced from the \( H_2 \) in the background.

For the 40 vol. % water WS experiment, 200 sccm of pure steam was flowed with 300 sccm of Ar as a carrier gas during oxidation. The RRR experiments were performed with controlled amounts of \( H_2 \) mixed in steam. For the high ratio of 1000:1, 4 sccm of 5% \( H_2 \) (balanced with Ar) was added to 200 sccm of steam and then balanced with Ar to reach 500 sccm of total flow. The lower ratios of 100:1, 10:1 and 2:1 were achieved by mixing 200 sccm of pure steam with 2, 20 and 100 sccm of 100% \( H_2 \), again with the balance to 500 sccm being Ar.

4.2 Acknowledgments

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4.3 Co-authors contribution

This work was realized by researchers over three different institutions. As the first author I was responsible for all the experimental work, coordination of the discussions and writing the manuscript. Ms. Nadia Ahlborg, Ph.D student at Stanford University is the second author in this manuscript and is responsible for the close-system thermodynamic modeling as well as writing. Prof. Michael Sanders was responsible for revisions and helped with discussions and data analysis. All the remainder co-authors helped with revisions.

4.4 Supporting information

This section will describe the simulation of thermodynamic favorability for water splitting and predicted fuel productivity details.

In a “closed reactor”, the partial pressure of oxygen in the gas can be calculated as a function of oxide nonstoichiometry change $\Delta \delta$ by applying simple mass balance equations to known initial and final states. For the reduction half-cycles, it was assumed that the reactor was filled with $n_{\text{inert}}^0$ moles of pure inert gas and $n_{\text{MO}_2}^0$ moles of oxide with initial oxygen stoichiometry $\delta_i$ at temperature $T_{\text{H}}$ (high
temperature. Based on the reaction given in equation (1), the number of moles of oxygen as a function of $\delta$ is then:

$$n_{O_2}(\delta) = \frac{1}{2}n_{MO_2}^0$$ (4.6)

Assuming the total gas pressure is fixed at 1 bar, the partial pressure of oxygen in units of bar is

$$P_{O_2} = \frac{n_{O_2}^0}{n_{inert}^{O_2} + \frac{1}{2}(\delta - \delta_i)} = \left(\frac{n_{inert}^0}{n_{MO_2}^0} \times \frac{2}{\delta - \delta_i} + 1\right)^{-1}$$ (4.7)

and the parameter $n_{inert}^0/n_{MO_2}^{\delta-\delta_0}$ is a measure of how much excess inert gas was added to the reactor. The end-reaction-state is reached when the gas and solid are in equilibrium. Equilibrium $P_{O_2}, \delta$ isotherms have been measured or calculated for many nonstoichiometric oxides and are available in the literature. In this simulation, $P_{O_2}(\delta)$ was compared to the equilibrium isotherms for cerium oxide [52] and La$_{0.6}$Sr$_{0.4}$MnO$_3$ [47] at $T_{HI}$. Numerical methods were used to solve for the intersection point between $P_{O_2}(\delta)$ and the isotherm for each material. The resulting nonstoichiometry $\delta_f$ was considered as the starting point for the next half-cycle.

For the oxidation-with-water half-cycle, it was assumed that the reactor was initially filled with $n_{H_2O}^0$ moles of pure steam and $n_{MO_2}^0$ of oxide with initial non-stoichiometry $\delta_f$. At the $T_{LO}$ (low temperature) values investigated in this work, water dissociates to form non-negligible amounts of oxygen and hydrogen.

$$2H_2O(g) \leftrightarrow 2H_2(g) + O_2(g)$$ (4.8)

Thus, one needs to consider both oxygen uptake by the oxide as given in equation (2) also the dissociation of water to form $y$ moles of oxygen and $2y$ moles of hydrogen.

$$n_{O_2}(\delta) = y$$ (4.9)

$$n_{H_2}(\delta) = 2y + (\delta_f - \delta)n_{MO_2}^0$$ (4.10)

$$n_{H_2O}(\delta) = n_{H_2O}^0 - 2y - vn_{MO_2}^0$$ (4.11)

$$n_{tot} = n_{O_2}(\delta) + n_{H_2}(\delta) + n_{H_2O}(\delta) = y + n_{H_2O}^0$$ (4.12)
The partial pressure of each gas is thus:

\[ P_{O_2}(\delta) = \frac{y}{y+n_{H_2O}^0} \]  
(4.13)

\[ P_{H_2}(\delta) = \frac{2y+(\delta_f-\delta)n_{MO_2}^0}{y+n_{H_2O}^0} \]  
(4.14)

\[ P_{H_2O}(\delta) = \frac{n_{H_2O}^0-2y-(\delta_f-\delta)n_{MO_2}^0}{y+n_{H_2O}^0} \]  
(4.15)

Equilibrium is reached when \( y \) and \( \delta \) are chosen such that \( P_{O_2}(\delta) \) falls on the relevant equilibrium isotherm line at TLO and the equilibrium constant expression for water dissociation is satisfied.

\[
\ln[K_{eq}(T_{LO})] = \ln[P_{O_2}] + 2 \ln \left[ \frac{P_{H_2}}{P_{H_2O}} \right] 
\]  
(4.16)

\[
\ln[K_{eq}(T_{LO})] = -\ln \left[ \frac{n_{H_2O}^0}{y} + 1 \right] - 2 \ln \left[ \frac{n_{H_2O}^0}{2y+(\delta_f-\delta)n_{MO_2}^0} - 1 \right] 
\]  
(4.17)

Rearranging the expression for \( P_{O_2} \)

\[ y = \frac{n_{H_2O}^0}{n_{O_2}^0-1} \]  
(4.18)

Substituting the above equation for \( y \), we now have an equation describing mass balance of oxygen between the gas and solid phases during the water-splitting step:

\[
\ln[K_{eq}(T_{LO})] = \ln[P_{O_2}] - 2 \ln \left[ \frac{\frac{1}{n_{MO_2}^0(\delta_f-\delta)}}{\frac{1}{n_{H_2O}^0} + \frac{1}{n_{MO_2}^0(\delta_f-\delta)}} - 1 \right] 
\]  
(4.19)

Again, \( \frac{n_{H_2O}^0}{n_{MO_2}^0} \) is a measure of how much excess water was added to the reactor. Once again, the end-reaction-state is the nonstoichiometry value where \( P_{O_2}(\delta) \) intersects the material-specific equilibrium isotherm. If the resulting nonstoichiometry \( \delta_i \neq \delta_f \) from the previous reduction half-cycle, up to 10 additional iterations were performed until a “stable cycle”, in which the reduction starting point and the oxidation endpoint differed by less than \( \delta = 10^{-5} \) was reached.
CHAPTER 5

BaCe$_{0.25}$Mn$_{0.75}$O$_{3-δ}$ — A PROMISING PEROVSKITE-TYPE OXIDE FOR SOLAR
THERMOCHEMICAL HYDROGEN PRODUCTION

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Abstract

Solar-thermal based hydrogen production technologies employing two-step metal oxide water-splitting cycles are emerging as a viable approach to renewable and sustainable solar fuels. However, materials innovations that overcome thermodynamic constraints native to the current class of solar-thermal water splitting oxides are required to increase solar utilization and process efficiency. Lowering oxide thermal reduction temperature while maintaining high water-splitting favorability are important ways to enhance such performance metrics. Recent attention to perovskite-type oxides as an alternative to ceria, which is widely viewed as the state-of-the art redox material, is driven by demonstrated thermodynamic and structural tuning derived through engineered composition. Here we discuss the unique properties of BaCe$_{0.25}$Mn$_{0.75}$O$_3$ (BCM) within the context of thermochemical water splitting materials. Firstly, BCM is a novel example of a line compound with B-site substitution of Mn by Ce. It also exhibits a polymorph phase transition during thermal reduction and yields nearly $3 \times$ more H$_2$ than ceria when reduced at lower...
temperature (1350 °C). More importantly, BCM exhibits faster oxidation kinetics and higher water-splitting favorability than Sr$_x$La$_{1-x}$Mn$_y$Al$_{1-y}$O$_3$ (x, y = 0.4, 0.6), which is a well-studied and popular Mn-based perovskite formulation. The unique properties manifested by BCM through engineered composition offer new pathways towards unlocking higher performing materials for solar thermochemical water splitting.

5.1 Introduction

A solar-driven two-step thermochemical cycle for splitting either water (so called STCH or STC hydrogen) or carbon dioxide utilizing metal oxides has the potential to provide industrial-scale quantities of renewable solar fuels. First proposed by Nakamura [21], the cycle chemistry is deceptively simple and avoids known technological barriers associated with other multistep gas-splitting cycles [95], [104]. Unfortunately even the simple stoichiometric cycle chemistries proposed by Nakamura and others are subject to undesired thermally-driven phenomena, such as phase change, metal volatilization, sintering, and complex solid solution behavior, that have thus far confounded further development of the approach [17], [32]. Recently, non-stoichiometric oxides have emerged as the preferred redox-active material for two-step gas-splitting cycles because they are able to maintain phase stability under the extreme thermal and chemical stresses encountered in a solar thermochemical reactor environment [105]. In this approach, a suitable oxide is defected by driving oxygen spontaneously from the lattice at high temperature. However, unlike the stoichiometric reaction, the oxygen deficiency does not result in phase change, decomposition, or disproportionation. When the reduced oxide is exposed to steam or carbon dioxide at conditions suitable for spontaneous reoxidation, oxygen is stripped from the gas molecule and transferred back into the oxide. And as in the stoichiometric cycle, hydrogen or carbon monoxide is the net product of the reactions.

Ceria (CeO$_2$) remains the benchmark material for single-phase non-stoichiometric STCH cycling [105]. It is favored because of a combination of phase stability, fast redox kinetics, and high fuel selectivity [23], [38]. One of ceria’s greatest attributes is high tolerance to the presence of hydrogen during reoxidation.
Ceria will thermodynamically favor net hydrogen production over deeper metal oxide reduction when splitting water under exceedingly low gas-phase oxygen chemical potential (i.e., at high fuel selectivity and low steam-to-hydrogen ratio; ~2:1 [53]). This attribute results in reasonable fuel selectivity for reoxidation conditions with gas-phase oxygen chemical potential many orders of magnitude below that of the thermal reduction condition. Unfortunately, these benefits are offset by the extremely high temperature (>1550 °C) required to reduce ceria to an extent deemed commercially viable [51], [106]. The combination of complicated engineering, exotic materials, and greatly reduced solar receiver efficiencies necessary to support such temperatures make the need for reduction temperatures below 1400 °C imperative.[50], [107] Efforts to overcome ceria’s thermal reduction limitation have largely failed [42], [64], [67], [68], [108], [109], thus necessitating a search for new redox materials that can sustain both high fuel selectivity and high fuel yield, but at lower thermal reduction temperatures.

Increasingly, the search for new STCH cycle materials has turned towards perovskite-structured oxides [110]. Perovskites have many desirable traits, including high structural tolerance for non-stoichiometry, tunable point-defect thermodynamics, good chemical stability and a long history of application in related fields that require oxygen exchange functionality (such as solid oxide fuel cells [111], chemical looping [112], and electrochemical water splitting [113]). While research into perovskite-based STCH materials is still in its infancy, several compounds including Sr$_x$La$_{1-x}$Mn$_y$Al$_{1-y}$O$_{3-\delta}$ (SLMA) [66] and La$_{0.6}$Ca$_{0.4}$Mn$_{1-y}$Al$_y$O$_{3-\delta}$ (LCMA) [43] have shown promise.

Based on the insights provided by these prior perovskite oxide candidates, we identified the BaCe$_x$Mn$_{1-x}$O$_{3-\delta}$ perovskite as a potential source of new STCH materials. Our selection of this system is based on leveraging the desired perovskite-associated traits mentioned above, particularly the ability to tune the point defect thermodynamics. Here this is achieved by double occupancy of the B-site using both cerium and manganese cations. We hypothesize that the multi-valent transition metal Mn cation will act in the accommodation of charge accumulation during redox (likely as Mn$^{4+}$/Mn$^{3+}$) while the Ce-Mn site mixing will allow for optimization of the oxygen vacancy formation energy. As shown in Table 1, the estimated oxygen vacancy formation energy ($E_v$) for BaMnO$_3$ is extremely low (near zero) while $E_v$ for BaCeO$_3$ is
extremely high (near 20 eV). Although sufficient experimental data is not available to satisfactorily establish $E_v$ with high confidence in these compounds, alternative measures for $E_v$ (e.g., based on a recent simple formula for estimating $E_v$ in oxides developed by Deml et al. [83]) or comparisons of the bond dissociation energies for Mn-O and Ce-O bonds show the same trends: BaMnO$_3$ is easy to reduce as the Mn-O bond is relatively weak, while BaCeO$_3$ is difficult to reduce because the Ce-O bond is relatively strong. Thus, Mn/Ce B-site mixing in the BaCe$_x$Mn$_{1-x}$O$_{3-\delta}$ system may provide a pathway to optimize $E_v$ between these two extremes. Furthermore, this strategy enables thrifting of the expensive rare-earth element Ce in a STCH-active compound while still retaining its beneficial properties. Ceria has long been understood to yield beneficial thermodynamics based on its rare increase in entropy during reduction over the range of defect concentrations in the fluorite phase relevant to STC. This has been recently shown to be related directly to cerium’s electronic structure [85], [114], and leads to the possibility of cerium additions to other systems having positive entropic impacts.

In this paper, we explore the water splitting efficacy of BaCe$_x$Mn$_{1-x}$O$_{3-\delta}$ and compare the redox activity of this material system against a CeO$_2$ benchmark and SLMA. Of particular interest here, and unique to this effort, is our exploration of the extent to which BaCe$_x$Mn$_{1-x}$O$_{3-\delta}$ maintains water splitting favorability under reoxidation conditions that are challenged by low gas-phase oxygen chemical potential (e.g., H$_2$O:H$_2$ ratio <2000). Such water splitting conditions are rarely investigated by this research community, yet considered a key metric when screening for commercial viability [44], [53].

Table 5.1: Oxygen vacancy formation energies and oxygen-cation bond dissociation energies for the two family end-member compounds (BaMnO$_3$ and BaCeO$_3$). See supplemental information for details on the calculation of $E_v$ based on Deml’s model.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_v$ reported in the literature (eV)</th>
<th>$E_v$ calculated based on Deml’s model (eV) [83]</th>
<th>Bond dissociation energy Ce-O or Mn-O (eV) [115]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaMnO$_3$</td>
<td>0.04[96]</td>
<td>4.1</td>
<td>3.75</td>
</tr>
<tr>
<td>BaCeO$_3$</td>
<td>19.20[116]</td>
<td>15.1</td>
<td>8.19</td>
</tr>
</tbody>
</table>
5.2 Experimental

Initially, seven different compound formulations were synthesized to test the redox behavior of a large breadth of the BaCe$_{1-x}$Mn$_x$O$_{3-δ}$ compositional range: $x = 0, 0.05, 0.15, 0.25, 0.50, 0.75$, and $1$, which we label BMO, BC05M95, BC15M85, BC25M75, BC50M50, BC75M25, and BCO respectively. All seven compositions were synthesized using a sol-gel modified Pechini method [117]. In brief, stoichiometric amounts of the precursors, barium nitrate (Alfa Aesar 99 %), cerium nitrate (Alfa Aesar 99.5 %) and manganese acetate tetrahydrate (Alfa Aesar 98 %) were dissolved in deionized water and constantly stirred with ethylenediaminetetraacetic acid (EDTA) and citric acid under heat. Ammonium hydroxide was used to adjust the pH. Once the gels were formed, they were dried at 165 °C and subsequently calcined using a two-step heat-treatment profile designed to avoid Mn loss; first, the powders were calcined at 800 °C for 10 h at a ramp rate of 10 °C/min and cooled back to 75 °C; then the powders were calcined at the final temperature of 1400 °C for 5 h at the same heating rate. Later, pure phase BaCe$_{0.25}$Mn$_{0.75}$O$_{3-δ}$ was produced using the same technique.

Sr$_{0.4}$La$_{0.6}$Mn$_{0.6}$Al$_{0.4}$O$_{3-δ}$ (SLMA4664) and Sr$_{0.6}$La$_{0.4}$Mn$_{0.6}$Al$_{0.4}$O$_{3-δ}$ (SLMA6464) were synthesized following a similar approach. Strontium nitrate, aluminum nitrate, manganese nitrate tetrahydrate, and lanthanum nitrate hexahydrate were dissolved in deionized water and added to ammonium hydroxide, EDTA and citric acid heated at 80-120 °C until a gel formed. The gel was transferred to a drying oven at 250 °C for 3 h. The sample was crushed and calcined at 800 °C for 6 h. A second calcination was done at 1350 °C for 24 h. Commercial cerium oxide powder (Sigma Aldrich 99.995 %) was used for comparison.

Powder X-ray diffraction (XRD) was performed on all samples using a PANalytical PW3040 diffractometer in Bragg-Brentano geometry surveying the $2θ$ range between 20° and 120° at a step size of 0.008° and Cu Kα radiation of $λ = 1.540598$ and 1.54439 Å. PANalytical Highscore Plus software was used for Rietveld refinement.
High-temperature X-ray diffraction (HTXRD) was carried out at Sandia National Laboratories in Albuquerque at a Brag-Bretano configuration XRD surveying the 2θ range between 19° and 50° with CuKα radiation of λ = 1.540598 and 1.54439 Å, using programmable divergence slit equipped with a Pt heating stage and controlled atmosphere. UHP He was used during the reduction step, flown through an oxygen getter which ensured a pO₂ of about 10⁻⁶.

The samples were prepared by firstly crushing them using a mortar and pestle and adding methanol to form a liquid solution. This solution was carefully deposited onto the (110) yttrium stabilized zirconia single crystal plate (10 x 10 x 0.5 mm) to obtain an even layer of sample. The XRD stage was rotated about 2° in the xz direction to skip the single crystal diffraction peak during normal scan.

The HTXRD run was carried out by heating the sample at 10 °C/min from room temperature (RT) to 1350 °C in He flow taking a scan at every 50 °C from 850 °C to 1350 °C (each scan taking about 10 min to be completed). The 1350 °C isotherm was carried out for 1h 30min.

Temperature Program Reduction (TPR) experiments were accomplished using a Setaram Setsys Evolution configured for thermal gravimetric analysis (TGA) with alumina crucibles to test the samples oxygen extent of reduction. The TPR experiment consisted of heating a sample at 10 °C/min to 1350 °C in UHP N₂ and holding isothermally for 1 h. The sample was subsequently cooled to 1000 °C followed by the introduction of air to initiate reoxidation. The change in mass was measured as a function of temperature and time.

The materials’ water splitting capabilities were tested at Sandia National Laboratories in a stagnation flow reactor (SFR) coupled with a laser-based sample heater and a mass spectrometer downstream from the reactor. All systems were operated at sub ambient pressure (75 Torr), the details of which have been published elsewhere [102], [103], [118]. The mass spectrometer was calibrated using aliquots of O₂ and H₂ prepared by mass flow controllers and taken from known gas mixture standards (25% O₂ in Ar and 5% H₂ in Ar). Powder samples (~100 mg) were placed on a zirconia platform forming a loosely-packed shallow bed, and the reactor was heated to the oxidation temperature (T_{OX}) under UHP Ar atmosphere. Samples were heated by the laser at 10 °C/s from T_{OX} to the reduction temperature (T_{RE}), where
they were held for 330 s, unless indicated otherwise. Upon turning off the laser, the samples cooled to $T_{\text{ox}}$ in a matter of seconds, minimizing the potential for reoxidation with any trace amount of $O_2$ still in the chamber. 40 vol.% water vapor (in Ar gas flow) was introduced to initiate reoxidation. The total amounts of $O_2$ released and $H_2$ produced were calculated by integrating the baseline-corrected mass spectrometer signals over the entire gas evolution envelope. A numerical approach developed by McDaniel et al. [65], [66], [103] was used to extract pseudo second-order rate constants for $H_2$ production from the transient response function of the mass spectrometer. This procedure corrects the measured instrument response for physical phenomena such as gas mixing and detector time lag, which enables more accurate quantification of the materials’ true solid-state kinetic response (see SI).

Finally, water splitting performance was tested under lower steam-to-hydrogen ratios to assess the material’s performance under more realistic (i.e., “higher-conversion”) WS conditions. Controlled amounts of hydrogen were mixed with steam, essentially fixing the initial gas-phase oxygen chemical potential prior to the reoxidation (WS) step. The steam-to-hydrogen ratios tested, with associated log($p_{O_2}$) values (in atm) at 850 °C, were 1333:1 (-11.6), 1000:1 (-11.9), 750:1 (-12.1), 500:1 (-12.5) and 285:1 (-13). In some instances, the controlled amounts of hydrogen introduced to the chamber generate a background hydrogen signal that is often much larger than the hydrogen produced by water splitting. Due to this limitation in the measurement, the amount of hydrogen produced during the oxidation step was inferred from the oxygen peak measured during a subsequent reduction cycle. The material will only reduce in a subsequent cycle if it has oxidized in the previous cycle, ensuring validity of this indirect measurement approach. If no oxidation was achieved, then no subsequent reduction is detected in the following cycle.

5.3 Results and discussion

X-ray diffraction of all seven samples are reported in Figure 5.10. The identified phases, and their relative amounts as calculated by Rietveld refinement are shown in Figure 5.1. Analysis reveals that while
the predicted mixed B-site occupancy occurs, all BaCe\(_{0.25}\)Mn\(_{0.75}\)O\(_3\)-\(\delta\) compositions besides the BCO and BMO end-members produce a perovskite-related line compound, BaCe\(_{0.25}\)Mn\(_{0.75}\)O\(_3\)-\(\delta\), with the excess Ce and/or Mn accommodated by additional simple perovskite secondary phases such as BaCeO\(_3\), BaMnO\(_3\), and cerium oxide. Our observations of the BaCe\(_{x}\)Mn\(_{1-x}\)O\(_3\)-\(\delta\) phase behavior are consistent with Fuentes et al. [119], who concluded that the Ce/Mn B-site shared perovskite can only be formed in the 25% Ce/75% Mn ratio.

![Figure 5.1: Summary of phases present in five of the target compositions.](image)

Interestingly, the BaCe\(_{0.25}\)Mn\(_{0.75}\)O\(_3\)-\(\delta\) line compound exhibits two known polytypes: 12\(R\) and 10\(H\) [120], [121], with the 12\(R\) polytype generally believed to be the thermodynamically stable low-temperature phase. In our as-prepared samples, the 12\(R\) polytype dominates. Furthermore, Rietveld analysis of the BC25M75 sample before and after the first reduction/oxidation cycle indicates that the minority 10\(H\) polymorph phase converts almost completely to the 12\(R\) phase after the first cycle (see Supplementary section and Figure 5.11).
Thus, upon cycling, the BC25M75 sample attains >95% $12R$-BaCe$_{0.25}$Mn$_{0.75}$O$_{3-\delta}$ phase purity, with only minor traces of $10H$-Ba$_3$Ce$_{1.25}$Mn$_{3.75}$O$_{15-\delta}$ and CeO$_2$.

To better understand the $12R$ to $10H$ behavior, HTXRD was performed at Sandia National Laboratories in Albuquerque. As Figure 5.2 demonstrates, under thermally reducing conditions the $12R$ phase slowly begins to convert to $10H$ upon heating above 1150 °C. The oxygen non-stoichiometry appears to be required for this transition to occur, as HTXRD scans of $12R$ performed under air do not show this phase transformation at 1150 °C. With further heating under highly reducing conditions, the phase conversion behavior extends to a new, previously unreported, polytype $H$, that begins to appear around 1350 °C and grows during the high temperature soak. This new phase requires even further non-stoichiometry to appear (the oxygen getter used on the HTXRD produces the required low oxygen partial pressure, only known to be below the 100 ppb sensitivity limit of the attached oxygen sensor) and also appears to be fully reversible. Initially, it was suspected that this phase was evidence of decomposition, however, we have successfully obtained nearly pure-phase $H$ polytype after long high-temperature reductions and quenching. XRD analysis of this new polytype shows no evidence of additional phases (e.g. such as ceria or barium cerate) that would indicate decomposition. In retrospect, the polytype behavior observed here for BCM should not be surprising, since the parent perovskite BMO also shows polytypes with increasing oxygen non-stoichiometry [122]. The phase changes in BMO are related to distortions caused by different ordering of octahedral layers. As first shown by Matias et al. [120], [121], the polytypes for $12R$ and $10H$ also include cerium cation ordering. This makes the phase transitions relatively slow. STCH WS cycle tests are insufficient in duration (~ 5 minutes) to permit the $12R$ to $10H$ phase change; the $10H$ phase can only be obtained when reducing the BCM material at higher temperatures for long times (several hours). We produced a pure $10H$ sample and did simulated WS cycles in the TGA with O$_2$ flow instead of steam (results shown in the SI). After several redox runs, the $10H$ sample converted fully to $12R$ phase (demonstrated by the XRD) and subsequently remained in the $12R$ phase. The detailed thermodynamics of this system and its various polytypes is the subject of ongoing study. The intriguing nature of these distortional-type phase changes, which do not coincide with full changes in oxygen
stoichiometry, (like those of early STCH materials like FeO to Fe₂O₃ [21], [26]) points towards a potentially exciting new mechanism for enhancing the per-cycle hydrogen productivity in BCM and related STCH-active perovskite systems.

Figure 5.2: High Temperature XRD done on a 12R-BaCe₀.₂₅Mn₀.₇₅O₃₋δ sample, heating from room temperature to 1350 °C in He flow. At 1150 °C the 12R phase starts to convert to 10H phase and by 1350 °C the onset of a new H polytype phase (N) is also apparent.

The samples were subjected to our Temperature Programmed Reduction screening protocol in order to quantify their redox behavior in comparison to previously identified STCH candidates (ceria, SLMA4664 and SLMA6464), as shown in Figure 3. SLMA4664 and SLMA6464 are used for comparison here because they are perovskite oxides with promising water splitting capacity [65], [66], despite showing
very strong kinetic limitations, while ceria (a fluorite) is the current benchmark material for STCH application. Ceria and SLMA6464 essentially represent boundaries of the STCH performance space of interest. Ceria provides an upper boundary with its unmatched reoxidation capability but low extent of reduction, while SLMA6464 provides a lower boundary due to its large extent of reduction but poor reoxidation performance. From a cycle thermodynamic perspective, any promising material will likely need to fall in between these two limits [53].

Figure 5.3: Temperature Programmed Reduction experiment evaluates the extent of reduction (formation of oxygen vacancies or $\delta$) and reversibility of samples BCO, ceria, SLMA 4664, BC25M75, SLMA6464 and BMO. Reduction at 1350 °C for 1 h and Oxidation in air at 1000 °C.

The TPR experiment reveals that BCO has no significant reduction and poor reoxidation for the water splitting application. BMO, on the other hand, reduces to an extreme (i.e., to a far greater extent than
even BCM), which indicates that the driving force for reoxidation will likely be too low to split water. These TPR results are consistent with the $E_v$ and oxygen bond strength estimates for BMO and BCO provided in Table 5.1.

As viable STCH materials must be cycle-able, mass recovery upon reoxidation is also an important consideration. While it should be noted that none of the experiments in Figure 5.3 show a complete return to zero upon oxidation, that is not necessarily indicative of whether samples experienced complete reoxidation. Testing is conducted on as-calcined powders with only a low temperature burnout (500 °C in air) before the experiment. While this removes most sources of irreversible mass loss, e.g., largely surface adsorbed water and stray organics, some irreversible mass losses not related to reduction may still occur upon heating to 1350 °C (e.g., strongly bound water, residual surface carbonates and hydroxides, etc.). As a general guideline, we typically consider materials that reoxidize to within a net difference in oxygen non-stoichiometry ($\Delta\delta$) of < 0.05 (representing a recovery to within ~0.2% of the starting mass) to be fully reoxidized, and therefore reversible/cycle-able.

BMO did not return to its original stoichiometry after reoxidation, which may indicate stability issues such as sintering and/or partial decomposition. BC25M75 also failed to completely reoxidize during initial testing, however, on subsequent cycling, no further unrecoverable reduction occurred (as shown in Figure S4).

The water splitting capability of six materials; BMO, BC25M75, BC50M50, BC75M25, BCO, and ceria (used as a reference) were tested at the SFR under the reduction condition of $T_{re} \ 1350$ °C and oxidation condition of $T_{ox} \ 1000$ °C with 40 vol. % of H$_2$O. H$_2$ production was highest for the BC25M75 composition, falling off sharply for compositions on either side. Neither end-member composition (BCO, BMO) splits water under the test conditions used. Based on the prior TPR results, we conjecture that BCO does not sufficiently reduce at $T_{re} = 1350$ °C, and therefore does not split a detectable amount of water upon exposure to steam in the reoxidation step at 1000 °C. In contrast, BMO reduces too easily, and therefore likely does not provide sufficient driving force for water splitting upon exposure to steam at $T_{ox} \ 1000$°C. As shown in Figure 5.4, the average H$_2$ production for the intermediate compositions (BC25M75,
BC50M50, and BC75M25) closely correlates with the amount of $12R$-$\text{BaCe}_{0.25}\text{Mn}_{0.75}O_{3-\delta}$ phase present in each sample. Early on, we therefore concluded that the $12R$-$\text{BaCe}_{0.25}\text{Mn}_{0.75}O_{3-\delta}$ phase represents the dominant active water splitting compound in this compositional family. Only later, as discussed above, did it become apparent that the distinction between the 10H and 12R was unnecessary for this analysis.

Figure 5.4: Average $H_2$ productivity over 3 cycles ($\mu$mol $H_2$/g sample) for BMO, BC25M75, BC50M50, BC75M25, BCO, and ceria (included as a reference). Superimposed on this data is the relative phase fraction of the hypothesized active water-splitting phase ($12R$-$\text{BaCe}_{0.25}\text{Mn}_{0.75}O_{3-\delta}$) in each sample. $H_2$ productivity closely correlates with the percentage of $12R$-$\text{BaCe}_{0.25}\text{Mn}_{0.75}O_{3-\delta}$ present in each sample.

It is important to note that the BC25M75 and BC50M50 samples contain small amounts (less than 5 %) of ceria as a secondary phase, and ceria is clearly an active WS material. Scaling the $H_2$ productivity of ceria by the percentage of ceria phase present in these samples, however, suggests that ceria is responsible for only a small portion of the total WS response of these materials under the applied test conditions. In BC25M75 and BC50M50, for example, the residual ceria should contribute less than ~1 $\mu$mol/g to the $H_2$ production, far smaller than the 135 $\mu$mol/g and 97 $\mu$mol/g of total $H_2$ production measured for these samples respectively. Even for BC75M25, which contains ~15 % ceria, only ~5$\mu$mol/g of $H_2$ can be attributed to the ceria phase, with the rest of the ~40 $\mu$mol/g of total $H_2$ production attributable to the $12R$-
BaCe$_{0.25}$Mn$_{0.75}$O$_{3-\delta}$ phase. This analysis supports our supposition that BaCe$_{0.25}$Mn$_{0.75}$O$_{3-\delta}$ is the dominant water splitting phase in these samples under the applied test conditions. Subsequently, pure phase 12$R$-BaCe$_{0.25}$Mn$_{0.75}$O$_{3-\delta}$ (which for simplicity we abbreviate as BCM hereinafter) was synthesized and became the primary material for continued investigations.

BCM was tested for water splitting and compared to ceria (the benchmark STCH material) and SLMA4664 (currently the most promising STCH perovskite). Performance comparisons are generally only meaningful when carried out at same cycle conditions due to different materials thermodynamic properties and kinetic limitations, therefore all three materials were tested under the same experimental conditions using the same testing protocol. A further comparison of BCM to other promising WS materials (albeit tested under non-identical conditions) can be found in the SI for reference.

Representative water splitting cycle data for BCM, SLMA4664, and ceria are shown in Figure 5.5. Each sample was subjected to an initial reduction step from a fully oxidized state followed by two complete water splitting cycles, each comprised of a reoxidation step and a subsequent reduction step.

While SLMA4664 releases a much larger amount of O$_2$ during the initial reduction than the other materials, significantly less O$_2$ (~60-70% of the initial cycle amount) is released during subsequent reduction cycles. This is because the water splitting step is strongly kinetically and thermodynamically limited in SLMA. SLMA4664 is unable to fully reoxidize during the allotted cycle time, which was chosen to approximate cycle times associated with a commercial water splitting reactor that does not incorporate material storage.

BCM shows a similar, but far less severe kinetic limitation, as the O$_2$ evolved during the initial reduction step is slightly greater than that evolved in subsequent reduction cycles.
Figure 5.5: Water splitting experiment at T_{RE} 1350 °C for 330 s and T_{OX} 850 °C with 40 vol% H_{2}O for 1200 s. Ceria was oxidized for 300 s. O_{2} peaks (blue) and H_{2} peaks (red) record the amount of oxygen and hydrogen evolved per gram of sample as a function of time. Integrated totals for the first three peaks are listed in the legend.
Ceria, in contrast, evolves the same amount of O\(_2\) in the initial reduction and in subsequent reduction cycles, indicating that its WS kinetics are sufficiently fast to permit full reoxidation within the experimental cycle time.

In order to quantitatively compare the water splitting kinetics of BCM, SLMA4664, and ceria, all three were evaluated using a simplified solid-state kinetics model, the details of which are briefly described in the Supplemental Information. The second-order “F2” kinetic model has been shown to produce a good fit for ceria, and we find that it can also nicely fit the BCM kinetic behavior. We therefore applied this model to analyze all three materials. The broad SLMA4664 H\(_2\) peak shape (as shown in Figure 5.5b), suggests a strong transport limitation and therefore doesn’t provide a good fit using only F2. As reported previously,[65], [66] SLMA4664 requires a coupled kinetic model where first-order reaction and diffusion are considered in concert. While such analysis is outside the scope of the present study, this observation further reinforces the fact that SLMA4664 presents additional kinetic limitations compared to BCM and ceria. Table 5. summarizes the rate constants (k\(_o\)) determined for ceria, BCM, and SLMA4664 fit to the F2 model at \(T_{RE}\) 1350 °C and \(T_{OX}\) 850 °C and 1000 °C, respectively.

It is worth noticing that the calculated rate constants for BCM increase with the increase in \(T_{OX}\), whereas for ceria k\(_o\) decreases about 2.5 times with the increase in temperature. This indicates that ceria’s reaction kinetics are slower at the 1000 °C compared to 850 °C. SLMA’s reoxidation kinetics are the slowest of all three materials. This behavior is further evident when analyzing Figure 5.6. In this plot, the as-measured mass normalized H\(_2\) production rate for each material (scattered dots) is compared against the kinetic model (solid lines). Time is plotted in logarithmic scale for better visualization of the plot features.
Table 5.2: Summary of the oxidation reaction rate constants using the second-order kinetics model F2 for BCM and Ceria at $T_{\text{ox}}$ 850 °C and 1000 °C.

<table>
<thead>
<tr>
<th>$T_{\text{ox}}$ (°C)</th>
<th>Sample</th>
<th>$r_{H_2} \propto k_o Y_{H_2O} (1 - \alpha)^2 \text{ [s}^{-1}\text{]}$</th>
<th>$k_o$ [s(^{-1})]</th>
<th>log $k_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$H_2$ peaks average</td>
<td>Standard deviation</td>
<td></td>
</tr>
<tr>
<td>850</td>
<td>SLMA4664</td>
<td>0.0075</td>
<td>0.0005</td>
<td>-2.12</td>
</tr>
<tr>
<td></td>
<td>BCM</td>
<td>0.0131</td>
<td>0.0005</td>
<td>-1.88</td>
</tr>
<tr>
<td></td>
<td>CeO(_2)</td>
<td>0.1827</td>
<td>0.0189</td>
<td>-0.74</td>
</tr>
<tr>
<td>1000</td>
<td>SLMA4664</td>
<td>0.0078</td>
<td>0.0005</td>
<td>-2.11</td>
</tr>
<tr>
<td></td>
<td>BCM</td>
<td>0.0161</td>
<td>0.0005</td>
<td>-1.79</td>
</tr>
<tr>
<td></td>
<td>CeO(_2)</td>
<td>0.0756</td>
<td>0.0015</td>
<td>-1.12</td>
</tr>
</tbody>
</table>

To further evaluate and compare BCM’s hydrogen production capacity against our implied standards, all three materials were examined under a range of oxidation and reduction conditions; namely variable $T_{\text{ox}}$ and oxidizing potential of the argon-steam mixture.

Figure 5.7 summarizes the total amount of $H_2$ produced by ceria, BCM, and SLMA4664 during STCH cycling in the SFR with 40% steam, $T_{\text{re}} = 1350$ °C, and $T_{\text{ox}} = 750$, 850, and 1000 °C, respectively.

The BCM, SLMA4664, and ceria hydrogen production data for two other reduction temperatures is compiled in Table S4 of the Supporting Information.
Ceria’s net hydrogen capacity is essentially independent of oxidation temperature for the conditions investigated. On the other hand, the positive slopes for BCM and SLMA4664 demonstrate that their oxidation kinetic limitations can be countered, to an extent, by increasing the oxidation temperature. SLMA4664, in particular, benefits greatly by the 150 °C increase from 850 °C to 1000 °C and shows larger H₂ productivity than ceria and BCM over all the temperatures tested. In considering a comparative analysis
between these STCH materials, it should be noted that $\text{H}_2$ yield is highly sensitive to absolute cycle times making direct comparisons to previous works uninformative [66].

Figure 5.7: Total $\text{H}_2$ produced per cycle by BCM (square), SLMA4664 (circle) and ceria (triangle) at $T_{\text{RE}}$ of 1350 °C with 40 vol. % steam and various oxidation temperatures. Reduction heating rate is 10 °C/s, with a reduction time of 330 s and a reoxidation time of 1200 s.

Materials that support STCH cycle operation at lower $T_{\text{RE}}$ and $T_{\text{OX}}$ are greatly desired for practical reactor applications as this relaxes high-temperature reactor materials requirements and generally improves overall reactor efficiency, due to decreased thermal losses and less energy required to heat both redox material and steam.
From this perspective, SLMA4664 appears highly attractive as it yields significantly more \( \text{H}_2 \) than either ceria or BCM across a range of \( T_{\text{RE}} \) and \( T_{\text{OX}} \) conditions, and particularly at lower \( T_{\text{RE}} \) and \( T_{\text{OX}} \) (see Figures S5a and S5b in the Supporting Information). BCM (at \( T_{\text{RE}} 1350 \, ^\circ\text{C} \) and \( T_{\text{OX}} 1000 \, ^\circ\text{C} \)) does approach ceria’s high-temperature performance window by \( \frac{2}{3} \) (at \( T_{\text{RE}} 1500 \, ^\circ\text{C} \) and \( T_{\text{OX}} = 1000 \, ^\circ\text{C} \)) [65], but at a substantially lower cycle \( \Delta T \). However, BCM yields less \( \text{H}_2 \) than SLMA4664 at all temperatures placing its performance characteristics in between our two material endpoint standards when a relatively high oxidizing potential of the argon-steam mixture is used to drive the reoxidation reaction to near completion.

Next, we address BCM’s capability to perform under oxidizing conditions (i.e., water splitting) that are more reducing than a mixture of 40 vol. % steam in argon. This is of extreme importance because the solar-to-hydrogen conversion efficiency and commercial viability of STCH production technology are tightly coupled to the process steam requirement [53]. Preferably, a STCH material should maintain water splitting favorability under “high conversion” conditions, where the ratio of \( \text{H}_2\text{O}:\text{H}_2 \) needed to drive the cycle to completion is substantially below 1000:1 (and ideally less than 10:1 [53]), otherwise the energy required to produce the necessary steam greatly reduces the efficiency of the cycle.

In order to examine the performance of candidate materials under high conversion conditions, we supplied a mixture of \( \text{H}_2 \) and argon to the 40 % steam (rather than balancing the 40 % steam with inert gas only) during the water splitting step. We tested ceria, SLMA4664, and BCM with steam-to-hydrogen ratios of 1333:1, 1000:1, 750:1, 500:1 and 285:1 using \( T_{\text{RE}} 1350 \, ^\circ\text{C} \) and \( T_{\text{OX}} 850 \, ^\circ\text{C} \) as thermal conditions for the cycle. The results are presented in Figure 5.8.

Ceria’s net hydrogen production capacity is unchanged when the initial oxidizing potential of the WS gas mixture is held at equivalent \( \text{O}_2 \) partial pressures between \( 2.5 \times 10^{-12} \) (1333:1) and \( 1.0 \times 10^{-13} \) (285:1) atmospheres.
Figure 5.8: “High conversion” water splitting performed at various steam to hydrogen mixture ratios for all three materials: BCM (square), SLMA4664 (circle), and ceria (triangle) at \( T_{\text{RE}} 1350 \) °C and \( T_{\text{OX}} 850 \) °C.

This insensitivity to low H₂O:H₂ ratios is due in part to the high oxygen vacancy formation energy found in ceria, which provides a strong thermodynamic driving force for water splitting even under strongly reducing conditions. SLMA4664 on the other hand, sharply deactivates in the presence of residual hydrogen (water splitting no longer proceeds at H₂O:H₂ ratios of 500:1). Thus, although SLMA4664 is promising due to its high extent of reduction and large H₂ production capacity under abundancy of steam, the economics of using SLMA in practical water splitting reactors is severely challenged because of low WS favorability under realistic H₂O:H₂ ratios desired for efficient reactor operation [43]. BCM, on the other hand, shows promising tolerance to high conversion conditions.
While water splitting capacity in BCM gradually falls off as the H₂O:H₂ ratio decreases, it does not suffer from the drastic drop in performance seen in SLMA, and it maintains H₂ production close to that of ceria all the way down to the 285:1 H₂O:H₂ ratio. This is the first known perovskite-based oxide to demonstrate acceptable performance under high conversion conditions.

It has been recently shown by Zhai et al. [123] that the poly-cation oxide (FeMgCoNi)Oₓ also has the ability to split water under similar high conversion conditions (1000:1 H₂O:H₂) under similar temperature conditions $T_{RE}$ 1300 °C and $T_{OX}$ 800 °C. This material showed promising performance yielding more H₂ than ceria at that ratio and showing a similar trend to BCM, with a decrease in H₂ yield with an increase in conversion ratio to about 100:1, however at the cost of long reduction and oxidation cycles of 5 h each. Within the same time frame of 10 hours, BCM would surpass the H₂ production at the high conversion ratios tested to about 300:1.

Structural and compositional durability is an additional concern for any proposed redox active material because of the extreme chemical and thermal stresses encountered in a STCH cycle. Limited lifetime testing has been performed on BCM through rapid redox cycling (210 s reduction and 10 min oxidation) in the SFR showing no deterioration in performance over 50 water-splitting cycles ($\Delta T$ between $T_{RE}$ 1350 °C and $T_{OX}$ 850 °C) under 40 vol. % steam as shown in Figure 5.9. It is worth noting that the scattering in the integrated hydrogen peaks for each cycle shown in Figure 5.9b, is due to variations in the mass spectrometer detection.

While it is believed that the 12R/10H phase change does not have sufficient time to occur during rapid STCH cycling, this preliminary lifetime testing suggests that even if the phase change does occur, it is clearly not detrimental to the water splitting performance.
Figure 5.9: Stability experiment done in the BCM sample. The fifty hydrogen peaks are shown in (a) and the integrated amounts of O$_2$ and H$_2$ obtained in each cycle are plotted in (b). Reduction was done at $T_{RE}$ 1350 °C for 210 s and oxidation with 40 vol. % steam was carried out at $T_{OX}$ 850 °C for 10 min. The data was collected over three days of experiment.

Post-mortem XRD performed after the 50 cycles experiment reveals only the presence of the 12$R$ phase. This is a promising result because poor durability and phase instability have hampered other prospective STCH redox materials systems [27], [50]. We speculate that if the conditions were altered such that the phase change could occur during cycling, the phase change thermodynamics could in fact boost the WS performance. The molar volume per formula unit of 12$R$ is slightly lower than that of the 10$H$ phase,
suggesting a slight increase in the standard absolute entropy of the system upon phase conversion [124]. If this phenomenon could be successfully exploited, it would represent the first example of a perovskite where nonstoichiometry participates in both phases during reaction.

5.4 Conclusions

The search for viable STCH materials within the vast perovskite oxide space has led to the discovery of a potentially attractive alternative to ceria, BaCe$_{0.25}$Mn$_{0.75}$O$_3$. With greatly improved reduction capacity at temperatures < 1400 °C, BCM produces 140 µmol/g of hydrogen at $T_{RE} = 1350$ °C and $T_{OX} = 850$ °C, nearly a three-fold improvement over ceria at these same conditions. And while BCM does not ultimately have the large production capacity exhibited by another notable Mn-based candidate perovskite (Sr$_{0.4}$La$_{0.6}$Mn$_{0.6}$Al$_{0.4}$O$_3$) under oxidation in excess steam, it does have distinctively faster reoxidation kinetics and greatly improved tolerance to the presence of hydrogen in the oxidation half cycle. In fact, BCM is the first example of a perovskite demonstrated to retain water splitting capability under high conversion conditions (steam-to-hydrogen ratio in the order of 285:1). This combination points to the potential of much higher overall solar-to-hydrogen conversion efficiencies than previous solar thermochemical water splitting candidates based on nonstoichiometry in perovskite or fluorite crystal structures.

Perhaps more important than BCM’s performance is its novel combination of properties that opens new paths towards STCH materials discovery. The presence of cerium on the B-site of the perovskite and its positive contribution to water-splitting opens the possibility of further focused search for other candidate materials that can accommodate the addition of cerium as a major dopant.
And the intriguing prospect of leveraging polytypes with different thermodynamics and oxygen non-stoichiometry creates further new avenues for investigation.

5.5 Acknowledgments

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5.6 Co-authors contribution

As the first author I did all the experimental work, data analysis and paper writing. Prof. Michael Sanders as the second author helped with discussions, data analysis, TGA experiments and paper revisions. Dr. Eric Coker helped with the high temperature XRD and DSC data during the week I sent in Sandia Albuquerque. All the remainder co-authors helped with discussions and paper revisions.
5.7 Supporting information

Theoretical bond strength analysis

The $E_v$ values provided in Table 1 column 3 were calculated according to Deml’s[79] model equation:

$$E_v = 0.67 \left| \Delta H_f \right| + 0.6 \left( E_{O 2p} + \frac{1.5}{2} E_{gDFT+U} \right) + 2.6 \left\langle \Delta \chi \right\rangle - 1.49$$ (5.1)

where $\Delta H_f$ is the oxide formation enthalpy in eV/atom, $E_{O 2p}$ is the energy difference between the valence band maximum and the center of the O 2p band in eV (inferred from DOS diagrams reported in the literature), $E_{gDFT+U}$ is the calculated band gap in eV, and $\Delta \chi$ is the unitless average Pauling electronegativity difference between O atoms and the atoms forming their first coordination shell, meaning O electronegativity subtracted from Mn and Ce electronegativities. The quantities used for BMO and BCO are given in Table 5..

Table 5.3: Reported calculated values used to approximate the oxygen vacancy formation energy

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H_f$ (eV/atom)</th>
<th>$E_{O 2p}$ (eV)</th>
<th>$E_{gDFT+U}$ (eV)</th>
<th>$\Delta \chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaMnO$_3$</td>
<td>2.0 [125]</td>
<td>1.0 [126]</td>
<td>1.6 [126]</td>
<td>1.9</td>
</tr>
<tr>
<td>BaCeO$_3$</td>
<td>17.5 [127]</td>
<td>0.8 [128]</td>
<td>1.5 [128]</td>
<td>2.3</td>
</tr>
</tbody>
</table>

X-ray diffraction analysis

Figure 5.10 demonstrates the XRD patterns obtained for the BaCexMn1-xO3 samples synthesized, where $x = 0$, 0.05, 0.15, 0.25, 0.50, 0.75 and 1 named respectively as BMO, BC05M95, BC15M85, BC25M75 (BCM), BC50M50, BC75M25 and BCO.
Figure 5.10: X-ray diffraction comparison between the samples BaCe$_x$Mn$_{1-x}$O$_3$, where $x = 0, 0.05, 0.15, 0.25, 0.50, 0.75,$ and 1.

From the diffraction patterns, it can be noticed that the pure phase structures predicted could not be achieved, but instead a mixture of crystal structures compose most of the samples. It can also be noticed that the samples BC25M75, BC50M50 and BC75M25 have the phases BaCe$_{0.25}$Mn$_{0.75}$O$_{3-\delta}$ (R-3m), BaCeO$_3$ (Pnma) and CeO$_2$ (Fm-3m) in common. Rietveld refinement results are shown in the Supplementary section. Rietveld Refinement quantification was not possible for samples BC05M95 and BC15M85 due to the multitude of secondary phases formed. It is evident from the Rietveld refinement results that there is only one exact amount of Ce that can be added to the structure to form the Ce/Mn shared B-site layered perovskite, which is 0.25 mol of Ce and 0.75 mol of Mn.
Table 5.4: Crystal structures determined from Rietveld Refinement for each of the 5 samples studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Space Group (ICSD)</th>
<th>( \text{BaCe}<em>{0.25}\text{Mn}</em>{0.75}\text{O}_3 )</th>
<th>( \text{BaCeO}_3 )</th>
<th>( \text{CeO}_2 )</th>
<th>( \text{Ba}<em>5\text{Ce}</em>{1.25}\text{Mn}<em>{3.75}\text{O}</em>{15} )</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMO</td>
<td>R-3m (166)</td>
<td>Pnma (62)</td>
<td>Fm-3m (225)</td>
<td>P6/m/mmc (194)</td>
<td>58% ( \text{BaMnO}_3 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>28% ( \text{Ba}_5\text{Mn}<em>5\text{O}</em>{16} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \text{Ba}_4\text{Mn}<em>3\text{O}</em>{10} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cmca (64)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7% ( \text{BaMnO}_3 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P63 mc (186)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7% ( \text{Mn}_3\text{O}_4 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>I41/amd (141)</td>
<td></td>
</tr>
<tr>
<td>BC25M75</td>
<td>83%</td>
<td>-</td>
<td>3%</td>
<td>14%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC25M75 cycled</td>
<td>95%</td>
<td>3%</td>
<td>1%</td>
<td>1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC50M50</td>
<td>61%</td>
<td>36%</td>
<td>3%</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC75M25</td>
<td>28%</td>
<td>58%</td>
<td>14%</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCO</td>
<td>-</td>
<td>94%</td>
<td>6%</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This behavior was confirmed in the literature by Fuentes et al. It was indicated that although predictions suggest the potential occurrence of other amounts of Ce in the B-site, affecting the layering sequence, however no attempts to synthesize \( \text{BaCe}_{x}\text{Mn}_{1-x}\text{O}_3 \) with different amounts of Ce were successful.
Macias et al. though were able to synthesize a polytype of the BaCe$_{0.25}$Mn$_{0.75}$O$_{3-\delta}$ (R-3m), identified as 10$H$-Ba$_5$Ce$_{1.25}$Mn$_{3.75}$O$_{15}$ (P63/mmc). This polytype has the same stoichiometric cation ratios Ba:Ce:Mn, respectively, 1:0.25:0.75, but has a difference in symmetry, forming a hexagonal structure. We were able to obtain this structure in very small quantity (14\%) in the BC25M75 sample. However, after one TPR cycle, (Figure 5.11), where the sample was reduced at a high temperature and then re-oxidized at a lower temperature, the polytype structure disappeared, forming a purer sample (95\% of the 12$R$ structure with simple oxides as secondary phases).

Figure 5.11: X-ray diffraction results for BC25M75 sample as calcined and after the first TPR cycle (reduction at 1350 °C and re-oxidation at 1000 °C) shows the increase of the 12$R$ structure and decrease of the 10$H$ structure.
Temperature Programmed Reduction

The extent of the reduction, as well as the onset temperatures from the Temperature Programmed Reduction (TPR) experiment, are summarized on Table 5. The onset temperatures were obtained at the temperature where $\delta$ is equal to 0.025. The BC25M75 onset temperature is similar to SLMA, but lower than ceria.

Table 5.5: Extent of reduction and onset temperature at $\delta = 0.025$. Data obtained from TPR experiment where $T_{\text{RE}}$ 1350 °C at 10 °C/min and held for 4 h and $T_{\text{OX}}$ 1000 °C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Extent of reduction (mol O/ mol sample) or $(\delta)$</th>
<th>Onset Temperature (°C) at $\delta = 0.025$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceria</td>
<td>0.049</td>
<td>1270</td>
</tr>
<tr>
<td>BCO</td>
<td>0.039</td>
<td>900</td>
</tr>
<tr>
<td>SLMA</td>
<td>0.088</td>
<td>1230</td>
</tr>
<tr>
<td>BC75M25</td>
<td>0.157</td>
<td>620</td>
</tr>
<tr>
<td>BC50M50</td>
<td>0.103</td>
<td>1300</td>
</tr>
<tr>
<td>BCM</td>
<td>0.182</td>
<td>850</td>
</tr>
<tr>
<td>BC15M85</td>
<td>0.227</td>
<td>1200</td>
</tr>
<tr>
<td>BC05M95</td>
<td>0.345</td>
<td>950</td>
</tr>
<tr>
<td>BMO</td>
<td>0.424</td>
<td>790</td>
</tr>
</tbody>
</table>

The compositions between BCO and BMO generally follow the trend of manganese rich phases reducing further than ceria rich phases, though the BC75M25 and BC50M50 positions reverse (Figure 5.12). This trend would likely be expected to hold if all compositions were single phase “alloys” of the two end members, but since the compositions are mixed-phase, the deviations should perhaps be unsurprising.
Figure 5.12: Temperature Programmed Reduction experiment evaluates the extent of reduction (formation of oxygen vacancies or $\delta$) and reversibility of samples BCO, ceria, SLMA, BC75M25, BC50M50, BC25M75, BC15M85, BC05M95 and BMO. Reduction at 1350 °C for 1 h in UHP N$_2$ and Oxidation in air at 1000 °C.

The compositions between BCO and BMO generally follow the trend of manganese rich phases reducing further than ceria rich phases, though the BC75M25 and BC50M50 positions reverse. This trend would likely be expected to hold if all compositions were single phase “alloys” of the two end members, but since the compositions are mixed-phase, the deviations should perhaps be unsurprising.

TPR was performed on the BCM sample, where three consecutive reduction (1350 °C) and oxidation (1000 °C) cycles are shown in Figure 5.13.
Figure 5.13: BCM three consecutive reduction and oxidation cycles at 1350 °C in UHP N₂ for 4 h and 1000 °C for 30 min in air respectively. The experiment indicates that after the first redox cycle BCM two polytypes were all converted to the main phase 12R.

Figure 5.13 suggests that the first BCM cycle reduces to a higher extent and doesn’t completely recover its mass. However, upon further cycling the sample demonstrates complete redox reversibility. This behavior might be attributed to the 10H secondary phase conversion to 12R primary phase, as shown by XRD.

Water-splitting experiments using Stagnation Flow Reactor

In the main text, BCM’s water splitting performance was compared to STCH 4664 and ceria under identical testing conditions. Direct comparison with other promising materials reported in the literature is not easy because of the diversity of cycle conditions used. A brief list of some of other promising materials for STCH reported in the literature can be found in Table 5, below.
Table 5.6: Non-exhaustive list of promising STCH materials reported in the literature for comparison of performance.

<table>
<thead>
<tr>
<th>Material</th>
<th>H\textsubscript{2} production (μmol/g)</th>
<th>Reduction step conditions</th>
<th>Oxidation step conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce\textsubscript{0.75}Zr\textsubscript{0.25}O\textsubscript{2}</td>
<td>354 [71]</td>
<td>1400 °C for 45 min</td>
<td>1000 °C for 35 min – 80% RH</td>
</tr>
<tr>
<td>Ce\textsubscript{0.75}Zr\textsubscript{0.25}O\textsubscript{2}</td>
<td>162 [58]</td>
<td>1450 °C for 45 min</td>
<td>950 °C for 25 min – 80% RH</td>
</tr>
<tr>
<td>Ce\textsubscript{0.85}Fe\textsubscript{0.15}O\textsubscript{2}</td>
<td>536 [67]</td>
<td>1500 °C for 30 min</td>
<td>1150 °C for 30 min – pH\textsubscript{2}O 0.5-0.84 atm</td>
</tr>
<tr>
<td>Ce\textsubscript{0.85}Co\textsubscript{0.15}O\textsubscript{2}</td>
<td>768 [67]</td>
<td>1500 °C for 30 min</td>
<td>1150 °C for 30 min – pH\textsubscript{2}O 0.5-0.84 atm</td>
</tr>
<tr>
<td>Ce\textsubscript{0.85}Ni\textsubscript{0.15}O\textsubscript{2}</td>
<td>688 [67]</td>
<td>1500 °C for 30 min</td>
<td>1150 °C for 30 min – pH\textsubscript{2}O 0.5-0.84 atm</td>
</tr>
<tr>
<td>Ce\textsubscript{0.85}Mn\textsubscript{0.15}O\textsubscript{2}</td>
<td>491 [67]</td>
<td>1500 °C for 30 min</td>
<td>1150 °C for 30 min – pH\textsubscript{2}O 0.5-0.84 atm</td>
</tr>
<tr>
<td>Sr\textsubscript{0.4}La\textsubscript{0.6}Mn\textsubscript{0.6}Al\textsubscript{0.4}O\textsubscript{3}</td>
<td>307 [65]</td>
<td>1350 °C for 30 min</td>
<td>1000 °C for 1000s – 40 vol% H\textsubscript{2}O</td>
</tr>
<tr>
<td>Sr\textsubscript{0.6}La\textsubscript{0.4}Mn\textsubscript{0.6}Al\textsubscript{0.4}O\textsubscript{3}</td>
<td>277 [65]</td>
<td>1350 °C for 30 min</td>
<td>1000 °C for 1000s – 40 vol% H\textsubscript{2}O</td>
</tr>
<tr>
<td>Sr\textsubscript{0.4}La\textsubscript{0.8}Mn\textsubscript{0.4}Al\textsubscript{0.6}O\textsubscript{3}</td>
<td>220 [65]</td>
<td>1350 °C for 30 min</td>
<td>1000 °C for 1000s – 40 vol% H\textsubscript{2}O</td>
</tr>
<tr>
<td>CaTi\textsubscript{0.7}Fe\textsubscript{0.3}O\textsubscript{3}</td>
<td>39 [65]</td>
<td>1400 °C for 30 min</td>
<td>1100 °C for 1000s – 40 vol% H\textsubscript{2}O</td>
</tr>
</tbody>
</table>
The three samples BC25M75 (BCM), SLMA and ceria (powder samples of surface area 0.20 m$^2$/g, 0.99 m$^2$/g and 2.24 m$^2$/g respectively) were tested for water splitting under various T$^\text{OX}$ and T$^\text{RE}$ conditions. The experiment was accomplished at Sandia in the Stagnation Flow Reactor (SFR) as described in the experimental section. Three oxidation temperatures and three reduction temperatures were probed maintaining the same reduction and oxidation times of 330 s and 20 min respectively, except for ceria where the oxidation hold time was only of 5 minutes. 40 vol. % of steam was used in all conditions. The average of the amounts of hydrogen produced per mass of material during each cycle is reported in Table 5. and Figure 5.14.

<table>
<thead>
<tr>
<th>T$^\text{OX}$ (°C)</th>
<th>Sample</th>
<th>T$^\text{RE}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1250</td>
</tr>
<tr>
<td>750</td>
<td>BCM</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>SLMA</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>Ceria</td>
<td>28</td>
</tr>
<tr>
<td>850</td>
<td>BCM</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>SLMA</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>Ceria</td>
<td>26</td>
</tr>
<tr>
<td>1000</td>
<td>BCM</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>SLMA</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>Ceria</td>
<td>26</td>
</tr>
</tbody>
</table>
In considering this comparative analysis of ceria, BCM, and SLMA4664, it should be noted that at $T_{\text{RE}}$ 1350 °C and $T_{\text{OX}}$ 1000 °C, we have previously reported per-cycle SLMA4664 H$_2$ production values significantly higher (as high as 277 µmol/g [66]) than those presented here. STCH H$_2$ yield is highly sensitive to cycle time. In the present analysis, we used a 330 s reduction time to better match realistic STCH reactor cycle durations. In our previous work, a reduction time of 1800 s was used [66], which increases the extent of reduction and thus increases the measured water splitting capacity of the material.
Numerical kinetics analysis

The kinetic behavior of the samples was analyzed by using a numerical approach developed by McDaniel et al. to separate the solid-state chemistry kinetic process from mainly three other events: 1- the time it takes for steam to enter the reactor, 2- the time lag of detection and 3- the dispersion effects of H₂ being produced and transported to the detector. A simulated oxidation experiment was performed where an empty zirconia boat was held at two oxidation temperatures 850 °C and 1000 °C. Instead of only steam, trace amounts of hydrogen in 40 vol. % steam were inserted in the reactor and detected in the mass spectrometer. The effects of the three events intrinsic to the experiment setup are then numerically determined by fitting a continuous stirred tank reactor (CSTR) model consisting, in this case of seven serial tanks to the resulting hydrogen signal. The fitted parameters for the reactor can then be applied to simple kinetic model curves, such as reaction-order, diffusion among other ones to produce simulated hydrogen production curves. Finally, using numerical methods, the kinetic model parameters are adjusted to fit the simulated curve to the actual experimental data and therefore extract the true rate-governing mechanisms in the materials such as surface reactions and bulk diffusion. The computational methods are discussed in further detail in McDaniel et al. [65] and Scheffe et al. [103]. Table 5. compiles the fitted parameters for the reactor using four blank runs.

Table 5. and Table 5. compile the calculated rate constants for each material and condition using all the four mixing models. The r-square is also reported as an indication of fitting suitability. An average of the rate constants as well as the standard deviation for each T_{ox} condition and material is reported in the main manuscript.
Table 5.8: Fitted parameters for the reactor calculated from four blank runs that used 2 sccm and 4 sccm trace amount of H\textsubscript{2} (5 % H\textsubscript{2} balanced in Ar) mixed in the 40 vol. % steam flow.

<table>
<thead>
<tr>
<th>T\textsubscript{OX} (°C)</th>
<th>Mixing model identification</th>
<th>Trace H\textsubscript{2} flow (sccm)</th>
<th>t\textsubscript{0} (s)</th>
<th>tau</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>M850-1</td>
<td>2</td>
<td>17.7</td>
<td>0.2617</td>
</tr>
<tr>
<td></td>
<td>M850-2</td>
<td>2</td>
<td>20.7</td>
<td>0.2887</td>
</tr>
<tr>
<td></td>
<td>M850-3</td>
<td>4</td>
<td>18.4</td>
<td>0.2740</td>
</tr>
<tr>
<td></td>
<td>M850-4</td>
<td>4</td>
<td>19.2</td>
<td>0.2929</td>
</tr>
<tr>
<td>1000</td>
<td>M1000-1</td>
<td>2</td>
<td>19.0</td>
<td>0.2613</td>
</tr>
<tr>
<td></td>
<td>M1000-2</td>
<td>2</td>
<td>16.2</td>
<td>0.2486</td>
</tr>
<tr>
<td></td>
<td>M1000-3</td>
<td>4</td>
<td>17.5</td>
<td>0.2580</td>
</tr>
<tr>
<td></td>
<td>M1000-4</td>
<td>4</td>
<td>18.2</td>
<td>0.2741</td>
</tr>
</tbody>
</table>

Table 5.9: Rate constants calculated for BCM using the four different mixing models at 850 °C and 1000 °C.

<table>
<thead>
<tr>
<th>T\textsubscript{OX} (°C)</th>
<th>H\textsubscript{2} peak</th>
<th>Mixing model</th>
<th>k\textsubscript{0}</th>
<th>r-square</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>1st</td>
<td>M850-1</td>
<td>0.0132</td>
<td>0.9960</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-2</td>
<td>0.0131</td>
<td>0.9950</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-3</td>
<td>0.0121</td>
<td>0.9956</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-4</td>
<td>0.0130</td>
<td>0.9949</td>
</tr>
<tr>
<td>850</td>
<td>2nd</td>
<td>M850-1</td>
<td>0.0129</td>
<td>0.9942</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-2</td>
<td>0.0128</td>
<td>0.9942</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-3</td>
<td>0.0128</td>
<td>0.9944</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-4</td>
<td>0.0127</td>
<td>0.9944</td>
</tr>
</tbody>
</table>
To ensure that the WS results measured in this study could be fully attributed to the 12$R$ phase, we conducted a simulated WS cycle on the 10$H$ phase using TGA. We prepared a phase-pure 10$H$ sample by reducing a BCM 12$R$ sample for 24 h under UHP N$_2$ flow at 1350 °C. 50.3mg of 10$H$ sample was loaded into a Pt crucible and heated under 100 sccm UHP N$_2$ at 10 °C/min to $T_{OX}$ 850 °C.

The reduction step was carried out heating the sample to TRE 1350 °C at 99°C/min (the fastest we could heat in the TGA to simulate the laser heating) and holding the temperature for 330 s. The sample was then cooled to $T_{OX}$ at the same fast ramp rate and 16 sccm of synthetic air was flowed for 10 min to initiate oxidation.

The synthetic air flow was turned off and UHP N$_2$ gas was flowed for 10 min to purge the O$_2$ from the chamber before the subsequent reduction step. Figure S6 shows the TGA simulated run results.

<table>
<thead>
<tr>
<th>$T_{OX}$ (°C)</th>
<th>H$_2$ peak</th>
<th>Mixing model</th>
<th>$k_0$</th>
<th>r-square</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>1st</td>
<td>M1000-1</td>
<td>0.0168</td>
<td>0.9946</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-2</td>
<td>0.0167</td>
<td>0.9980</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-3</td>
<td>0.0168</td>
<td>0.9971</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-4</td>
<td>0.0167</td>
<td>0.9974</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>M1000-1</td>
<td>0.0157</td>
<td>0.9886</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-2</td>
<td>0.0157</td>
<td>0.9943</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-3</td>
<td>0.0158</td>
<td>0.9924</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-4</td>
<td>0.0157</td>
<td>0.9933</td>
</tr>
</tbody>
</table>
Table 5.10: Rate constants calculated for ceria using the four different mixing models at 850 °C and 1000 °C.

<table>
<thead>
<tr>
<th>$T_{ox}$ (°C)</th>
<th>H$_2$ peak</th>
<th>Mixing model</th>
<th>$k_0$</th>
<th>r-square</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>1st</td>
<td>M850-1</td>
<td>0.1784</td>
<td>0.9858</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-2</td>
<td>0.1697</td>
<td>0.9693</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-3</td>
<td>0.1703</td>
<td>0.9892</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-4</td>
<td>0.1561</td>
<td>0.9915</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>M850-1</td>
<td>0.2134</td>
<td>0.9935</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-2</td>
<td>0.2010</td>
<td>0.9792</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-3</td>
<td>0.1953</td>
<td>0.9936</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M850-4</td>
<td>0.1774</td>
<td>0.9937</td>
</tr>
<tr>
<td>1000</td>
<td>1st</td>
<td>M1000-1</td>
<td>0.0768</td>
<td>0.9705</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-2</td>
<td>0.0764</td>
<td>0.9881</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-3</td>
<td>0.0780</td>
<td>0.9836</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-4</td>
<td>0.0756</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>M1000-1</td>
<td>0.0744</td>
<td>0.9781</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-2</td>
<td>0.0737</td>
<td>0.9915</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-3</td>
<td>0.0759</td>
<td>0.9891</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M1000-4</td>
<td>0.0738</td>
<td>0.9896</td>
</tr>
</tbody>
</table>

Figure 5.15 shows the XRD results on the 10$H$ sample before and after the simulated run. Before TGA cycling, the sample presents only the 10$H$ phase.
Figure 5.15: 10H sample tested on 5 simulated WS cycles carried out in a TGA. The sample was heated at 10 °C/min to $T_{OX} \ 850$ °C in UHP $N_2$. The reduction step was done by heating the sample at 99 °C/min to $T_{RE} \ 1350$ °C and held for 330s. The sample was then cooled to $T_{OX}$ at 99 °C/min and 16 sccm of synthetic air (21% $O_2$ balanced in $N_2$) mixed with 100 sccm of UHP $N_2$ was flowed for 10 min. The oxidizing flow was turned off and 100 sccm of UHP $N_2$ purged the chamber for another 10 min preparing the sample for the subsequent reduction cycle.

However, after TGA cycle, the sample is converted entirely to the 12$R$ phase. This demonstrates that under the SFR WS conditions used in this study, any reminiscent 10$H$ phase is converted to the 12$R$ phase.
Figure 5.16: XRD done on 10H samples before and after WS simulated runs done in TGA. The as prepared sample indicates the presence of 10H phase, whereas the sample after the TGA WS simulated run indicates that the 10H phase was converted to 12R phase.
CHAPTER 6

PHASE IDENTIFICATION OF THE LAYERED PEROVSKITE CE\textsubscript{A}SR\textsubscript{2-a}MNO\textsubscript{4} AND APPLICATION FOR SOLAR THERMOCHEMICAL WATER SPLITTING

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\textsuperscript{b}Department of Materials Science and Eng., Northwestern University, Evanston IL, USA
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\textsuperscript{d}Sandia National Laboratory, Livermore CA, USA

Abstract

Ruddlesden-Popper (layered perovskite) phases are attracting significant interest because of their unique potential for many applications requiring mixed ionic and electronic conductivity. Here we report a new, previously undiscovered layered perovskite of composition, Ce\textsubscript{a}Sr\textsubscript{2-a}MnO\textsubscript{4} (a = 0.1, 0.2, and 0.3). Furthermore, we demonstrate that this new system is suitable for solar thermochemical hydrogen production (STCH). Synchrotron radiation X-ray diffraction and Transmission Electron Microscopy are performed to characterize this new system. Density Functional Theory calculations of phase stability and oxygen vacancy formation energy (1.76, 2.24 and 2.66 eV/O atom, respectively with increasing Ce content) reinforce the potential of this phase for STCH application. Experimental hydrogen production results show
that this materials system produces 2-3X more hydrogen than the benchmark STCH oxide ceria at a reduction temperature of 1400 °C and an oxidation temperature of 1000 °C.

6.1 Introduction

Perovskite oxides are of great scientific interest due to their compositional versatility and the resulting breadth of physical properties they exhibit. Perovskite oxides are widely studied for numerous applications including solid oxide fuel cells [72], colossal magnetoresistors [74], multiferroics [75], chemical looping [73], and solar thermochemical hydrogen production (STCH) [20]. Currently, there are about 254 confirmed, experimentally synthesized inorganic perovskites.[86] However, recent density functional theory (DFT) and machine learning (ML) screening efforts suggest that there are yet hundreds more stable perovskite or perovskite-related oxides remaining to be discovered and synthesized [84], [86], [129]. In this paper, we report one such new perovskite-related compound, Ce$_2$Sr$_2$MnO$_4$ (CSM), a K$_2$NiF$_4$-type[130] layered perovskite which is a known Ruddlesden-Popper phase. Our discovery of CSM was triggered by a search for new STCH-active materials. Here, we provide detailed analysis validating its structure and show that CSM indeed possesses intriguing thermochemical water splitting behavior that makes it potentially attractive for STCH application.

In a two-step thermochemical water-splitting process, a STCH-active oxide is reduced at a high temperature ($T_{\text{RE}}$, typically 1300-1500 °C) in low oxygen environments, driving the production of oxygen vacancies. The oxide is then cooled to a lower temperature ($T_{\text{OX}}$, typically 800-1000 °C), where steam is introduced, and the driving force for reoxidation leads to the dissociation of the hydrogen-oxygen bonds, thereby reoxidizing the STCH material and liberating hydrogen gas. The suitability of a prospective oxide material for STCH application is intrinsically tied to the energy required to create/fill oxygen vacancies during this cyclic reduction/oxidation process. Ceria, the benchmark material for STCH, represents the upper limit in the range of viable oxygen vacancy formation energy ($E_v$) at about 5 eV/O atom [131]. Any
material having an $E_v$ at or above this value will likely require impractically high temperatures (above 1550 °C) for meaningful reduction to occur. The cubic perovskite Sr$_{1-a}$La$_a$Mn$_b$Al$_{1-b}$O$_3$ [66] (SLMA), having an $E_v$ between 1.5 and 2.5 eV/O atom [80], depending on exact composition, represents the potential lower limit for STCH materials [84], [98], because $E_v$ also directly impacts the driving force for oxide reoxidation in the presence of steam. In essence, $E_v$ must be low enough to allow a reasonable level of nonstoichiometry during reduction at reactor-attainable conditions (i.e., $T_{RE} < 1400$ °C) but must be high enough to overcome the O-H bond strength of water to ensure sufficient driving force for water splitting during the reoxidation step.

In the search for new STCH-active materials, perovskite and perovskite-related oxides provide fertile hunting grounds because of their compositional flexibility and tolerance for large degrees of nonstoichiometry. A and B-site cation selection, site-substitution (doping), order/disorder effects, and structural distortions can all be used to alter the thermodynamics of oxygen vacancy formation. The tradeoff between the energy requirements for reduction and oxidation, and the demonstrable ability to tune $E_v$ [80], [83], is crucial to the continued search for suitable STCH candidates.

We have recently shown that the perovskite oxide BaCe$_{0.25}$Mn$_{0.75}$O$_3$ (BCM) attains good STCH performance. However, BCM forms a line compound, *i.e.*, it can only form with an exact composition, a Ce/Mn ratio of 0.25/0.75, likely due to size constraints on the A and B-sites, which eliminates the possibility for redox tunability via substitutional doping. Motivated by the success of BCM, but with the goal of identifying related perovskites possessing greater compositional tunability, we hypothesized that Ce could be analogously doped on the B-site of SrMnO$_3$. However, we instead obtained an unexpected structure, part of the Ruddlesden-Popper family AO(ABO$_3$)$_n$ (where $n = 1$) [132], known as a K$_2$NiF$_4$-type [130] layered perovskite, where Ce shares the A-site with Sr. Layered perovskites are of great interest for their increased oxygen ion mobility due to the rock salt interlayers formed by AO (where the A cation in the rock salt layer is the same as the A cation in the ABO$_3$ perovskite layer). The AO layers may potentially serve as highways for oxygen ion transport because they can accommodate interstitial oxygen [133], [134].
The layered perovskite we discovered here, Ce$_a$Sr$_{2-a}$MnO$_4$ (Figure 6.1), has never been reported in the literature, motivating the detailed structural analysis from synchrotron radiation X-ray diffraction and high-resolution transmission electron microscopy (HR-TEM) reported in this paper.

![Figure 6.1: Illustration of the Ce$_a$Sr$_{2-a}$MnO$_4$ Ruddlesden-Popper layered perovskite crystal structure. Purple octahedra are MnO$_6$ and green/yellow atoms denote the A-site positions which are randomly shared between Sr and Ce atoms.](image)

DFT calculations and preliminary WS experiments suggested that this phase has the potential for water splitting. This phase is one of the few layered-perovskites suggested for STCH application [93]. More extensive testing on purified phase samples corroborate these encouraging observations, highlighting the promise of this structure for STCH and opening new avenues of exploration for the next generation of water splitting materials.
6.2 Experimental

In this section the synthesis and characterization techniques parameters are described in detail. Parameters for the DFT calculations are discussed and the water splitting test parameters are also explained in detail.

*Synthesis*

Five samples spanning the nominal \( \text{SrCe}_{0.3}\text{Mn}_{0.7}\text{O}_3 \) compositional space were synthesized with \( b = 0, 0.3, 0.5, 0.7 \) and 1 using the sol-gel modified Pechini synthesis route described by Shang et al. [117]. Stoichiometric amounts of strontium nitrate (Alfa Aesar 99%), cerium nitrate hexahydrate (Alfa Aesar 99.5%) and manganese acetate tetrahydrate (Alfa Aesar 98+%) were stirred in deionized water, with ethylenediaminetetraacetic acid (EDTA), citric acid, and ammonium hydroxide for pH adjustment while heating at 90 °C. Once the gel was formed, it was transferred to a drying oven at 160 °C to dry completely. The resulting charcoal-like samples were calcined first at 800 °C for 10 h and then subsequently at 1400 °C for 5 h.

Three \( \text{Ce}_{a}\text{Sr}_{2-a}\text{MnO}_4 \) samples \( (a = 0.1, 0.2 \) and 0.3) were synthesized following the evaporation-to-dryness procedure of Karita et al. [135], [136], where nitrates of the metal precursors, in this case strontium nitrate (Alfa Aesar 99%), cerium nitrate hexahydrate (Alfa Aesar 99%) and manganese nitrate tetrahydrate (Alfa Aesar 99%) in the stoichiometric ratios were stirred in deionized water and heated at 180 °C until dry. The samples were calcined at 350 °C for 4 h to allow for the decomposition of the nitrates and then at 1000 °C for 10 h. A second calcination took place at 1400 °C for 10 h.
Characterization

Powder X-ray diffraction (XRD) patterns were measured on a PANalytical PW3040 diffractometer surveying the 2θ range between 20° and 120° at a step size of 0.008° with Cu-Kα radiation of λ=1.540598 and 1.54439 Å.

For structural characterization of the new phase (CeₐSr₂₋₃MnO₄), three samples were probed by synchrotron radiation through the mail-in program offered by the Advanced Photon Source (APS) 11-BM at Argonne National Laboratory (λ = 0.412628 Å powder XRD). Rietveld refinement of the resulting diffraction patterns was conducted using the free software GSAS-II [137] by indexing the patterns to the tetragonal structure of space group I4/mmm (139).

Selected samples were also analyzed by Transmission Electron Microscopy (TEM) using a FEI Talos operating at 200 kV. The microscope was equipped with four Energy Dispersive X-Ray Spectroscopy (EDS) detectors optimized for compositional mapping. The TEM samples were prepared by Focused Ion Beam (FIB) on a FEI Helios equipped with a dual-beam system that uses an electron gun as well as a Ga gun for the milling steps. The milling was performed at 30 kV, but a final thinning step at 2 kV was performed to minimize surface damage.

High-resolution electron microscopy images (HRTEM) were processed using the CRISP software [138] following the standard procedure described elsewhere [139] to identify the unit cell in the image by the Fourier Transform, averaging over a region of several unit cells and imposing the known symmetry. Only the Fourier components with resolution smaller than the first crossover of the image were used for the image at the Scherzer defocus condition. The regions from the image that yielded the smallest phase residuals were used; that also coincided with the thinnest regions of the crystal. These processed images were compared with Multislice simulations performed using the jEMS software for different defocus and thickness values. Once the thickness was discovered by finding the best match between the simulated and experimental images, the other defocus images were compared with the respective defocus simulated image for the same thickness.
DFT calculations

DFT calculations were employed to check for phase stability using the Vienna ab-initio simulation package (VASP) [140], [141] with projector-augmented wave method (PAW) [142] potentials with the Perdew-Burke-Ernzerhof generalized gradient approximation[143] to the XC functional. DFT+U [144], [145] was used for Mn and Ce elements (\( U = 3.8 \) and 5 eV, respectively, \( J = 0 \)). The stability of the compounds was calculated with respect to all phases in the Sr-Ce-Mn-O system present in the Open Quantum Materials Database (OQMD) [146]. We note that all compounds containing cerium were not simply taken from OQMD, but were recalculated (in the present work) with the Ce pseudopotential containing 12 valence electrons. The total number of phases for this set of 4 elements is 230. Among those, 23 were stable before adding the Sr\(_a\)Ce\(_b\)Mn\(_c\)O\(_d\) phases. The stability, or hull distance, for any arbitrary Sr\(_a\)Ce\(_b\)Mn\(_c\)O\(_d\) compound is defined as in Equation 6.1:

\[
\Delta H_{\text{stab}}^{\text{Sr}_a\text{Ce}_b\text{Mn}_c\text{O}_d} = \Delta H_f^{\text{Sr}_a\text{Ce}_b\text{Mn}_c\text{O}_d} - \Delta H_f
\]

where \( \Delta H_f \) is the convex hull energy at the Sr\(_a\)Ce\(_b\)Mn\(_c\)O\(_d\) composition and \( \Delta H_f^{\text{Sr}_a\text{Ce}_b\text{Mn}_c\text{O}_d} \) is the formation energy of the Sr\(_a\)Ce\(_b\)Mn\(_c\)O\(_d\) compound calculated in Equation 6.2 as:

\[
\Delta H_f = E(Sr_aCe_bMn_cO_d) - a\mu_{Sr} - b\mu_{Ce} - c\mu_{Mn} - d\mu_{O}
\]

where, \( E(Sr_aCe_bMn_cO_d) \) is the DFT total energy of the Sr\(_a\)Ce\(_b\)Mn\(_c\)O\(_d\) compound, and \( \mu_{Sr}, \mu_{Ce}, \mu_{Mn} \) and \( \mu_{O} \) are the chemical potentials of strontium, cerium, manganese and oxygen, respectively. The chemical potential of Sr is the DFT 0 K energy of the element. For Ce, Mn and O, the chemical potentials are fitted to experimental data using the FERE technique [147] because of the use of DFT+U (Ce and Mn) and the phase transition between 0 K and 300 K (O) [146]. Compounds that are stable have a zero or negative hull distance whereas compounds that are unstable have a positive hull distance.

The Sr\(_a\)Ce\(_b\)Mn\(_{1-b}\)O\(_3\) compounds were generated by mixing Ce and Mn on the Mn site of the cubic SrMnO\(_3\) perovskite with the special quasirandom structure approach (SQS) [148]. SQS are structures generated so that their short-range correlation functions (\( \Pi_f(\sigma) \)) match those of a random alloy, thus
allowing the calculation of random mixing despite periodic boundary conditions. SQS were generated using the Monte Carlo semi quasirandom structure (mcsqs) as implemented in the Alloy Theoretic Automated Toolkit (ATAT).

The structures of Ce$_{a}$Sr$_{2-a}$MnO$_{4}$ were created by taking LaSrMnO$_{4}$ from the ICSD (collection code number 153645) and substituting Ce for La. The SQS approach was used to model the cation mixing on the (Ce-Sr) A-site.

Oxygen vacancy formation energy was calculated according to Equation 6.3:

$$\Delta E^O_v = E(Sr_aCe_bMn_cO_{d-1}) + \mu_O - E(Sr_aCe_bMn_cO_d)$$  \hspace{1cm} (6.4)

where $E(Sr_aCe_bMn_cO_{d-1})$ and $E(Sr_aCe_bMn_cO_d)$ are the DFT total energies of the defected and pristine structures, respectively and $\mu_O$ is the chemical potential of oxygen, which was detailed above.

**Testing for Solar Thermochemical Hydrogen Production**

Temperature Programmed Reduction (TPR) was conducted to measure extent of reduction as a function of temperature, as a preliminary indicator of a materials’ potential for STCH. About 50 mg of sample was loaded into a Pt crucible and heated in a Setaram SetSys Evo Thermogravimetric Analyzer (TGA) to the reduction temperature ($T_{RE}$) of 1350 °C in UHP nitrogen at a ramp rate of 10 °C/min. After a dwell of 1 h, the sample was cooled down to the oxidation temperature ($T_{OX}$) of 1000 °C at the same temperature ramp rate and air was introduced. An oxygen sensor connected to the exhaust of the system monitored the oxygen content to confirm that the mass loss was due to oxygen release. The mass profile was converted into moles of atomic oxygen per mole of sample (or $\delta$ as in the ABO$_{3-\delta}$) and was compared for all the samples tested.

Water splitting performance tests were performed in the Stagnation Flow Reactor (SFR) at Sandia National Laboratories (configurations of the system and experiment are detailed elsewhere [102], [150]). Briefly, a powder sample on a zirconia platform was maintained at the oxidation temperature (1000 °C) by a tubular furnace in argon atmosphere at 75 torr. The sample was heated at the controlled rate of 10 °C/s to
1400 °C by a laser. The reduction temperature was held for 330 s and the amount of oxygen released during reduction was measured in a calibrated mass spectrometer. The samples were then immediately cooled back down to the oxidation temperature by turning off the laser and steam (40 vol. % balanced in argon) was introduced to the reactor. The amount of hydrogen produced during the oxidation step and oxygen evolved from the samples during the reduction step were measured by a mass spectrometer and the detected amounts of hydrogen and oxygen were normalized by the mass of sample.

6.3 Results and discussion

Motivated by the perovskite BaCe$_{0.25}$Mn$_{0.75}$O$_3$, first synthesized by Fuentes et al. [119] and found to be a promising STCH candidate, we attempted to synthesize five samples in the SrCe$_b$Mn$_{1-b}$O$_3$ system ($b = 0, 0.3, 0.5, 0.7$ and $1$; denoted SMO, SCM3070, SCM5050, SCM7030, and SCO respectively) via sol-gel with the goal of having the Ce cation sharing the perovskite B-site with Mn. The Goldschmidt tolerance factor calculations (0.99, 0.96 and 0.93 respectively) indicated that it should be possible to form cubic SrCe$_{0.3}$Mn$_{0.7}$O$_3$, SrCe$_{0.5}$Mn$_{0.5}$O$_3$ and SrCe$_{0.7}$Mn$_{0.3}$O$_3$ respectively. However, powder X-ray diffraction patterns obtained from the calcined samples revealed that the target compositions were not formed, and all samples showed the presence of mixed phases. Moreover, Rietveld refinement summarized in Table 6.4, indicated the presence of an unexpected phase common to all the Ce-containing samples. This phase was identified as belonging to the space group I4/mmm (139), known as a K$_2$NiF$_4$-type[130] Ruddlesden-Popper phase, with a structure similar to that of SrLaCoO$_4$ [151].

We turned to DFT calculations to corroborate the relative stability of this previously unknown phase within the Sr-Ce-Mn-O system. The DFT-predicted relative phase stabilities and decomposition reactions are summarized in Table 6.1.
Table 6.1: DFT calculations of stability, decomposition reactions and oxygen vacancy formation energy of SrCe\textsubscript{b}Mn\textsubscript{1-b}O\textsubscript{3} (b = 0, 0.25, 0.5, 0.75, 1).

<table>
<thead>
<tr>
<th>Formula</th>
<th>Stability [eV/atom]</th>
<th>Decomposition reactions</th>
<th>Oxygen vacancy formation energy [eV/O atom]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrMnO\textsubscript{3}</td>
<td>-0.026</td>
<td>Stable</td>
<td>1.418</td>
</tr>
<tr>
<td>SrCe\textsubscript{0.25}Mn\textsubscript{0.75}O\textsubscript{3}</td>
<td>0.057</td>
<td>0.250 CeO\textsubscript{2} + 0.250 Sr\textsubscript{3}Mn\textsubscript{2}O\textsubscript{10}</td>
<td>-</td>
</tr>
<tr>
<td>SrCe\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3}</td>
<td>0.062</td>
<td>0.450 CeO\textsubscript{2} + 0.050 SrO\textsubscript{2} + 0.500 Sr\textsubscript{1.9}Ce\textsubscript{0.1}MnO\textsubscript{4}</td>
<td>-</td>
</tr>
<tr>
<td>SrCe\textsubscript{0.75}Mn\textsubscript{0.25}O\textsubscript{3}</td>
<td>0.059</td>
<td>0.475 CeO\textsubscript{2} + 0.025 SrO\textsubscript{2} + 0.250 Sr\textsubscript{1.9}Ce\textsubscript{0.1}MnO\textsubscript{4} + 0.250 Sr\textsubscript{2}CeO\textsubscript{4}</td>
<td>-</td>
</tr>
<tr>
<td>SrCeO\textsubscript{3}</td>
<td>0.018</td>
<td>0.500 CeO\textsubscript{2} + 0.500 Sr\textsubscript{2}CeO\textsubscript{4}</td>
<td>-</td>
</tr>
</tbody>
</table>

The calculated stabilities indicate that the SrMnO\textsubscript{3} perovskite is stable, whereas doping this compound with Ce on the B-site results in an instability and decomposition into other phases, one of them being the layered perovskite.

The confirmation of the formation of the layered perovskite led to additional DFT calculations to further examine the stability of this phase as a function of the Ce content. DFT stability calculations not only confirmed the probability of formation of three materials Ce\textsubscript{a}Sr\textsubscript{2-a}MnO\textsubscript{4} (a = 0.1, 0.2, 0.3, 1) but also predicted that these materials could be suitable for WS based on model predictions of the oxygen vacancy formation energy (results summarized in Table 6.2). Results showed that Ce can be fully incorporated into the structure in all three synthesized samples. While the reported limit for La into the La\textsubscript{a}Sr\textsubscript{2-a}MnO\textsubscript{4} structure is a = 1, [152] our results suggest that less Ce can be incorporated in the Ce\textsubscript{a}Sr\textsubscript{2-a}MnO\textsubscript{4} structure, i.e., the solubility limit for Ce in Ce\textsubscript{a}Sr\textsubscript{2-a}MnO\textsubscript{4} is likely to be significantly lower, probably close to a = 0.3.
Table 6.2: DFT stability and oxygen vacancy formation energy calculations on CSM1, CSM2 and CSM3.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Stability [eV/atom]</th>
<th>Decomposition reactions</th>
<th>Oxygen vacancy formation energy [eV/O atom]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.1}$Sr$</em>{1.9}$MnO$_4$</td>
<td>-0.012</td>
<td>stable</td>
<td>1.763</td>
</tr>
<tr>
<td>Ce$<em>{0.2}$Sr$</em>{1.8}$MnO$_4$</td>
<td>0.000</td>
<td>stable</td>
<td>2.243</td>
</tr>
<tr>
<td>Ce$<em>{0.3}$Sr$</em>{1.7}$MnO$_4$</td>
<td>-0.007</td>
<td>Stable</td>
<td>2.661</td>
</tr>
<tr>
<td>CeSrMnO$_4$</td>
<td>0.061</td>
<td>0.500 Ce$_2$O$_3$ + 0.500 Sr$_2$Mn$_2$O$_5$</td>
<td>-</td>
</tr>
</tbody>
</table>

Preliminary WS experiments (Table 6.5 and Figure 6.5) performed on the samples with the largest amounts of this new phase (SCM5050 and SCM7030), as well as on the end members, indicated that this K$_2$NiF$_4$-type phase is in fact thermochemically active.

To facilitate further study, we attempted to isolate the new phase in high purity via evaporation-to-dryness synthesis approach, as further described in the experimental section. This relatively simple synthesis approach utilizes nitrate precursors (rather than carbonates) for all cations. This factor likely contributes to its success in producing a phase-pure compound as the nitrate precursor decompositions occurs at much lower temperatures than corresponding carbonate decompositions, thereby kinetically promoting the formation of the K$_2$NiF$_4$-type structure. Ultimately, three samples, Ce$_{0.1}$Sr$_{1.9}$MnO$_4$ (CSM1), Ce$_{0.2}$Sr$_{1.8}$MnO$_4$ (CSM2), and Ce$_{0.3}$Sr$_{1.7}$MnO$_4$ (CSM3), were successfully synthesized by the evaporation-to-dryness method.

Synchrotron radiation XRD was employed for structural analysis and the obtained diffractograms are shown below in Figure 6.2 (a,b, and c) for the samples CSM1, CSM2 and CSM3, respectively. XRD reveals minor secondary phase peaks that increase with increasing Ce content. However, the amount of secondary phase is minimal and is most likely due to inefficient mixing during synthesis, and/or incomplete calcination.
Figure 6.2: Powder X-ray diffraction using synchrotron radiation ($\lambda = 0.412628$ Å) on (a) Ce$_{0.1}$Sr$_{1.9}$MnO$_4$ (CSM1), (b) Ce$_{0.2}$Sr$_{1.8}$MnO$_4$ (CSM2), and (c) Ce$_{0.3}$Sr$_{1.7}$MnO$_4$ (CSM3). Observed (dark), calculated (light grey), difference plot (bottom) and expected phase peaks (vertical marks).
Rietveld refinement was performed with GSAS-II [137] using the Powder Diffraction File number 04-002-4381 on Sr$_{0.8}$La$_{1.2}$CoO$_4$, modified using the software VESTA [153] to account for the different A-site cation ratios and cation species Ce and Mn instead of La and Co respectively. Using the layered perovskite nomenclature, (AO)(A$_{1-a}$A'_aBO$_3$)$_n$ where $n=1$, the Ce cations were modelled as sharing the perovskite A-sites randomly. The refinement analysis results are shown below in Table 2. As expected, the lattice parameters increase with increasing Ce content, from CSM1 to CSM3. The site fraction refinement confirms that Ce is being incorporated into the structure and that CSM3 has the largest amount of Ce compared to CSM2 and CSM1.

Table 6.3: Final structural parameters for Ce$_{0.1}$Sr$_{1.9}$MnO$_4$, Ce$_{0.2}$Sr$_{1.8}$MnO$_4$ and Ce$_{0.3}$Sr$_{1.7}$MnO$_4$.

<table>
<thead>
<tr>
<th>Atom site</th>
<th>Sr (1)</th>
<th>Ce (1)</th>
<th>Mn (1)</th>
<th>O (1)</th>
<th>O (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.1}$Sr$</em>{1.9}$MnO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x/a$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$y/b$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>$z/c$</td>
<td>0.35674</td>
<td>0.35655</td>
<td>0.0</td>
<td>0.0</td>
<td>0.15415</td>
</tr>
<tr>
<td>$U_{iso}$</td>
<td>0.01063</td>
<td>0.00473</td>
<td>0.00756</td>
<td>0.00795</td>
<td>0.01344</td>
</tr>
<tr>
<td>Frac. site</td>
<td>0.915</td>
<td>0.0854</td>
<td>1.0</td>
<td>1.024</td>
<td>0.9764</td>
</tr>
<tr>
<td>Ce$<em>{0.2}$Sr$</em>{1.8}$MnO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x/a$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$y/b$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>$z/c$</td>
<td>0.35747</td>
<td>0.35528</td>
<td>0.0</td>
<td>0.0</td>
<td>0.15331</td>
</tr>
<tr>
<td>$U_{iso}$</td>
<td>0.00634</td>
<td>0.00209</td>
<td>0.00394</td>
<td>0.00736</td>
<td>0.00516</td>
</tr>
<tr>
<td>Frac. site</td>
<td>0.888</td>
<td>0.112</td>
<td>1.0</td>
<td>0.983</td>
<td>1.0464</td>
</tr>
<tr>
<td>Ce$<em>{0.3}$Sr$</em>{1.7}$MnO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x/a$</td>
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</tr>
<tr>
<td>$y/b$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>$z/c$</td>
<td>0.35674</td>
<td>0.36017</td>
<td>0.0</td>
<td>0.0</td>
<td>0.15779</td>
</tr>
</tbody>
</table>
Table 6.3: continued

<table>
<thead>
<tr>
<th>Atom site&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Sr (1)</th>
<th>Ce (1)</th>
<th>Mn (1)</th>
<th>O (1)</th>
<th>O (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( U_{iso} )</td>
<td>0.00802</td>
<td>0.00820</td>
<td>0.00615</td>
<td>0.01381</td>
<td>0.02012</td>
</tr>
<tr>
<td>Frac. site</td>
<td>0.8624</td>
<td>0.1384</td>
<td>1.0</td>
<td>1.050</td>
<td>1.2424</td>
</tr>
</tbody>
</table>

<sup>a</sup> Space group: I4/mmm (139)

<sup>b</sup> For Ce<sub>0.1</sub>Sr<sub>1.9</sub>MnO<sub>4</sub>, \( a = 3.81477 \) Å, \( c = 12.45533 \) Å; \( V = 181.256 \) Å³, \( GOF = 2.76 \)

<sup>c</sup> For Ce<sub>0.3</sub>Sr<sub>1.7</sub>MnO<sub>4</sub>, \( a = 3.82784 \) Å, \( c = 12.45831 \) Å; \( V = 182.543 \) Å³, \( GOF = 3.73 \)

<sup>d</sup> For Ce<sub>0.5</sub>Sr<sub>1.5</sub>MnO<sub>4</sub>, \( a = 3.82548 \) Å, \( c = 12.46784 \) Å; \( V = 182.458 \) Å³, \( GOF = 4.85 \)

A thorough Transmission Electron Microscopy (TEM) study using a combination of electron diffraction and high-resolution transmission electron microscopy (HRTEM) was performed on sample CSM1, which is the closest to pure phase, to further characterize its structure. The first step of the TEM analysis consisted of taking a series of selected area diffraction patterns (SADP) and convergent beam electron diffractions (CBED). The combination of these two techniques can confirm the symmetry of a given phase. SADP and CBED patterns of all three major zone axis, namely the [001], [100] and [110], are given in Figure 6.3.

The CBED pattern from the [001] zone axis reveals a 4mm symmetry while the [100] and [110] patterns both reveal a 2mm symmetry. The diffraction pattern in Figure 3a is rotated 90° relative to the diffraction patterns in b and c.

The SADPs displayed in Figure 6.3 also confirm the I centering of the phase, due to the systematic absence of the \( h+k+l=(2n-1) \) reflections.
Figure 6.2: Indexed SADPs (left) and CBED patterns (right) of the three main zone axes of the Ce$_{0.1}$Sr$_{1.9}$MnO$_4$ layered perovskite: a) [001], b) [100], and c) [110]. The yellow lines represent the mirror symmetries present in each CBED pattern and they confirm the I4/mmm space group. The diffraction patterns are not necessarily at the same scale.
No other systematic absences were observed; therefore, the space group is symmorphic. Overall, the electron diffraction results confirm that the space group of the perovskite is I4/mmm. The measured lattice parameters by TEM are $a = 3.8 \, \text{Å}$ and $c = 12.5 \, \text{Å}$, which match the values measured from synchrotron XRD (Table 6.3), further confirming this is indeed the phase present in the CSM1 sample. The CSM2 and CSM3 samples were also analyzed by TEM electron diffraction, confirming presence of the same phase (Figure 6.6 in the supporting information section).

The layered structure was confirmed using HRTEM by a combination of image processing and simulation using a defocus series. HRTEM images were acquired in the two shortest projection axes, the [100] and the [110], under different defocus conditions. Two processing steps were performed on the images using the software CRISP [154]. The first imposed an average over hundreds of unit cells to remove the random noise from the HRTEM images, while the second consisted of taking a Fourier transform of the image to extract its Fourier coefficients, which in turn were related to the structure factor of the sample. The 2mm symmetry was imposed in both zone axes, which forces phase and amplitude restrictions on symmetrically related reflections, and an image was reconstructed from these modified structure factors. This procedure, valid since the symmetry of the zone axis is known and has been proved by CBED, corrects several aberrations from the microscope and the image acquisition process. These experimental images were compared to multi-slice simulations produced by the jEMS software, with information derived from the refined atomic positions of the synchrotron XRD patterns. The multi-slice calculations were performed by varying the defocus and the sample thickness. Based on image comparison, the thickness of the sample was determined to be around 28 nm; the simulated and experimental images for different defocus conditions can be seen in Figure 6.3. The simulated images match well with the experimental ones; the heavier Ce and Sr atoms can be easily distinguished, especially on the [100] projection, in which the layered structure is confirmed.
EDS analysis was also performed in the TEM to verify that the chemical composition of the layered perovskite was consistent with expectations. The Sr to Ce ratios measured in samples CSM1, CSM2 and CSM3 were 16.9, 8.9 and 5.9, respectively, close to the nominal expected values of 19, 9 and 5.7. Table 6.6 in the supporting information shows the EDS results.

The DFT calculated oxygen vacancy formation energies of the CSM family (1.8, 2.2 and 2.7 eV/O atom for CSM1, CSM2 and CSM3 respectively, see Table 6.2) are within the target range of 1.5 to 5 eV/O atom required for potential STCH materials [80], [84]. In addition, layered perovskites also potentially enable enhanced oxygen ion mobility (e.g., Ivanov et al. [155], [156] have attributed the increased mobility of the layered perovskite La$_x$Sr$_{2-x}$MnO$_4$ compared to the regular La$_y$Sr$_{1-y}$MnO$_3$ to the layered aspect of this structure).
These characteristics make CSM an excellent potential candidate for STCH application.

To confirm the potential for water splitting seen in the preliminary testing, TPR was conducted on the three samples (shown in Figure 6.7). All three samples show complete redox reversibility under the TPR test cycle conditions. Consistent with the oxygen vacancy formation energy calculations, CSM1, having the smallest amount of Ce (and the lowest oxygen vacancy formation energy), has the largest extent of reduction ($\delta$). CSM3, which contains the largest amount of Ce (and therefore the highest oxygen vacancy formation energy), has the smallest $\delta$.

Motivated by these promising TPR results, we tested all three samples’ water splitting capability using Sandia National Laboratories SFR test facility using a $T_{RE}$ of 1400 °C and a $T_{OX}$ of 1000 °C with 40 vol. % steam (Figure 6.5). CSM2 shows the greatest per-cycle H$_2$ productivity (247 $\mu$mol/g) because it balances a moderate extent of reduction with adequate driving force (as quantified by the oxygen vacancy formation energy) to approach complete reoxidation in steam. CSM1 yields a larger extent of reduction but cannot fully reoxidize in steam due to the relatively low oxygen vacancy formation energy. Thus, its full redox capacity is not utilized. CSM3 has a relatively small extent of reduction (and therefore a small redox capacity) because it has the highest oxygen vacancy formation energy of the three compositions. In general, under the same testing conditions, the hydrogen production performance of CSM3 is comparable to that of BCM, at 181 $\mu$mol/g, and much better than ceria’s 71 $\mu$mol/g. The behavior of all three compositions is generally consistent with that of STCH materials having the $E_v$ values predicted by our DFT calculations. This agreement represents an important advancement in expanding the use of DFT calculations to probe for new STCH materials.
Figure 6.5: Water splitting results for two complete cycles at $T_{RE} = 1400 \, ^\circ C$ for 330 s and at $T_{OX} = 1000 \, ^\circ C$ for 1200 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, with the second value corresponding to the subsequent cycles average. The hydrogen value refers to the average hydrogen production.
6.4 Conclusions

Motivated by the development of BCM as a successful perovskite material for STCH, we expanded our search for new Ce and Mn-containing perovskites. We replaced Ba by Sr on the A-site to permit greater structural and compositional flexibility, since BCM is a line-compound material that lacks this compositional tunability. In the process of synthesizing the SrCe$_b$Mn$_{1.6}$O$_3$ compositional family, however, we identified the unexpected formation of a layered perovskite Ce$_a$Sr$_{2-a}$MnO$_4$, previously unreported in the literature for this compositional family.

Nearly phase-pure Ce$_{0.1}$Sr$_{1.9}$MnO$_4$, Ce$_{0.2}$Sr$_{1.8}$MnO$_4$, and Ce$_{0.3}$Sr$_{1.7}$MnO$_4$ compositions were successfully synthesized by the evaporation-to-dryness method and the structures were characterized by synchrotron radiation X-ray diffraction and transmission electron microscopy.

By correctly predicting the stability of Ce$_{0.1}$Sr$_{1.9}$MnO$_4$, Ce$_{0.2}$Sr$_{1.8}$MnO$_4$, and Ce$_{0.3}$Sr$_{1.7}$MnO$_4$, DFT calculations played a key role in the computational and experimental iterative work corroborating the existence of those phases and the prediction for STCH application. The oxygen vacancy formation energy calculated from first-principles flagged those compounds as good candidates for water splitting, values that were found to be consistent with results from TPR. The samples were then tested for water splitting and two of the compositions were shown to produce more hydrogen than ceria and BCM under identical test conditions. This new phase and its promising performance further motivates the search for perovskite related compounds with unique and potentially valuable STCH properties. The DFT stability calculations and the calculated oxygen vacancy formation energy predictions of WS performance highlight the possibility of harnessing computation to accelerate the development of new STCH-active materials.
6.5 Acknowledgments

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6.6 Co-authors contribution

I as the first author was responsible for all the experimental data, analysis, discussions and writing the manuscript. Dr. Francisco Coury as the second author was responsible for the TEM work, discussions and writing the paper. Dr. Michael Sanders was responsible for discussions, data analysis and revisions. All the remainder co-authors were responsible for discussions and revisions.

6.7 Supporting information

Five samples of composition SrCe$_b$Mn$_{1-b}$O$_3$, where $b = 0, 0.3, 0.5, 0.7$ and 1 were synthesized via sol-gel. The samples were named SMO, SCM3070, SCM5050, SCM7030 and SCO accordingly.

Powder X-ray diffraction (XRD) patterns are shown in Figure 6.4.

![XRD of samples SMO, SCM3070, SCM5050, SCM7030 and SCO](image)

Figure 6.4: XRD of samples SMO, SCM3070, SCM5050, SCM7030 and SCO.
Rietveld refinement was performed on the patterns using the PANalytical Highscore Plus software in semi-automatic mode. The quantification of the identified phases is reported in weight % in Table 6.4.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Target structure</th>
<th>Identified phases (from XRD)</th>
<th>Pnma (SrCeO₃)</th>
<th>I4/mmm (CeₓSr₂₋ₓMnO₄)</th>
<th>Fm-3m (CeO₂)</th>
<th>- (SrMnO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMO</td>
<td>SrMnO₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>93% P63/mmc + 7% Cmca</td>
</tr>
<tr>
<td>SCM3070</td>
<td>SrCe₀.3Mn₀.7O₃</td>
<td>-</td>
<td>21%</td>
<td>14%</td>
<td>-</td>
<td>65% P4/mbm</td>
</tr>
<tr>
<td>SCM5050</td>
<td>SrCe₀.5Mn₀.5O₃</td>
<td>8%</td>
<td>53%</td>
<td>27%</td>
<td>12%</td>
<td>P4/mbm</td>
</tr>
<tr>
<td>SCM7030</td>
<td>SrCe₀.7Mn₀.3O₃</td>
<td>52%</td>
<td>33%</td>
<td>15%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SCO</td>
<td>SrCeO₃</td>
<td>100%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Preliminary WS was done on all samples and the results are reported on the active phase plot (Figure 6.5). The left y-axis gives the amount of the two possible water splitting active phases, ceria and CeₓSr₂₋ₓMnO₄ (layered-perovskite), contained in all the samples, the compositions of which proceed in increasing at.% Ce along the x-axis. The analysis of the active phases can be done by comparing the left-axis i.e. the relative amount of active phase present and the right y-axis i.e. the amount of hydrogen produced by each sample, which is quantified in µmol of H₂ per gram of sample.
Figure 6.5: Active phase plot. Comparison between SCM5050 and SCM7030 hydrogen production and amount of water splitting active phases present in each sample. WS experiment was performed at reduction temperature of 1400 °C in Ar and oxidation temperature of 1000 °C with 50 vol% H2O for 1000 s. Ceria was tested at the same temperature conditions.

Table 6.5: Preliminary water splitting summary. WS was performed at $T_{RE}$ 1400 °C for 330 s and at $T_{OX}$ 1000 °C for 1000 s in 50 vol.% steam balanced with argon.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Target structure</th>
<th>$H_2$ production (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCO</td>
<td>SrCeO$_3$</td>
<td>0</td>
</tr>
<tr>
<td>SCM7030</td>
<td>SrCe$<em>{0.7}$Mn$</em>{0.3}$O$_3$</td>
<td>100</td>
</tr>
<tr>
<td>SCM5050</td>
<td>SrCe$<em>{0.5}$Mn$</em>{0.5}$O$_3$</td>
<td>140</td>
</tr>
<tr>
<td>SCM3070</td>
<td>SrCe$<em>{0.3}$Mn$</em>{0.7}$O$_3$</td>
<td>NA</td>
</tr>
<tr>
<td>SMO</td>
<td>SrMnO$_3$</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 6.6: Additional TEM characterization results of the CSM samples. (a) SADP of [100] zone axis of the layered perovskite in the CSM 2 sample. (b) SADP of [001] zone axis of the layered perovskite in the CSM 3 sample and (c) EDS map with bright field – scanning transmission electron microscopy image of CSM 1 sample showing its single-phase character.
The sample’s phase composition was evaluated through EDS measurements performed in TEM. The EDS results are expected to have an error of approximately 5 at. %.

Table 6.6: Atomic composition obtained from EDS measurements on samples CSM1, CSM2 and CSM3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sr (at. %)</th>
<th>Mn (at. %)</th>
<th>Ce (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSM1</td>
<td>64.3</td>
<td>31.9</td>
<td>3.8</td>
</tr>
<tr>
<td>CSM2</td>
<td>61.9</td>
<td>31.1</td>
<td>7.0</td>
</tr>
<tr>
<td>CSM3</td>
<td>57.6</td>
<td>32.7</td>
<td>9.7</td>
</tr>
</tbody>
</table>

The Temperature Programmed Reduction (TPR) screening protocol was used as a method to evaluate the redox behavior of the three layered perovskite materials (CSM1, CSM2 and CSM3) as shown in Figure 6.7. Ceria and BCM (BaCe$_{0.25}$Mn$_{0.75}$O$_3$) redox curves are added for comparison. Ceria is the current state-of-the-art STCH material while BCM has been shown to be a promising perovskite for STCH because of its potential to split water under reducing environments (under high conversion conditions).
Figure 6.7: Temperature Programmed Reduction performed on CSM1, CSM2 and CSM3. BCM (BaCe$_{0.25}$Mn$_{0.75}$O$_3$) and ceria (CeO$_2$) are added for comparison. In this experiment, we measured extent of reduction as a function of temperature. Reduction was done at $T_{RE}$ $1350$ °C for 1 h in nitrogen followed by oxidation at $T_{OX}$ $1000$ °C for 1 h in air.
CHAPTER 7
CONCLUSIONS

The main objective of this work was to find new materials for STCH and this dissertation introduces two products of that work, the perovskite BCM and the layered perovskite CSM, that can produce more hydrogen than the state-of-the-art material ceria.

To facilitate this search for new materials, it was necessary to both improve the speed at which materials couple be tested and better define the design requirements. Throughput was greatly improved by the developed of the TPR rapid screening method, which can quickly evaluate the material’s redox capacity and suitability for water splitting. This method was employed to screen over 100 compositions. And fuel conversion has slowly begun to be understood as one of the most important design requirement for water splitting materials. Its rise in importance is tied to the recognition that under currently developed reactor schemes, steam production is a cost and efficiency driver and most testing of candidate materials has occurred under conditions where the supply of steam is essentially limitless. The impact of constraining this condition was shown through detailed thermodynamic analysis to greatly impact the hydrogen production potential of many STCH candidates. But this thermodynamic information is not often known for newly developed candidates, so an experimental protocol for testing under these high conversion conditions was developed. With this protocol, SLMA, previously considered as a promising candidate for STCH, fails to split water when tested under true high conversion conditions, making the case for why researchers should take this key requirement into account when designing and testing materials.

BCM and CSM, identified by TPR as promising, break the trend of STCH perovskites derived from LaMnO$_3$. The different compositions, specifically the inclusion of Ce, introduced not only good performance but new pathways of materials discovery. And although BCM was shown to have a decreased H$_2$ yield compared to SLMA, it is still much larger than ceria under the same WS conditions and improved on the redox kinetics of SLMA. It is also the first non-stoichiometry STCH material to have multiple polytypes, 12$R$ and 10$H$, although they were not found to be present under the normal cycle conditions.
BCM was shown to operate at moderate high conversion conditions, surpassing SLMA’s H₂ production at all steam-to-hydrogen ratios tested. It still fails to split water at the ultimate steam-to-hydrogen ratio target of 10:1, however, its vast improvement over previous perovskites is encouraging.

CSM is one of the first Ruddlesden-Popper phase materials to be tested for STCH and represents a previously unreported compositional family. Diffraction information was obtained for these new phases using synchrotron XRD and TEM. Two of the compositions tested had higher H₂ production than BCM, however all three showed poorer high conversion performance. CSM opens new design directions such as new compounds containing Ce and new possible layered perovskites.

Finally, BCM’s interesting polytype behavior and improved high-conversion performance prompted a deeper investigation into its phase change and thermodynamic properties. Synthesis and post-synthesis processing conditions were found that allow for pure phase samples of each polytype to be produced, including a new, previously unreported, polytype H. Testing of these pure phases showed that each may have different redox thermodynamics, a tantalizing hint that alterations in cycle conditions may allow for the accessing of these phase changes to further improve BCM’s hydrogen production.

7.1 Future Work

Overall, STCH is still in its infancy and there is a vast amount of work left to be done, even when only considering the search for improved redox materials. This work falls into two broad categories: 1) better understand the existing materials and correlate their material properties to hydrogen production; and 2) follow new material development pathways to produce improved materials.

On the existing materials front, BCM is the most intriguing yet least understood material system. The thermodynamic properties of BCM need to be explored further, more specifically by isolating the 10H and H polytypes into their temperature and reduction level regimes and evaluate their independent redox properties. A computational investigation, in conjunction with experimental study, could answer questions
about whether it is possible to take advantage of the phase change during WS. Cerium’s role in BCM’s performance is also not well understood, and a better understanding could at least advise future materials development.

BCM, being a line-compound, is incapable of \( E_v \) tuning through compositional variation, unlike SLMA for example. However, by further doping BCM with new cations one may be able to modify the lattice to accommodate for a different Ce/Mn ratio, or otherwise alter \( E_v \), and potentially improve WS ability.

Water-splitting experiments have not been performed on SCM yet and the role of structure vs. composition is also up for debate. SCM and its sister material CSM are reasonably close in composition while having different structures, making them a perfect subject of study to improve our understanding of the correlation.

When looking to new pathways of development, once again, BCM, lights the way. Until BCM’s discovery, it was generally believed that phase changes were detrimental to WS thermodynamics, but that is no longer seen as a certainty. Many of the manganates appear to have similar polytype behavior in response to oxygen non-stoichiometry, so there may be other compositional families with phase changes that are better suited to WS.

A last suggestion for future development is the further exploration of Ruddlesten-Popper phases for STCH. The \( \text{Ce}_a \text{Sr}_{2-a} \text{CoO}_4 \) could be compared to CSM as well as other Mn/Co compositions. More importantly, only a few \( \text{A}_2 \text{BO}_4 \) structures have been studied for STCH [93]. The universe of these RP phases is vast and might lead to surprisingly interesting \( \text{H}_2 \) production performance.
Table A.1: Fluorite oxide materials CO production via thermochemical CO₂ splitting compiled from Jiang et al. [57].

<table>
<thead>
<tr>
<th>Material [ref]</th>
<th>CO production (µmol/g)</th>
<th>Reduction step conditions</th>
<th>Oxidation step conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂ [57]</td>
<td>201</td>
<td>1400 °C for 40 min</td>
<td>700 °C for 3-5 min – 500 sccm CO₂</td>
</tr>
<tr>
<td>CeO₂ [57]</td>
<td>241</td>
<td>1500 °C for 40 min</td>
<td>700 °C for 3-5 min – 500 sccm CO₂</td>
</tr>
<tr>
<td>CeO₂ [57]</td>
<td>348</td>
<td>1500 °C for 40 min</td>
<td>800 °C for 3-5 min – 500 sccm CO₂</td>
</tr>
<tr>
<td>CeO₂ [57]</td>
<td>250</td>
<td>1500 °C for 40 min</td>
<td>900 °C for 3-5 min – 500 sccm CO₂</td>
</tr>
<tr>
<td>CeO₂ [57]</td>
<td>147</td>
<td>1500 °C for 40 min</td>
<td>1000 °C for 3-5 min – 500 sccm CO₂</td>
</tr>
<tr>
<td>CeO₂ [57]</td>
<td>161</td>
<td>1500 °C for 40 min</td>
<td>1100 °C for 3-5 min – 500 sccm CO₂</td>
</tr>
<tr>
<td>Ce₀.7₅Zr₀.2₅O₂ [57]</td>
<td>335</td>
<td>1400 °C for 40 min</td>
<td>700 °C for 30-120 min – 500 sccm CO₂</td>
</tr>
<tr>
<td>Ce₀.7₅Zr₀.2₅O₂ [57]</td>
<td>446</td>
<td>1400 °C for 40 min</td>
<td>800 °C for 30-120 min – 500 sccm CO₂</td>
</tr>
</tbody>
</table>
Table A.1: continued

<table>
<thead>
<tr>
<th>Material [ref]</th>
<th>CO production (µmol/g)</th>
<th>Reduction step conditions</th>
<th>Oxidation step conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ce}<em>{0.75}\text{Zr}</em>{0.25}\text{O}_2$ [57]</td>
<td>473</td>
<td>1400 °C for 40 min</td>
<td>900 °C for 30-120 min – 500 sccm CO$_2$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.75}\text{Zr}</em>{0.25}\text{O}_2$ [57]</td>
<td>420</td>
<td>1400 °C for 40 min</td>
<td>1000 °C for 30-120 min – 500 sccm CO$_2$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.75}\text{Zr}</em>{0.25}\text{O}_2$ [57]</td>
<td>451</td>
<td>1400 °C for 40 min</td>
<td>1100 °C for 30-120 min – 500 sccm CO$_2$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.75}\text{Hf}</em>{0.25}\text{O}_2$ [57]</td>
<td>112</td>
<td>1400 °C for 40 min</td>
<td>1100 °C for 90-130 min – 500 sccm CO$_2$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.80}\text{Ti}</em>{0.20}\text{O}_2$ [57]</td>
<td>54</td>
<td>1400 °C for 40 min</td>
<td>900 °C for 1-5 min – 500 sccm CO$_2$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.80}\text{Ti}</em>{0.20}\text{O}_2$ [57]</td>
<td>36</td>
<td>1400 °C for 40 min</td>
<td>1000 °C for 1-5 min – 500 sccm CO$_2$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.80}\text{Ti}</em>{0.20}\text{O}_2$ [57]</td>
<td>18</td>
<td>1400 °C for 40 min</td>
<td>1100 °C for 1-5 min – 500 sccm CO$_2$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.85}\text{La}</em>{0.15}\text{O}_2$ [57]</td>
<td>250</td>
<td>1500 °C for 40 min</td>
<td>700 °C for 30-120 min – 500 sccm CO$_2$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.85}\text{La}</em>{0.15}\text{O}_2$ [57]</td>
<td>272</td>
<td>1500 °C for 40 min</td>
<td>800 °C for 30-120 min – 500 sccm CO$_2$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.85}\text{La}</em>{0.15}\text{O}_2$ [57]</td>
<td>228</td>
<td>1500 °C for 40 min</td>
<td>900 °C for 30-120 min – 500 sccm CO$_2$</td>
</tr>
</tbody>
</table>
Table A.2: Fluorite oxide materials H\textsubscript{2} production via thermochemical H\textsubscript{2}O splitting compiled from the literature.

<table>
<thead>
<tr>
<th>Material [ref]</th>
<th>H\textsubscript{2} production (µmol/g)</th>
<th>Reduction step conditions</th>
<th>Oxidation step conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceria [59]</td>
<td>9</td>
<td>1500 °C for 10 min</td>
<td>1000 °C for 5 min – 0.02 mol H\textsubscript{2}O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ceria [59]</td>
<td>13</td>
<td>1400 °C for 10 min</td>
<td>1000 °C for 5 min – 0.02 mol H\textsubscript{2}O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ceria [59]</td>
<td>34</td>
<td>1300 °C for 10 min</td>
<td>1000 °C for 5 min – 0.02 mol H\textsubscript{2}O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce\textsubscript{0.75}Zr\textsubscript{0.25}O\textsubscript{2} [71]</td>
<td>354</td>
<td>1400 °C for 45 min</td>
<td>1000 °C for 35 min – 80 % RH</td>
</tr>
<tr>
<td>Ce\textsubscript{0.75}Zr\textsubscript{0.25}O\textsubscript{2} [58]</td>
<td>140</td>
<td>1450 °C for 120 min</td>
<td>845 °C for 60 min – 20-30 mol.%</td>
</tr>
<tr>
<td>Ce\textsubscript{0.75}Zr\textsubscript{0.25}O\textsubscript{2} [58]</td>
<td>168</td>
<td>1450 °C for 120 min</td>
<td>945 °C for 60 min – 20-30 mol.%</td>
</tr>
<tr>
<td>Ce\textsubscript{0.75}Zr\textsubscript{0.25}O\textsubscript{2} [58]</td>
<td>238</td>
<td>1450 °C for 120 min</td>
<td>1045 °C for 60 min – 20-30 mol.%</td>
</tr>
<tr>
<td>Ce\textsubscript{0.85}Fe\textsubscript{0.15}O\textsubscript{2} [67]</td>
<td>536</td>
<td>1500 °C for 30 min</td>
<td>1150 °C for 30 min – pH\textsubscript{2}O 0.5-0.84 atm</td>
</tr>
<tr>
<td>Ce\textsubscript{0.85}Co\textsubscript{0.15}O\textsubscript{2} [67]</td>
<td>768</td>
<td>1500 °C for 30 min</td>
<td>1150 °C for 30 min – pH\textsubscript{2}O 0.5-0.84 atm</td>
</tr>
</tbody>
</table>
Table A.2: continued

<table>
<thead>
<tr>
<th>Material [ref]</th>
<th>H₂ production (µmol/g)</th>
<th>Reduction step conditions</th>
<th>Oxidation step conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₀.₈₅Ni₀.₁₅O₂ [67]</td>
<td>688</td>
<td>1500 °C for 30 min</td>
<td>1150 °C for 30 min – pH₂O 0.5-0.84 atm</td>
</tr>
<tr>
<td>Ce₀.₈₅Mn₀.₁₅O₂ [67]</td>
<td>491</td>
<td>1500 °C for 30 min</td>
<td>1150 °C for 30 min – pH₂O 0.5-0.84 atm</td>
</tr>
<tr>
<td>Ce₀.₉₀Mn₀.₁₀O₂ [59]</td>
<td>168</td>
<td>1500 °C for 10 min</td>
<td>1000 °C for 5min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce₀.₉₀Mn₀.₁₀O₂ [59]</td>
<td>88</td>
<td>1400 °C for 10 min</td>
<td>1000 °C for 5min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce₀.₉₀Mn₀.₁₀O₂ [59]</td>
<td>24</td>
<td>1300 °C for 10 min</td>
<td>1000 °C for 5min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce₀.₉₀Fe₀.₁₀O₂ [59]</td>
<td>87</td>
<td>1500 °C for 10 min</td>
<td>1000 °C for 5min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce₀.₉₀Fe₀.₁₀O₂ [59]</td>
<td>171</td>
<td>1400 °C for 10 min</td>
<td>1000 °C for 5min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce₀.₉₀Fe₀.₁₀O₂ [59]</td>
<td>10</td>
<td>1300 °C for 10 min</td>
<td>1000 °C for 5min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
</tbody>
</table>
Table A.2: continued

<table>
<thead>
<tr>
<th>Material [ref]</th>
<th>H₂ production (µmol/g)</th>
<th>Reduction step conditions</th>
<th>Oxidation step conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₀.₉₀Ni₀.₁₀O₂ [59]</td>
<td>122</td>
<td>1500 °C for 10 min</td>
<td>1000 °C for 5 min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce₀.₉₀Ni₀.₁₀O₂ [59]</td>
<td>48</td>
<td>1400 °C for 10 min</td>
<td>1000 °C for 5 min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce₀.₉₀Ni₀.₁₀O₂ [59]</td>
<td>27</td>
<td>1300 °C for 10 min</td>
<td>1000 °C for 5 min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce₀.₉₀Cu₀.₁₀O₂ [59]</td>
<td>44</td>
<td>1500 °C for 10 min</td>
<td>1000 °C for 5 min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce₀.₉₀Cu₀.₁₀O₂ [59]</td>
<td>6</td>
<td>1400 °C for 10 min</td>
<td>1000 °C for 5 min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
<tr>
<td>Ce₀.₉₀Cu₀.₁₀O₂ [59]</td>
<td>8</td>
<td>1300 °C for 10 min</td>
<td>1000 °C for 5 min – 0.02 mol H₂O in 100 sccm Ar</td>
</tr>
</tbody>
</table>
Table A.3: Perovskite oxide materials suggested for CO production via thermochemical CO$_2$ splitting extracted from the literature.

<table>
<thead>
<tr>
<th>Material [ref]</th>
<th>CO production (µmol/g)</th>
<th>Reduction step conditions</th>
<th>Oxidation step conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.65}$Sr$</em>{0.35}$MnO$_3$ [89]</td>
<td>138</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>La$<em>{0.50}$Sr$</em>{0.50}$MnO$_3$ [89]</td>
<td>325</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>La$<em>{0.65}$Ca$</em>{0.35}$MnO$_3$ [89]</td>
<td>175</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>La$<em>{0.50}$Ca$</em>{0.50}$MnO$_3$ [89]</td>
<td>525</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>La$<em>{0.50}$Ca$</em>{0.50}$MnO$_3$ [89]</td>
<td>481</td>
<td>1350 °C for 45 min</td>
<td>1000 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>La$<em>{0.35}$Ca$</em>{0.65}$MnO$_3$ [89]</td>
<td>350</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>La$<em>{0.70}$Sr$</em>{0.30}$FeO$_3$ [89]</td>
<td>72</td>
<td>1300 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>Y$<em>{0.50}$Ca$</em>{0.50}$MnO$_3$ [91]</td>
<td>671</td>
<td>1400 °C for 45 min</td>
<td>900 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>Nd$<em>{0.50}$Ca$</em>{0.50}$MnO$_3$ [91]</td>
<td>538</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>Sm$<em>{0.50}$Ca$</em>{0.50}$MnO$_3$ [91]</td>
<td>590</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
</tbody>
</table>
Table A.3: continued

<table>
<thead>
<tr>
<th>Material [ref]</th>
<th>CO production</th>
<th>Reduction step</th>
<th>Oxidation step</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(µmol/g)</td>
<td>conditions</td>
<td>conditions</td>
</tr>
<tr>
<td>Gd0.5Ca0.5MnO3 [91]</td>
<td>637</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>Dy0.5Ca0.5MnO3 [91]</td>
<td>566</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>Y0.5Sr0.5MnO3 [91]</td>
<td>757</td>
<td>1400 °C for 45 min</td>
<td>900 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>Nd0.5Sr0.5MnO3 [91]</td>
<td>441</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>Sm0.5Sr0.5MnO3 [91]</td>
<td>526</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>Gd0.5Sr0.5MnO3 [91]</td>
<td>487</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>Dy0.5Sr0.5MnO3 [91]</td>
<td>554</td>
<td>1400 °C for 45 min</td>
<td>1100 °C for 60 min – 40 vol.%</td>
</tr>
<tr>
<td>La0.5Ba0.5MnO3 [92]</td>
<td>159</td>
<td>1400 °C for 45 min</td>
<td>1050 °C for 60 min – 50 vol.%</td>
</tr>
<tr>
<td>La0.5Sr0.5Mn0.75Al0.25O3 [92]</td>
<td>186</td>
<td>1400 °C for 45 min</td>
<td>1050 °C for 60 min – 50 vol.%</td>
</tr>
<tr>
<td>La0.5Sr0.5Mn0.60Al0.40O3 [92]</td>
<td>187</td>
<td>1400 °C for 45 min</td>
<td>1050 °C for 60 min – 50 vol.%</td>
</tr>
</tbody>
</table>
Table A.3: continued

<table>
<thead>
<tr>
<th>Material [ref]</th>
<th>CO production (µmol/g)</th>
<th>Reduction step conditions</th>
<th>Oxidation step conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$Mn$<em>{0.83}$Mg$</em>{0.17}$O$_3$ [92]</td>
<td>207</td>
<td>1400 °C for 45 min</td>
<td>1050 °C for 60 min – 50 vol.%</td>
</tr>
<tr>
<td>La$<em>{0.6}$Sr$</em>{0.4}$Cr$<em>{0.80}$Co$</em>{0.20}$O$_3$ [88]</td>
<td>157</td>
<td>1200 °C for 60 min</td>
<td>800 °C for 30 min – 50 vol.%</td>
</tr>
</tbody>
</table>

Table A.4: Perovskite oxide materials suggested for H$_2$ production via thermochemical H$_2$O splitting extracted from the literature.

<table>
<thead>
<tr>
<th>Material [ref]</th>
<th>H$_2$ production (µmol/g)</th>
<th>Reduction step conditions</th>
<th>Oxidation step conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.5}$Sr$</em>{0.5}$MnO$_3$ [89]</td>
<td>308</td>
<td>1400 °C for 100 min</td>
<td>1000 °C for 100 min – 40 vol.%</td>
</tr>
<tr>
<td>La$<em>{0.5}$Ca$</em>{0.5}$MnO$_3$ [89]</td>
<td>407</td>
<td>1400 °C for 100 min</td>
<td>1000 °C for 100 min – 40 vol.%</td>
</tr>
<tr>
<td>Sr$<em>{0.4}$La$</em>{0.6}$Mn$<em>{0.6}$Al$</em>{0.4}$O$_3$ [65]</td>
<td>307</td>
<td>1350 °C for 30 min</td>
<td>1000 °C for 1000s – 40 vol% H$_2$O</td>
</tr>
<tr>
<td>Sr$<em>{0.6}$La$</em>{0.4}$Mn$<em>{0.6}$Al$</em>{0.4}$O$_3$ [65]</td>
<td>277</td>
<td>1350 °C for 30 min</td>
<td>1000 °C for 1000s – 40 vol% H$_2$O</td>
</tr>
<tr>
<td>Sr$<em>{0.4}$La$</em>{0.6}$Mn$<em>{0.4}$Al$</em>{0.6}$O$_3$ [65]</td>
<td>220</td>
<td>1350 °C for 30 min</td>
<td>1000 °C for 1000s – 40 vol% H$_2$O</td>
</tr>
<tr>
<td>CaTi$<em>{0.7}$Fe$</em>{0.3}$O$_3$ [65]</td>
<td>39</td>
<td>1400 °C for 30 min</td>
<td>1100 °C for 1000s – 40 vol% H$_2$O</td>
</tr>
<tr>
<td>LaSrCoO$_4$ [93]</td>
<td>107</td>
<td>1300 °C for 60 min</td>
<td>800 °C for 45 min – 80 vol.%</td>
</tr>
</tbody>
</table>
Table A.4: continued

<table>
<thead>
<tr>
<th>Material [ref]</th>
<th>H₂ production (µmol/g)</th>
<th>Reduction step conditions</th>
<th>Oxidation step conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba₀.₅₀Sr₀.₅₀Co₀.₈₀Fe₀.₂₀O₃ [93]</td>
<td>102</td>
<td>1000 °C for 60 min</td>
<td>800 °C for 45 min – 80 vol.%</td>
</tr>
<tr>
<td>La₀.₆₀Sr₀.₄₀Cr₀.₈₀Co₀.₂₀O₃ [88]</td>
<td>50</td>
<td>1200 °C for 60 min</td>
<td>800 °C for 30 min – 2.5 vol.%</td>
</tr>
</tbody>
</table>
APPENDIX B

TEMPERATURE PROGRAMMED REDUCTION RESULTS FOR PEROVSKITE FAMILIES

Figure B.1: Temperature programmed reduction results for CaZr$_{y}$Mn$_{1-y}$O$_{3}$ family. Reduction was carried in a TGA at 1350 ºC for 1h in UHP N$_{2}$ flow. Oxidation was carried for 5 min in synthetic air flow. Samples tested were CaZr$_{50}$Mn$_{50}$ = CaZr$_{0.50}$Mn$_{0.50}$O$_{3}$, CaZr$_{40}$Mn$_{60}$ = CaZr$_{0.40}$Mn$_{0.60}$O$_{3}$, CaZr$_{30}$Mn$_{70}$ = CaZr$_{0.30}$Mn$_{0.70}$O$_{3}$, CaZr$_{20}$Mn$_{80}$ = CaZr$_{0.20}$Mn$_{0.80}$O$_{3}$ and CaZr$_{10}$Mn$_{90}$ = CaZr$_{0.10}$Mn$_{0.90}$O$_{3}$.
Figure B.2: Temperature programmed reduction results for CaZr\textsubscript{x}Fe\textsubscript{1-x}O\textsubscript{3} family. Reduction was carried in a TGA at 1200 °C for 1h in UHP N\textsubscript{2} flow. Oxidation was carried for 5 min in synthetic air flow. Samples tested were CaZr\textsubscript{0.50}Fe\textsubscript{0.50}O\textsubscript{3}, CaZr\textsubscript{0.40}Fe\textsubscript{0.60}O\textsubscript{3}, CaZr\textsubscript{0.30}Fe\textsubscript{0.70}O\textsubscript{3}, CaZr\textsubscript{0.20}Fe\textsubscript{0.80}O\textsubscript{3} and CaZr\textsubscript{0.10}Fe\textsubscript{0.90}O\textsubscript{3}. Signal to noise ratio is very small, leading to noisy data.
Figure B.3: Temperature programmed reduction results for CaTi$_{y}$Nb$_{1-y}$O$_3$ family. Reduction was carried in a TGA at 1350 °C for 1h in UHP N$_2$ flow. Oxidation was carried for 5 min in synthetic air flow. Samples tested were CaTi$_{0.80}$Nb$_{0.20}$O$_3$, CaTi$_{0.90}$Nb$_{0.10}$O$_3$, CaTi$_{0.95}$Nb$_{0.05}$O$_3$. Signal to noise ratio is very small, leading to noisy data.
Figure B.4: Temperature programmed reduction results for AMnO$_3$ family as well as related compositions such as CeFe = CeFeO$_3$ and CaCe50Mn50 = CaCe$_{0.50}$Mn$_{0.50}$O$_3$. Reduction was carried in a TGA at 1350 ºC for 1h in UHP N$_2$ flow. Oxidation was carried for 5 min in synthetic air flow. Other samples tested were YMn = YMnO$_3$, CeMn = CeMnO$_3$, CaMn = CaMnO$_3$. 
Figure B.5: Temperature programmed reduction results for ASnO$_3$ family as well as related compositions such as CaSn = CaSnO$_3$, SrSn = SrSnO$_3$, and BaSn = BaSnO$_3$. Reduction was carried in a TGA at 1200 °C for 1h in UHP N$_2$ flow. Oxidation was carried for 5 min in synthetic air flow.
Figure B.6: Temperature programmed reduction results for SrZr$_{1-x}$Mn$_x$O$_3$ family as well as related compositions such as SrZr10Mn90 =SrZr$_{0.10}$Mn$_{0.90}$O$_3$, SrZr20Mn80 =SrZr$_{0.20}$Mn$_{0.80}$O$_3$, and SrZr30Mn70 =SrZr$_{0.30}$Mn$_{0.70}$O$_3$. Reduction was carried in a TGA at 1350 ºC for 1h in UHP N$_2$ flow. Oxidation was carried for 5 min in synthetic air flow.
Figure B.7: Temperature programmed reduction results for SrZr$_x$Fe$_{1-x}$O$_3$ family as well as related compositions such as SrZr10Fe90 = SrZr$_{0.10}$Fe$_{0.90}$O$_3$, SrZr20Fe80 = SrZr$_{0.20}$Fe$_{0.80}$O$_3$, and SrZr30Fe70 = SrZr$_{0.30}$Fe$_{0.70}$O$_3$, SrZr40Fe60 = SrZr$_{0.40}$Fe$_{0.60}$O$_3$, and SrZr50Fe50 = SrZr$_{0.50}$Fe$_{0.50}$O$_3$. Reduction was carried in a TGA at 1200 °C for 1h in UHP N$_2$ flow. Oxidation was carried for 5 min in synthetic air flow.
Figure B.8: Temperature programmed reduction results for La$_{x}$Sr$_{2-x}$MoO$_4$ family as well as related compositions such as LaMo = LaMo$_2$O$_4$, La$_{1.90}$Sr$_{0.10}$MoO$_4$, and La$_{1.80}$Sr$_{0.20}$MoO$_4$. Reduction was carried in a TGA at 1350 ºC for 1h in UHP N$_2$ flow. Oxidation was carried for 5 min in synthetic air flow.
Figure B.9: Temperature programmed reduction results for LaMn$_x$V$_{1-x}$O$_3$ family as well as related compositions such as LaV = LaVO$_3$, LaMn30V70 = LaMn$_{0.30}$V$_{0.70}$O$_3$, and LaMn50V50 = LaMn$_{0.50}$V$_{0.50}$O$_3$. Reduction was carried in a TGA at 1350 ºC for 1h in UHP N$_2$ flow. Oxidation was carried for 5 min in synthetic air flow.
Figure B.10: Temperature programmed reduction results for Sr$_{x}$La$_{1-x}$Mn$_{0.60}$Ce$_{0.40}$O$_{3}$ family as well as related compositions such as Sr$_{0.95}$La$_{0.05}$Mn$_{0.60}$Ce$_{0.40}$O$_{3}$, Sr$_{0.90}$La$_{0.10}$Mn$_{0.60}$Ce$_{0.40}$O$_{3}$, and Sr$_{0.80}$La$_{0.20}$Mn$_{0.60}$Ce$_{0.40}$O$_{3}$. Reduction was carried in a TGA at 1350 °C for 1h in UHP N$_{2}$ flow. Oxidation was carried for 5 min in synthetic air flow.
Figure B.11: Temperature programmed reduction results for SrTi$_{x}$Nb$_{1-x}$O$_{3}$ family as well as related compositions such as SrTi95Nb05 = SrTi$_{0.95}$Nb$_{0.05}$O$_{3}$, SrTi90Nb10 = SrTi$_{0.90}$Nb$_{0.10}$O$_{3}$, and SrTi80Nb20 = SrTi$_{0.80}$Nb$_{0.20}$O$_{3}$. Reduction was carried in a TGA at 1450 °C for 1h in UHP N$_{2}$ flow. Oxidation was carried for 5 min in synthetic air flow.
Figure B.12: Temperature programmed reduction results for SrFe$_x$Nb$_{1-x}$O$_3$ family as well as related compositions such as SrFe$_{90}$Nb$_{10}$ = SrFe$_{0.90}$Nb$_{0.10}$O$_3$, SrFe$_{80}$Nb$_{20}$ = SrFe$_{0.80}$Nb$_{0.20}$O$_3$, SrFe$_{70}$Nb$_{30}$ = SrFe$_{0.70}$Nb$_{0.30}$O$_3$ and SrFe$_{60}$Nb$_{40}$ = SrFe$_{0.60}$Nb$_{0.40}$O$_3$. Reduction was carried in a TGA at 1350 °C for 1h in UHP N$_2$ flow. Oxidation was carried for 5 min in synthetic air flow.
Figure B.13: Temperature programmed reduction results for SrTi$_{x}$V$_{1-x}$O$_3$ family as well as related compositions such as SrTi$_{0.95}$V$_{0.05}$O$_3$ and SrTi$_{0.90}$V$_{0.10}$O$_3$. Reduction was carried in a TGA at 1350 °C for 1h in UHP N$_2$ flow. Oxidation was carried for 5 min in synthetic air flow.
APPENDIX C
WATER SPLITTING RESULTS OBTAINED FOR PEROVSKITES

Table C.1: Water splitting experiment performed in SFR, under 40 vol. % steam. Reduction time was 300 s and oxidation time was 20 min.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature condition $T_{RE}$-$T_{OX}$ (°C)</th>
<th>Average O$_2$ released during reduction (µmol/g)</th>
<th>Average H$_2$ production (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$<em>{0.20}$Ce$</em>{0.80}$O$_2$</td>
<td>1350-1000</td>
<td>16</td>
<td>83</td>
</tr>
<tr>
<td>CeFeO$_2$</td>
<td>1350-1000</td>
<td>16</td>
<td>30</td>
</tr>
<tr>
<td>FeTiO$_3$</td>
<td>1350-850</td>
<td>90</td>
<td>108</td>
</tr>
<tr>
<td>FeTiO$_3$</td>
<td>1350-1000</td>
<td>94</td>
<td>146</td>
</tr>
<tr>
<td>Sr$<em>{0.60}$La$</em>{0.40}$Mn$<em>{0.55}$Al$</em>{0.40}$Nb$_{0.05}$O$_3$</td>
<td>1350-1000</td>
<td>143</td>
<td>290</td>
</tr>
<tr>
<td>Sr$<em>{0.60}$La$</em>{0.40}$Mn$<em>{0.55}$Al$</em>{0.40}$Nb$_{0.05}$O$_3$ impreg. 1% Ru particles</td>
<td>1350-1000</td>
<td>80</td>
<td>180</td>
</tr>
<tr>
<td>Sr$<em>{0.90}$La$</em>{0.10}$Mn$<em>{0.50}$Ce$</em>{0.50}$O$_3$</td>
<td>1350-850</td>
<td>38</td>
<td>127</td>
</tr>
<tr>
<td>Sr$<em>{0.90}$La$</em>{0.10}$Mn$<em>{0.50}$Ce$</em>{0.50}$O$_3$</td>
<td>1400-1000</td>
<td>45</td>
<td>151</td>
</tr>
<tr>
<td>Ca$<em>{0.90}$La$</em>{0.10}$Mn$<em>{0.50}$Ce$</em>{0.50}$O$_3$</td>
<td>1350-850</td>
<td>72</td>
<td>122</td>
</tr>
<tr>
<td>Ca$<em>{0.90}$La$</em>{0.10}$Mn$<em>{0.50}$Ce$</em>{0.50}$O$_3$</td>
<td>1400-1000</td>
<td>83</td>
<td>164</td>
</tr>
<tr>
<td>Ba$<em>{0.90}$La$</em>{0.10}$Mn$<em>{0.50}$Ce$</em>{0.50}$O$_3$</td>
<td>1350-850</td>
<td>88</td>
<td>42</td>
</tr>
<tr>
<td>Ba$<em>{0.90}$La$</em>{0.10}$Mn$<em>{0.50}$Ce$</em>{0.50}$O$_3$</td>
<td>1400-1000</td>
<td>160</td>
<td>50</td>
</tr>
<tr>
<td>SrFe$<em>{80}$Nb$</em>{20}$O$_3$</td>
<td>1350-850</td>
<td>16</td>
<td>35</td>
</tr>
<tr>
<td>CaMn$<em>{0.50}$Ce$</em>{0.50}$O$_3$</td>
<td>1350-850</td>
<td>42</td>
<td>115</td>
</tr>
</tbody>
</table>
Appendix D

Investigation of \( \text{BaCe}_{0.25} \text{Mn}_{0.75} \text{O}_3 \) Polytypes

Once \( \text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3 \) (BCM) was established as an interesting candidate for STCH (Chapter 5), particularly its improved performance under high conversion water splitting, further investigation required understanding BCM’s phase-change behavior to determine its thermodynamic properties.

D.1 Introduction

BCM was identified by Macias et al.\cite{120,121} to have multiple polytypes that could be achieved by altering the synthesis route. The 12\( R \) and 10\( H \) BCM polytypes were shown to assume a rhombohedral and hexagonal symmetries, respectively with manganese and cerium octahedra forming special arrangements, \textit{i.e.} ordering. The 12\( R \) nomenclature is represented by twelve cation octahedra forming a repeating block (nine MnO\(_6\) and three CeO\(_6\)), whereas the 10\( H \) nomenclature is due to ten octahedra (eight MnO\(_6\) and two CeO\(_6\)). The two polytypes are shown below in Figure D.1.

As was discussed previously, mixed phase samples (12\( R \) and 10\( H \)) convert completely to the 12\( R \) phase after the first redox cycle \( T_{\text{RE}} \) 1350 °C and \( T_{\text{OX}} \) 1000 °C. This suggests that the synthesis routes reported in Macias et al. are not the exclusive pathway to accessing these polytypes. Further evidence can be found in BCM’s parent system, BaMnO\(_{3-x}\). There are five reported polytypes, with each assuming a different oxygen nonstoichiometry. The most oxidized Ba-Mn-O phase is rhombohedral 15\( R \)-BaMnO\(_{2.99}\) and then it assumes hexagonal phases when reduced to 8\( H \)-BaMnO\(_{2.95}\). Further reduction forms the phases 6\( H \)-BaMnO\(_{2.92}\), 10\( H \)-BaMnO\(_{2.91}\), and 4\( H \)-BaMnO\(_{2.65}\).
Similar to the BCM polytypes, the number accompanying the symmetry is related to the number of repeating Mn octahedra. However, in the case of the BaMnO$_{3+\delta}$ system, the phases go from ordered octahedra to disordered in the case of the $4H$ phase. The Sr-Mn-O system was also shown to form a few polytypes that were dependent on the oxygen stoichiometry.

In this chapter I will describe all the study we did in identifying the conditions for obtaining the two polytypes. During high temperature XRD we detected the presence of a third BCM polytype. I will then describe all the thermodynamic characterization we have done on the $12R$ phase. I will finally comment on the potential for using one of the other polytypes for WS.
D.2 Experimental

Several experimental methods have been employed for this effort. In this section I describe the sample preparation and characterization techniques used for the identification of phases and quantification of oxygen nonstoichiometry.

Sample preparation

BaCe$_{0.25}$Mn$_{0.75}$O$_3$ (BCM) was prepared by the modified Pechini sol-gel method. Stoichiometric amounts of barium nitrate (Alfa Aesar 99 %), cerium nitrate hexahydrate (Alfa Aesar 99.5 %) and manganese nitrate (Alfa Aesar 98 %) were mixed in deionized water. Citric acid and EDTA in the molar ratio of 2:1 were added and the solution was heated in a hot plate under continuous stirring. Ammonium hydroxide was added for adjustment of the pH to about 11 and the solution was evaporated. Once the gel was formed, the sample was moved to a drying oven for 48 h at 160 °C where it dried to a charcoal-like powder.

The sample was then calcined in two steps. First at 800 °C for 10h followed by a second calcination at 1400 °C for 5 h. Both calcinations used a heating and cooling ramp rate of 10 °C/min and were performed in static air.

Once the powder sample was ready, it was subjected to a heat treatment for achievement of the desired BCM phase. The as-calcined starting BCM material was composed of 90% 12$R$ and 10% 10$H$ phase. 12$R$ sample was obtained by taking the starting powder and heating it to 1350 °C in UHP Ar with a dwell of 5 h. The sample was then cooled to 1000 °C and synthetic air (21% O$_2$ balanced with Ar) was introduced for 10h. This redox cycle was necessary to convert the “leftover” 10$H$ phase to 12$R$ phase.

The 10$H$ pure phase sample was obtained by taking the as-calcined sample and pressing it into a pellet with the addition of small amounts of binder (PVA 5% solution in water), sintering it at 1350 °C for 10 h at a slow ramp rate of 1 °C/min. The presence of binder burnout at higher temperatures decreased the
local pO$_2$ forcing the sample to stay “reduced” and allowing for the conversion to 10$H$ phase. Additionally, once sintered, the pellet could not easily reoxidize due to the much longer diffusion length, trapping the 10$H$ phase during cooling. Alternative methods were also tested to obtain the 10$H$ phase, such as taking an as-calcined BCM powder sample and heating it to 1350 °C and holding for 24 h and cooling in UHP N$_2$ or Ar. However, this method typically yields only about 75 to 85% 10$H$ phase, likely due to small amounts of O$_2$ still present in the reactor are enough to keep the pO$_2$ higher than necessary for full 10$H$ conversion and/or slightly oxidize the sample during cooling, which could lead to the conversion of the some 10$H$ phase back to 12$R$.

Attempts to mitigate the remnant oxygen lead to the formation of an unreported third polytype that’s existence was hinted at by the high-temperature XRD work. Finally, we discovered that by reducing the as-calcined sample at lower pO$_2$ atmospheres at the same temperature we may obtain a third polytype of the BCM phase, which we will call $H$ phase, due to its lower ordering sequence. To obtain near pure $H$, the as-calcined sample was heated to 1350 °C and held for 48 h in with a gas flowrate of 100 sccm of UHP Ar and 8.7 sccm of 1% H$_2$ balanced with Ar (there was residual 10H present in initial runs with only a 24 h dwell).

**X-ray diffraction characterization**

Powder X-ray diffraction (XRD) patterns were measured on a PANalytical PW3040 diffractometer surveying a $2\theta$ range between 20° and 70° at a step size of 0.008° with CuK$_\alpha$ radiation of $\lambda = 1.540598$ and 1.54439 Å. Incident slits of $\frac{1}{4}$° and $\frac{1}{2}$° and a detector slit of 5.0° was used. The powder samples were crushed using mortar and pestle to obtain a fine powder and then placed on a SiO$_2$ crystal zero background sample holder cut at an off-set angle, to skip the 110 diffraction peak. Quick Rietveld refinement for phase identification was done using X’pert Highscore Plus.

High-temperature XRD was carried out at Sandia National Laboratories in Albuquerque on a Bragg-Bretano configuration XRD surveying a $2\theta$ range between 19° and 50° with CuK$_\alpha$ radiation of $\lambda = 1.540598$
and 1.54439 Å, using programmable divergence slit equipped with a Pt heating stage and controlled atmosphere. UHP He was used during the reduction step, passing through an oxygen getter which ensured a pO\textsubscript{2} below 1 ppm, and synthetic air (21 % O\textsubscript{2} balanced in N\textsubscript{2}) was used during the oxidation steps.

The samples were prepared by firstly crushing them using a mortar and pestle and adding methanol to form a liquid solution. This solution was carefully deposited onto (110) yttrium stabilized zirconia single crystal plates (10 x 10 x 0.5 mm) to obtain an even layer of sample. The XRD stage was rotated about 2\textdegree\ in the xz direction to skip the single crystal diffraction peak during normal scans. All experiments were performed on samples that contained greater than 95% 12\textit{R} phase with a remainder of 10\textit{H} phase.

\textit{Simulated water splitting cycles}

Regular WS testing is carried out in the Stagnation Flow reactor (SFR) at Sandia, where the reduction step is done under Ar flow and heating rate of 10 °C/s to T\textsubscript{RE} 1350 °C for 5 min and the oxidation cycle is done at T\textsubscript{OX} 850 °C for 20 min under 200 sccm H\textsubscript{2}O flow and 300 sccm Ar (40 vol. % H\textsubscript{2}O). Simulated cycles were designed to mimic the thermal and redox conditions of the SFR using a Setaram Setsys Evolution Thermogravimetric Analyzer (TGA). This allowed for more rapid redox cycle/XRD iterations. Before cycle testing, powder of all three pure phase polytypes were loaded into the TGA and reoxidized in synthetic air by heating to 850 °C and holding for 1 h. Since this oxidation was below the 1100 °C phase change, oxidation occurred without reversion to a different polytype. Post oxidation XRD confirmed that all three phases remained unchanged. The now oxidized samples of 10\textit{H} and the new \textit{H} polytype, 50.3 mg and 50.2 mg respectively, were each loaded into a Pt crucible and cycled five times in the TGA under the simulated cycles. The samples were initially heated to the oxidation temperature T\textsubscript{OX} 850 °C \textdegree C in a flowing environment of 100 sccm of UHP N\textsubscript{2}. The first redox cycle was carried out by heating the sample to T\textsubscript{RE} 1350 °C at a ramp rate of 99 °C/min (simulating the laser fast heating rate) followed by a hold of 5 min. The sample was then cooled down at the same rapid ramp rate to T\textsubscript{OX} 850 °C.
and 16 sccm of synthetic air (21% O₂ balanced with N₂) was added for 10 min. The air flow was turned off and purged by the N₂ flow for another 10 min before the next.

D.3 Results and discussion

From early in the work on BCM, there were tantalizing hints in the XRD and redox behavior that phase changes might occur in this system. To determine the thermodynamic properties of BCM we first needed to understand these phase changes and determine the conditions for the formation of each one. The phase change analysis will be now discussed.

D.3.1 Phase change evaluation

While quench studies are useful, ultimately there is little substitute for in-situ evaluation of phase changes. To that end, HT-XRD was employed to test BCM under various temperature and oxygen partial pressure conditions.

Experiment 1 mimics a typical redox cycle. The sample was heated at 10 °C/min from room temperature (RT) to 1350 °C in He flow taking a scan at every 50 °C from 850 °C to 1350 °C (each scan taking about 10 min to be completed). The 1350 °C isotherm was held for 1h 30min. The sample was cooled to 1150 °C and synthetic air was introduced. The oxidation step dwell was 1 h and the sample was cooled down to RT. Figure D.2 shows selected spectra from important points of the experiment. The complete experiment results are shown in Figures D.8, D.9 and D.10.
Figure D.2: High temperature XRD done on $12R$-$\text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3$. The powder samples was deposited onto an YSZ 110 single crystal plate and was heated to 1350 °C under He atmosphere. After an isotherm of 1.5 h, the sample was cooled to 1150 °C and oxidized in synthetic air for 1 h. $12R$ phase converts to $10H$ phase as well as a new polytype phase upon reduction. Symbols represent the highlighted $12R$ (★), $10H$ (◇) and $H$ (◻) polytype phase peaks.

As expected during heating, all peaks shift to lower angles due to lattice thermal expansion. By the time the sample has reached 1150 °C, the first hints of the $10H$ phase can be seen, and by the time the 1350 °C isotherm has concluded, the $12R$ phase has completely converted to $10H$, characterized by the disappearance of the 27.7° peak and the increase of the 28.4° peak. The highest intensity peaks for the $12R$ and $10H$ phases nearly overlap, which makes it difficult to distinguish between the two. However, when comparing the beginning and the end of the reduction isotherm at 1350 °C there is a subtle but distinct shift from the $12R$ phase’s 30.4° peak to the 30.1° peak of the $10H$ phase. A new polytype phase also started to appear, identified by the 25.7° and 30.9° peaks. Upon cooling and oxidation, the $10H$ and the new polytype phases remained. Some peak broadening can be seen, a product of the lattice becoming increasingly...
stressed, but overall, there is no evidence of a return of the $12R$ phase. These temperature and time conditions we were apparently not conducive to a return to the original phase upon oxidation.

Early preliminary redox experiments indicated that the $12R$ to $10H$ phase transition could be dependent on both temperature (above $1150^\circ C$) and reduction level (oxygen nonstoichiometry). Experiment 2 (Figure D.3) was carried out to confirm this observation, by subjecting the sample to the same redox temperature profile as Experiment 1, however only synthetic air was used.

![XRD spectra](image)

Figure D.3: High temperature XRD done on $12R$-$BaCeO_{2.25}MnO_{0.75}$. The powder samples was deposited onto an YSZ 110 single crystal plate and was heated to $1350^\circ C$ under synthetic air flow atmosphere. After an isotherm of 1.5 h, the sample was cooled to $1150^\circ C$ followed by a dwell of 1 h. $12R$ phase decreases in intensity giving place to $10H$ phase and a small amount of the $H$ polytype phase. Symbols represent the highlighted $12R$ (★), $10H$ (◇) and $H$ (Ⅱ) polytype phase peaks.

$10H$ and the new $H$ polytype phase start to appear during heating at approximately the same time they appeared in the previous experiment, however, the $12R$ phase never completely disappears. By the end of the experiment all three phases are present.
A third scan, Experiment 3, was carried out while heating the sample to a lower temperature, 1150 °C for the same time duration of 1.5 h under He flow. The sample was then cooled to 1000 °C and synthetic air was introduced, followed by a dwell of 1 h before cooling back to room temperature. In this experiment (Figure D.4), the $12R$ phase starts to decrease in intensity and the $10H$ phase starts to increase, however upon cooling, the $10H$ phase slowly converts back to $12R$. The oxidation isotherm clearly did not allow enough time for complete reversibility. This indicates that this phase transition is kinetically limited, which is expected for a transition that requires some cation rearrangement. Surprisingly, there is some evidence that the $H$ phase starts to appear during the oxidation step, indicated by a few faint peaks at 25.7° and 30.9°. The reason for its appearance under these conditions is not yet understood.

Figure D.4: High temperature XRD done on $12R$-$\text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3$. The powder sample was deposited onto an YSZ 110 single crystal plate and was heated to 1150 °C under synthetic air flow atmosphere. After an isotherm of 1.5 h, the sample was cooled to 1050 °C followed by a dwell of 1 h. $12R$ phase starts to converts to $10H$ phase and upon oxidation it slowly converts back to $12R$. A small amount of $H$ polytype phase is present at the end of the experiment. Symbols represent the highlighted $12R$ (★), $10H$ (◇) and $H$ (□) polytype phase peaks.
Once the basic parameters for triggering the phase changes were defined by the HT-XRD, our attention turned to the possibility of preparing phase pure samples of each of the three polytypes. Ultimately, this was achieved using the sample preparation conditions detailed in the experimental section. A long reduction and reoxidation cycle is necessary to convert the $10\text{H}$ phase to $12\text{R}$, achieving samples above 95% $12\text{R}$ phase. Long oxidation alone has been found to be insufficient for the conversion of $10\text{H}$. It appears that once partially reoxidized, the $10\text{H}$ becomes a metastable phase until the oxygen nonstoichiometry is returned to pre-oxidation levels. To that end, high $10\text{H}$ content material can be achieved by heating the sample to 1350 °C in inert atmosphere for reduction of the sample with long reduction times on the order of 5 to 10 h. However, by pressing the powder into a pellet, with binder, the static air environment of a furnace could still initiate conversion. The local sample environment during binder burnout was reducing enough to force the sample to reduce and flip the phase to $10\text{H}$, this was then retained during cooling, even in air, due to the dense pellet’s greatly reduced oxygen diffusion rate. The $\text{H}$ polytype phase was accessible when $\text{H}_2$ was introduced during the heat treatment in order to drop the oxygen partial pressure below what is achievable in an inert environment alone (in our system, this is typically on the order of tens of ppm). Once 8.6 sccm of 1% $\text{H}_2$ balanced with Ar was added to the typical 100 sccm of UHP Ar (~40 ppm $\text{H}_2$ in Ar), the residual oxygen was consumed leaving an oxygen partial pressure on the order of $1\times10^{-9}$ atm at 1350 °C (~10-20 ppm $\text{H}_2$), and after very long reduction times, nearly pure $\text{H}$ phase was produced. This was consistent to the HT-XRD results that first showed small amounts of $\text{H}$, since the flowing $\text{He}$ in the XRD chamber passed through an oxygen getter, dropping the oxygen content to less than 100 ppb (the limit of the attached oxygen sensor).

The phase change from $12\text{R}$ to $10\text{H}$ was further studied using Differential Scanning Calorimetry (DSC). A $12\text{R}$ sample was heated to 1250 °C, followed by an isotherm of 10 min and the sample was then cooled to 1000 °C under synthetic air flow. This experiment was done at different heating rates and a heat flow peak was detected during heating, shown in Figure D.5.
Figure D.5: Differential Scanning Calorimetry performed on BaCe$_{0.25}$Mn$_{0.75}$O$_3$. The sample was heated from 1000 °C to 1250 °C under flowing UHP N$_2$ at various heating rates 10, 20 and 40 °C/min. The endothermic peak indicates the heat capacity required for the phase change from 12$^R$ to 10$^H$ phase. The data and plot presented here was a contribution from Dr. Eric Coker.

The peaks detected at the various heating rates, indicate the heat capacity of the phase transition from 12$^R$ to 10$^H$ at temperature about 1170 °C. A rough integration of the peak at the fast ramp rate (40 °C/min) indicates that the heat capacity of the phase transition is about + 0.6 J/g. This indicates that this is an endothermic phase change, as expected, requiring smaller amount of energy.

From all these TGA redox and XRD experiments one may conclude that the 12$^R$ phase is BaCe$_{0.25}$Mn$_{0.75}$O$_3$ most stable oxidized phase at lower temperature. The 10$^H$ phase can be achieved by about 1170 °C when the sample suffers oxygen reduction, shown by the DSC experiment. The 10$^H$ phase may achieve a larger reduction level than 12$^R$. The $H$ polytype is an even more reduced phase, achieved by reducing BCM for a long time at elevated temperature. It achieves a larger reduction level than 10$^H$. The phase change might be kinetically limited requiring cation rearrangement for it to happen which is the reason why the 10$^H$ and $H$ polytypes can be locked in and exist at lower temperatures. These polytypes are completely reversible to 12$^R$ after a few of redox cycles.
The 10H and the H polytype samples were tested in the TGA for 5 simulated WS cycles to evaluate their redox capacity under the regular WS temperature conditions ($T_{RE}$ 1350 °C and $T_{OX}$ 850 °C). Results are shown in Figure D.6.

Figure D.6: Simulated five WS cycles on 10H (blue) and H (black) polytype. Reduction was carried out in 100 sccm UHP N$_2$ flow at $T_{RE}$ 1350 °C for 5 min and oxidation carried out in 100 sccm N$_2$ and 16 sccm (21 % O$_2$ balanced with N$_2$) flow at $T_{OX}$ 850 °C for 20 min.

The 10H sample achieved consistent reduction levels of about 0.5 weight % (i.e., $\Delta \delta = 0.08$) across all five cycles. The mass gain during reoxidation was also similar for all cycles, however the sample never returns to its starting oxidation level. XRD performed on the sample (shown in Figure D.11) indicated that after the simulated cycles, the sample converted almost fully from 10H to 12R phase.
The $H$ polytype sample behaved differently. Like the 10$H$ sample, the initial reduction step experienced the largest mass loss, about 0.91 weight % (i.e. $\Delta \delta = 0.15$). This was nearly twice that of the 10$H$ sample. However, the reoxidation and later redox cycles saw larger oxidations followed by smaller reductions until an apparent equilibrium was reached by the last cycle, and overall the sample had actually gained mass. The final cycle of the $H$ experiment was nearly identical to that of the last 10$H$ cycle. This was explained by the post cycle XRD (Figure D.11) which once again showed nearly complete conversion back to 12$R$.

The simulated WS cycles suggested that the fully oxidized polytype phases 10$H$ and $H$ achieve higher reduction levels than the 12$R$ phase. This assumption was confirmed by the TPR performed on all three phases (Figure D.7).

![Figure D.7: Temperature programmed reduction performed on BaCe$_{0.25}$Mn$_{0.75}$O$_3$ 12$R$, 10$H$ and $H$ polytypes. Reduction was carried out under flowing N$_2$ for 1 h at 1350 °C and oxidation was carried out in flowing synthetic air for 1 h at 1000 °C.](image-url)
The 12R phase shows close to full oxygen recoverability by the end of the experiment. The 10H phase has the same onset reduction temperature compared to 12R (about 1050 °C), however it reduces more and does not completely recover all the oxygen released during reduction. Lastly, the H polytype starts to reduce at a much lower temperature around 850 °C and achieves the largest reduction level among all samples. It surprisingly recovers all the oxygen released during oxidation. XRD done on samples after TPR (shown in Figure D.12) indicate that the majority of 10H sample converted to 12R, leaving behind a small amount of 10H phase. The H sample, on the other hand, only partially converted to 10H and the remainder either stayed as the H polytype or converted to a possibly unidentified transition phase and there was no evidence of 12R. The lack of complete conversion during a single redox cycle is unsurprising in light of the TPR results that showed that a few cycles were necessary to completely revert samples back to the 12R phase. It is also possible that the higher oxidation temperature (1000 °C) contributed to the relative stability of the H phase.

D.4 Conclusion

BCM showed interesting STCH properties and was investigated concerning its thermodynamic properties for a fundamental understanding of its WS performance. However, from previous TPR experiments it was identified that BCM suffers a polytypic phase change during oxygen reduction. The phase change was further investigated by high temperature XRD and a new polytype was discovered, H when the sample is extremely reduced. The characterization experiments indicated that fully oxidized BCM assumes the 12R polytype, and when reduced above 1100 °C it changes phase to 10H. Upon further reduction, the samples suffer a second phase change to the H polytype.

We are fairly confident that during the WS experiments, the BCM sample is staying as 12R due to the short reduction times, however, as seen in the experiments performed, it is possible to initiate a phase change to the more reduced polytypes but increasing the reduction time. The phase change might be
beneficial for WS since we’ve shown that 10H and H phases might have a larger driving force for reduction. When combining the larger reduction capacity from the 10H and H polytypes and the larger driving force for reoxidation from the 12R, one may increase the H₂ production while still maintain the tolerance for high conversion water splitting.
Figure D.8: High temperature X-ray Diffraction on BaCe$_{0.25}$Mn$_{0.75}$O$_3$, Experiment 1. The sample starts at room temperature at He flow and is heated to 1350 °C with a dwell of 1.5 h. The sample is then cooled to 1150 °C and synthetic air is introduced (21% O$_2$ balanced with N$_2$). After a dwell of 1 h the sample is cooled down to room temperature. This experiment starts with a 12$R$ phase and at the reduction step, the sample suffers a phase change to 10$H$ and $H$ polytype.
Figure D.9: High temperature X-ray Diffraction on BaCe$_{0.25}$Mn$_{0.75}$O$_3$, Experiment 2. The sample starts at room temperature in air flow and is heated to 1350 °C with a dwell of 1.5 h. The sample is then cooled to 1150 °C. After a dwell of 1 h the sample is cooled down to room temperature. This experiment starts with a 12$R$ phase and a partial phase change occurs forming 10$H$ and $H$ polytype.
Figure D.10: High temperature X-ray Diffraction on BaCe$_{0.25}$Mn$_{0.75}$O$_3$, Experiment 3. The sample starts at room temperature in air flow and is heated to 1150 °C with a dwell of 1.5 h. The sample is then cooled to 1000 °C. After a dwell of 1 h the sample is cooled down to room temperature. A small amount of 10$H$ phase starts to appear at the end of the reduction step as well as the $H$ polytype.
Figure D.11: XRD on starting samples and after the cycle WS simulated cycles performed on TGA. a) 10H phase sample converted to 12R phase and b) H polytype sample converted to 12R phase.
Figure D.12: XRD performed on BaCe$_{0.25}$Mn$_{0.75}$O$_3$ 10\(H\) and \(H\) polytype samples after TPR run. The 10\(H\) sample converted its majority to 12\(R\) phase having a small amount of 10\(H\) phase still present. The \(H\) sample converted partially to 10\(H\).
Figure D.13: Differential Scanning Calorimetry performed on BaCe$_{0.25}$Mn$_{0.75}$O$_3$. The samples were loaded into an alumina crucible and heated to the oxidation temperature 1050 °C under UHP N$_2$ flow. The sample were further heated from the oxidation temperature to the reduction temperature 1250 °C at three different heating rates 10, 20 and 40 °C/min. After a dwell of 10 min, the temperature was dropped at same ramp rates to the oxidation temperature under synthetic air flow. The phase change from 12$R$ to 10$H$ phase was identified during heating.
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