

EVALUATING THE THERMAL STABILITY OF $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ (SVMO)
AND SVMO's PROMISE AS A SOLID OXIDE CELL
ELECTRODE MATERIAL

by

Bamidele Johnson Samuel

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Physical Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

May 2026

©COPYRIGHT

by

Bamidele Johnson Samuel

2026

All Rights Reserved

DEDICATION

To my family and friends, thank you for your constant support, encouragement, and belief in me throughout this journey. With love and gratitude.

ACKNOWLEDGEMENTS

First, I sincerely thank my advisor, Prof. Robert Walker, for his guidance, mentorship, and for encouraging me to pursue my own research ideas with confidence. I am also grateful to our collaborators at the Department of Mechanical and Industrial Engineering, Montana State University, Bozeman, especially Prof. Stephen Sofie, Dr. Stephen Heywood and Julia Esakoff, for their support in research and writing. I thank the past and present members of the Walker Research Group, particularly Dr. Elias Epomeroy, Dr. Marshall McNally, Dr. Steven Montoya and Keegan Walker for their useful suggestions and support in general. I am also deeply grateful to my committee members – Prof. Erik Grumstrup, Prof. Nick Stadie, Prof. Stephen Sofie, and Dr. Martin Mosquera – for their valuable insights, constructive feedback, and thoughtful discussions throughout this work. Special thanks to Dr. Doreen Brown for her dedicated help with graduate school processes and paperwork. I would also like to thank my parents Mr. and Mrs. Braimoh Samuel for their prayers and useful advice.

I would like to thank the U.S. Army Research Office for funding us through DEVCOM Army Research Office: under Cooperative Agreement (CA) Number W911NF-22-2-0021.

TABLE OF CONTENTS

1. INTRODUCTION	1
Motivation and Background	1
High Temperature Solid Oxide-based Electrochemistry	3
Solid Oxide Fuel Cells	3
Reversible Solid-Oxide Cells	5
Challenges in Triple Phase Boundary-based Electrodes	6
Mixed Ionic-Electronic Conductors	8
Perovskite and Double Perovskite Materials for High Temperature Energy Conversion	9
Single Perovskites	9
Double Perovskites	11
History of Double Perovskites Research	14
Structure of Double Perovskites	16
1. Random	18
2. Rock Salt	18
3. Layered	18
Properties of Double Perovskites	20
Electrical Conductivity	20
Ionic Conductivity	22
Catalysis	24
Stability	25
Applications of Double Perovskite Oxides	26
$\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ Double Perovskite Oxides	27
Techniques/Experimental Methods	31
Raman spectroscopy	32
Data acquisition using Raman spectroscopy	34
Thermogravimetric analysis	36
X-ray Diffractometry	38
2. CHEMICAL AND THERMAL STABILITY OF $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$: IMPLICATIONS FOR HIGH TEMPERATURE ENERGY CONVERSION APPLICATIONS	55
Manuscript Information	56
Introduction	58
Materials and Methods	61
$\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ (SVMO-19) synthesis	61
Chemical Stability Testing	62
Characterization – X-ray diffraction	62
Characterization – Raman spectroscopy	63
Characterization – Thermogravimetric analysis	63

Results	64
Phase composition and crystal structure of SVMO-19	64
SVMO-19 stability in inert, reducing and oxidizing atmospheres	65
Thermal analysis	72
Summary	83
3. THE ROLE OF A-SITE DEFICIENCY IN $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ STABILITY	89
Manuscript Information	90
Abstract	91
Introduction	92
EXPERIMENTAL	99
3. RESULTS AND DISCUSSION	104
3.1. SVMOs stability in inert and oxidizing atmospheres	104
3.1.1 Thermal analysis	105
3.1.1 Raman analysis	106
3.2.1 Kinetics with isothermal-Raman measurements	108
3.2.2 Kinetics with isothermal-Raman measurements	112
3.2.3 Comparing isothermal Raman and isothermal TGA results.	116
4. Conclusions	117
References	119
4. CONCLUSIONS AND FUTURE DIRECTIONS	125
Conclusions	125
Future Directions	127
Electrochemical Performance and Durability	129
APPENDICES	133
Supporting Information for Chapter 2	134
Supporting Information for Chapter 3	141
Kinetic Modeling Considerations	157

LIST OF TABLES

Table	Page
1. Table 1.1. Comparison of reported conductivities of selected single and double perovskite materials	12
2. Table 2.1. Crystallographic information for common double perovskites	19
3. Table 3.1. Reported electrical conductivities of Sr_2MMoO_6 and other relevant materials	29
4. Table 1.2. Rate constants determined from fitting data in Figures 5.2b and 6.2b to Eq. 1. Typical uncertainties in k_1 are $\pm 20\%$; typical uncertainties in k_2 are $\pm 5\%$	76
5. Table 2.2. Rate constant and exponent determined from fitting data in Figure 8.2b to Eq. 3.2. Typical uncertainties in rate constants are less than $\pm 25\%$	81
6. Table 1.3 Rate constants determined from fitting data from isothermal Raman data using the SrMoO_4 peak at 876 cm^{-1} intensity to Equation 2.3.	111

LIST OF FIGURES

Figure	Page
7. Figure 1.1. Schematic drawing showing the operating principle of a solid oxide fuel cell where oxygen is catalytically reduced at the LSM/YSZ cathode; oxygen ions diffuse through the YSZ electrolyte; and fuel is oxidized at the Ni/YSZ anode	4
8. Figure 3.1. Schematic representation showing electrochemical reactions at the three phase boundaries (TPB) inside the anode. Adapted from Chinda et al.....	7
9. Figure 5.1. Schematic illustration of a double perovskite structure (right), shown as a derivative of the simple perovskite structure (left).	12
10. Figure 6.1. Structural flexibility of oxide perovskites. The central image shows the simple cubic perovskite structure, while the surrounding figures illustrate the formation of double perovskites with different types of B-site ordering, including rock-salt, random, and layered arrangements. Octahedral tilting within the [BO ₆] framework can transform the cubic structure into several lower-symmetry tilt systems, three of which are shown at the bottom left. Under large octahedral distortions, the three-dimensional connectivity of the [BO ₆] network can break down, giving rise to two-dimensional and one-dimensional perovskite-derived structures.	17
11. Figure 7.1. Schematic representation of the crystal structure of Sr ₂ VMoO ₆ double perovskite.	28
12. Figure 8.1. Schematic energy level diagram illustrating scattering and absorption processes in vibrational spectroscopy	33
13. Figure 10.1. (a) TGA curves of SVMO in N ₂ and air from 25 to 900 °C (b) Isothermal TGA curves of SVMO in air at 500 °C, 600 °C and 700 °C. The dashed vertical lines correspond to the time when the sample has reached its target temperature. The dashed lines superimposed on the data correspond to fits generated by the double exponential kinetic model.....	37
14. Figure 1.2. XRD patterns of SVMO-19 double-perovskite as-fabricated. Inset: XRD patterns of the SVMO-19 showing the expanded view of 2θ = 10 -24° with features assigned to secondary phases.	64
15. Figure 6.2. (a) TGA curves of SVMO-19 in N ₂ and air from 25 to 900 °C (b) Isothermal TGA curves of SVMO-19 in air at 500 °C, 600 °C and 700	

°C. The dashed vertical lines correspond to the time when the sample has reached its target temperature. The dashed lines superimposed on the data correspond to fits generated by Eq. 1.2.....	73
16. Figure 7.2. XRD pattern from SVMO-19 sample after being heated to 800 °C in air. Rietveld refinement identifies 3 distinct secondary phases.	75
17. Figure 8.2. Isothermal TGA curves of SVMO-19 in air at 500 °C, 600 °C and 700 °C with fits to (a) the double exponential kinetic, and (b) the Avrami kinetic models	80
18. Figure 9.2. Arrhenius plots for SVMO-19 kinetic data from isothermal TGA measurements shown in Figure 6.2. Data in panel (a) correspond to a double exponential function describing two independent first order kinetic processes. (See Equation 1.) Data in panel (b) correspond to rate constants derived from an Avrami model. (See equation 3.) Experiments at each temperature were carried out a minimum of 4 times and the uncertainties represent two standard deviations. Note the break in scale between panels (a) and (b).....	82
19. Figure 1.3 XRD patterns of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ (SVMO: $x = 0.0, 0.05, 0.1, 0.15, 0.2$) double perovskites as-fabricated.	101
20. Figure 2.3 TGA curves of SVMO-20 in N_2 and air from 25 to 900 °C.	105
21. Figure 3.3 <i>In situ</i> Raman spectra of SVMO-20 in air from room temperature to 1000 °C.	107
22. Figure 4.3 <i>In situ</i> Raman spectra of SVMO ($x = 0.0, 0.1$, and 0.2) in air at 400 °C and 500 °C.	108
23. Figure 5.3 <i>In situ</i> Raman spectra of SVMO-20 in 5% $\text{H}_2/95\% \text{N}_2$ and air from room temperature to 700 °C; (b) Kinetic trace showing the normalized intensity of the SrMoO_4 secondary phase after exposure to air at 700 °C.....	110
24. Figure 6.3 Isothermal TGA curves of SVMO-20 in air at 500 °C, 600 °C, and 700 °C with fits to double exponential kinetic model. The dashed vertical lines correspond to the time when the sample has reached its target temperature. The markers superimposed on the data correspond to fits generated by Eq. 2.3.....	113
25. Figure 7.3 Asymptotic mass gain (%) as a function of A-site (Sr) deficiency (x) in $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ double perovskites, determined from isothermal TGA oxidation measurements in air at 500 °C, 600 °C and 700 °C.....	114

26. Figure 1.4 Schematics showing membrane electrode assemblies with SVMO/CeO ₂ fuel electrodes.....	130
27. Figure 2.4 <i>In situ</i> temperature dependent Raman spectra of SVMO/CeO ₂ cell at room temperature and in nitrogen at 800 °C	131
28. Figure 3.4 <i>In situ</i> temperature dependent Raman spectra of SVMO/CeO ₂ cell in nitrogen and 40 sccm H ₂ at 800 °C (sccm: standard cubic centimeters per minute)	132

GLOSSARY or NOMENCLATURE

SVMO: $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$

SVMO-20: $\text{Sr}_{2.0}\text{VMoO}_{6-\delta}$

SVMO-195: $\text{Sr}_{1.95}\text{VMoO}_{6-\delta}$

SVMO-19: $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$

SVMO-185: $\text{Sr}_{1.85}\text{VMoO}_{6-\delta}$

SVMO-18: $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$

x: A-site cation deficiency

δ : Oxygen vacancy concentration

SOFCs: Solid Oxide Fuel Cells

SOECs: Solid Oxide Electrolysis Cells

MIEC: Mixed Ionic-Electronic Conductors

rSOCs: Reversible Solid Oxide Cells

TPB: Triple Phase Boundary

TGA: Thermogravimetric Analysis

XRD: X-ray Diffraction

XPS: X-ray Photoelectron Spectroscopy

Cermet: Composite of ceramic and metal e.g., Ni-YSZ

ABSTRACT

A family of double perovskite materials $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ (SVMO, $x = 0-0.2$) shows exceptionally large conductivities under reducing atmospheres, making these materials attractive as electrode candidates for high temperature electrochemical devices. To function as electrodes, SVMO must be stable at elevated temperatures and under both oxidizing and reducing conditions. Work described in this dissertation examines SVMO stability as a function of temperature, P_{O_2} , and A-site deficiency. My research uses Raman spectroscopy, thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) to examine the behavior of SVMO under different atmospheres at temperatures up to 1000 °C. Raman spectra show that SVMO is stable under forming gas (5% H_2) at temperatures up to 1000 °C. Similar behavior is observed with humidified argon and CO_2 atmospheres. However, when heated above 600 °C in air, Raman spectra show that SVMO phase separates. Secondary phases include scheelite (SrMoO_4) and single perovskite (SrVO_3) phases. Phase separation is reversible under reducing atmospheres at high temperature, restoring the original SVMO structure and demonstrating its redox-sensitive and atmosphere-dependent structural stability. While Raman data suggest that SVMO will oxidize above 600 °C, TGA measurements show that oxygen uptake starts at temperatures as low as 400 °C. TGA data show that SVMO is stable under N_2 at temperatures as high as 900 °C, consistent with Raman data. SVMO oxidation kinetics in air are analyzed using a simple kinetic model consisting of two independent first-order processes with the faster process describing surface decomposition and the latter reaction describing conversion of the bulk material. An Arrhenius analysis results in an activation energy (E_a) between 0.1 and 0.8 eV for these processes depending on A-site deficiency. Activation energies show that SVMO stability is maximized with $x = 0.05$. These findings imply that SVMO can function as an anode in solid oxide fuel cells and the fuel electrode in solid oxide electrolysis cells.

CHAPTER ONE

INTRODUCTION

Motivation and Background

High-temperature electrochemical energy conversion systems, including solid oxide fuel cells (SOFCs), and solid oxide electrolysis cells (SOECs), typically operate between 600 and 1000 °C.¹ At these elevated temperatures, electrochemical reaction rates are significantly faster and oxide-ion conductivity through electrolytes is greatly enhanced.¹ Furthermore, the high-temperature exhaust heat can be recovered and used in combined heat and power (CHP) systems, thereby improving overall energy utilization and system efficiency.¹ In addition, non-precious metal catalysts can be used because reaction kinetics are sufficiently fast at high temperatures, which helps lower material costs.² When operated in electrolysis mode, SOECs can utilize thermal energy to supply part of the energy required for steam splitting, reducing electrical energy demand and enabling highly efficient hydrogen production.³

Despite these advantages, high operating temperatures also introduce significant challenges. Elevated temperatures accelerate degradation processes such as electrode coarsening, chromium poisoning, delamination, redox instability, and corrosion of seals and interconnects. These degradation mechanisms reduce long-term durability and increase system cost.⁴ In addition, high temperatures result in slow start-up, sensitivity to thermal cycling, and complex thermal management requirements, limiting operational flexibility and commercial scalability.⁵ Although high-temperature electrochemical systems offer high efficiency and fuel flexibility,

their widespread implementation depends on improving the stability, durability, and overall cost-effectiveness of device materials.

The need for sustainable and efficient energy conversion technologies has accelerated the development of more durable electrocatalytic materials that retain function at high-temperatures and in chemically reactive gas environments. Among these materials, double perovskite (DP) oxides ($A_2B'B''O_6$) are being considered as possible candidates because of their compositional flexibility, mixed ionic-electronic conductivity, and redox adaptability.⁶⁻⁸ The ability of DP oxide materials to accommodate diverse cation substitutions at both A- and B-sites allows modifications in a material's physical and chemical properties thus enabling them to be optimized for specific applications. By virtue of being able to have two different lanthanide or alkaline earth elements on the A sites and two transition metals on the B sites, DP oxides offer functional advantages over simple ABO_3 perovskite structures.

This dissertation describes a series of studies designed to test the chemical stability of one such double perovskite, $Sr_{2-x}VMoO_{6-\delta}$ (SVMO), under conditions commonly encountered in SOFCs and solid oxide electrolysis cells (SOECs). Previous reports suggest that SVMO has remarkably high conductivity for a ceramic material, undergoing a semi-conductor to metal transition at high temperatures under reducing conditions. If this material is going to be integrated into SOFCs and SOECs as an electrode, its resilience to high temperatures (up to 1000 °C), ambient atmosphere, and non-stoichiometric formulations must be well documented. Using thermal gravimetric analysis (TGA) and *in situ* high temperature Raman spectroscopy, experiments described in subsequent chapters examine SVMO's tendency to form secondary phases under application-relevant conditions.

To motivate the work described in this dissertation, Chapter 1 first describes SOFC and SOEC operation and the requirements materials must satisfy before they can be integrated into these high temperature membrane electrode assemblies. Also described in Chapter 1 are the general structures and properties of DP ceramics and a review of how different DP materials have been used previously. Chapter 1 concludes with a description of the primary experimental methods used in these studies and a summary of relevant findings.

High Temperature Solid Oxide-based Electrochemistry

Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFCs) are fuel flexible energy conversion devices, that directly convert fuel's chemical energy into electricity via electrochemical reaction. Compared to the conventional power plant, SOFCs could promise cleaner and more efficient energy conversion.⁹⁻

¹¹ An SOFC primarily consists of three components: a cathode, an electrolyte and an anode. Oxygen reduction takes place at the cathode, where oxygen gains electrons and is reduced to oxide ions. The electrolyte is a ceramic solid oxide that conducts oxide ions efficiently at high temperatures, typically between 600 and 1000 °C. High temperature is critical in SOFCs operation because it facilitates ionic conductivity, speeds up electronic kinetics, allows for flexible fuel use, and maximizes energy conversion efficiency. Fuel oxidation occurs at the anode, where fuel reacts with oxygen ions to form H₂O, while simultaneously releasing electrons to an external circuit as shown in Figure 1. The anode is usually a cermet, a material made by combining a ceramic and a metal – most commonly Ni-YSZ. In this composite, the ceramic conducts ions, while the metal conducts electrons. Electrochemical reactions occur at the triple

phase boundary (TPB), where the fuels (H_2 and CO), electronic conductor (Ni) and oxygen ion conducting phases meet.¹²⁻¹⁵

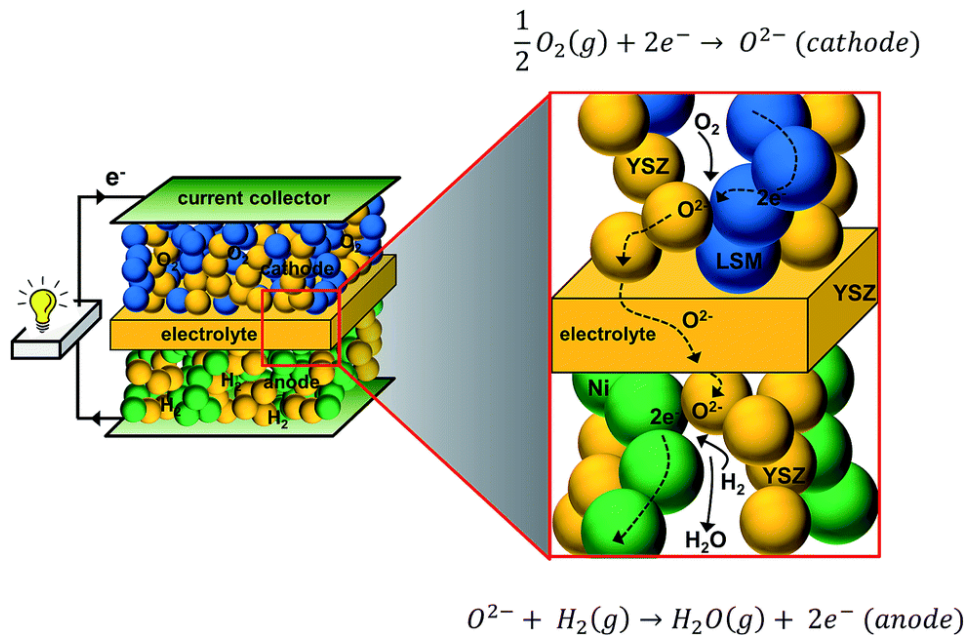
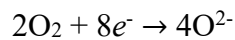


Figure 1.1. Schematic drawing showing the operating principle of a solid oxide fuel cell where oxygen is catalytically reduced at the LSM/YSZ cathode; oxygen ions diffuse through the YSZ electrolyte; and fuel is oxidized at the Ni/YSZ anode.¹⁶

Anodic reaction: Fuel oxidation for CH_4



Cathodic reaction: Oxygen reduction



The performance of an SOFC depends on how well ions and electrons move through the cell and how active the electrodes in promoting the reactions. It is also important to reduce energy losses and ensure that the materials remain stable during operation. As shown in Figure 1,

a well-distributed triple phase boundary and stable contact between the electrodes and electrolyte are essential for efficient and long-lasting SOFC performance.

Reversible Solid-Oxide Cells

Reversible solid-oxide cells (rSOCs) are high-temperature electrochemical systems that can function in two different operating modes.¹⁷ When operated as a solid oxide fuel cell (SOFC), they generate electrical power by converting the chemical energy of a fuel into electricity via electrochemical reactions. When operated as a solid oxide electrolysis cell (SOEC), the process is reversed: electrical energy is supplied to split steam (and in some cases carbon dioxide) to produce hydrogen (and carbon monoxide). Therefore, rSOCs can both generate electricity and store energy in the form of chemical fuels. This dual functionality makes SOECs attractive for integrating renewable energy sources with energy storage technologies.¹⁷

The operation of rSOCs relies on the movement of oxygen ions (O^{2-}) through a solid ceramic electrolyte, typically yttria-stabilized zirconia (YSZ).¹⁸ In fuel cell mode, oxygen molecules are reduced at the oxygen electrode to form O^{2-} ions. These ions travel through the electrolyte and react with hydrogen at the fuel electrode, producing water and releasing electrons that flow through the external circuit to generate power. In electrolysis mode, the reactions occur in the opposite direction, $SOFC \rightleftharpoons SOEC$, as shown in Figure 2. Steam is reduced at the fuel electrode to form hydrogen and O^{2-} ions, and oxygen gas is produced at the oxygen electrode. rSOCs operation require elevated temperatures (600 – 900 °C)¹⁸ which promotes ionic conductivity and reaction rates, leading to high energy conversion efficiency. However, repeated switching between the two modes imposes additional challenges related to electrode stability and long-term interface durability.¹⁸

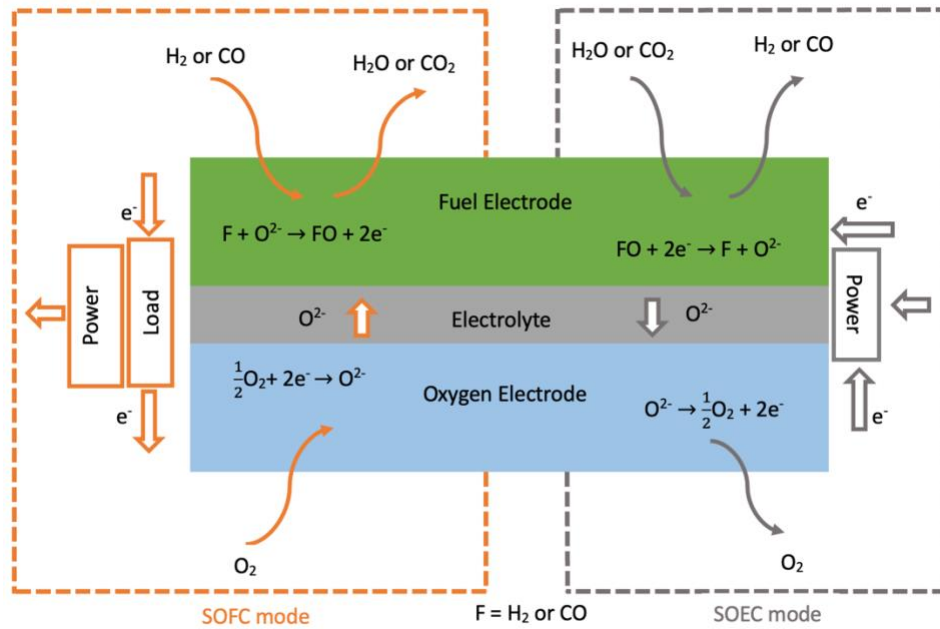


Figure 2.1. Schematic drawing showing the operating principle of a reversible solid oxide cell. Adapted from Gómez et al. ¹⁹ and Yang et al. ²⁰

For reliable performance, rSOCs must allow ions and electrons to move quickly in both modes of operation. The electrodes need to be highly active for both fuel oxidation and electrolysis, while remaining chemically and mechanically stable during repeated switching between operational modes. As shown in Figure 2, a well-connected triple phase boundary and strong, stable contact between the electrodes and electrolyte are key to efficient and long-lasting operation.

Challenges in Triple Phase Boundary-based Electrodes

In conventional SOFCs and in rSOCs, the kinetics of the electrochemical reactions at the TPB play a critical role in controlling device performance. As a TPB-based electrode, Ni/YSZ cermet suffers from redox instability, sulfur poisoning, and carbon deposition, and current limited by charge transfer, all of which can cause serious degradation in SOFC performance. ^{21, 22}

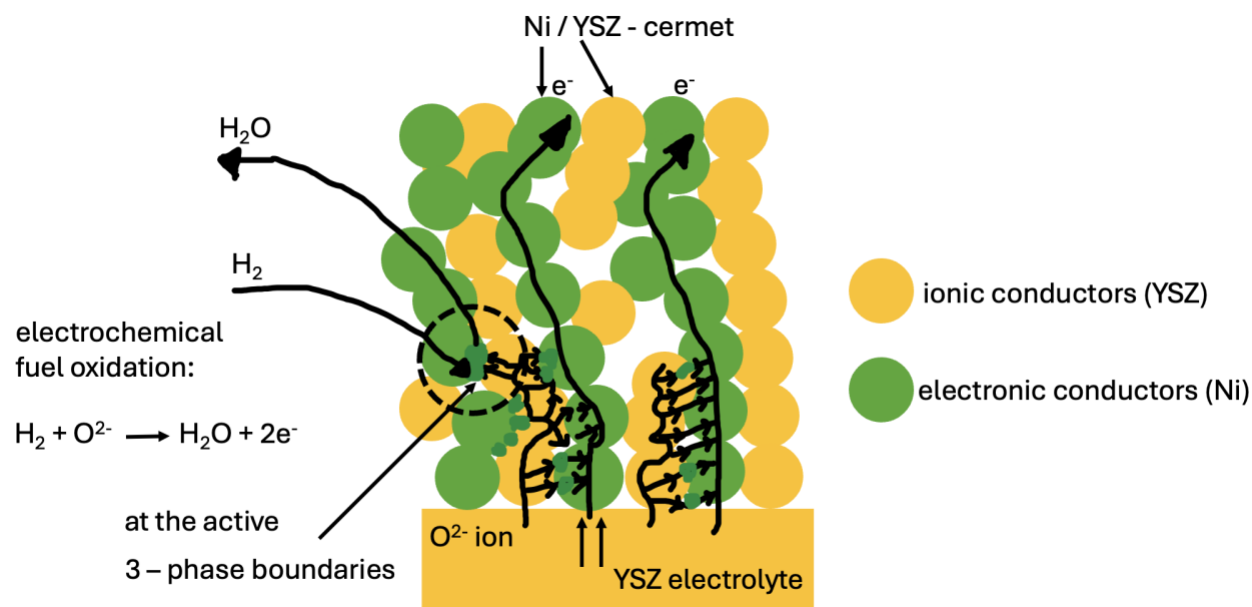


Figure 3.1. Schematic representation showing electrochemical reactions at the three phase boundaries (TPB) inside the anode. Adapted from Chinda et al.²³

In SOFCs and SOECs, secondary phases can form in electrode materials or between components during fabrication or operation.²⁴ These new phases block active sites and reduce efficiency.²⁴ Single perovskite cathodes such as LSCF and LSM are especially susceptible to Sr migration at high temperatures. Sr can segregate to the surface or interfaces and form Sr-rich phases like SrO or SrCrO₄.²⁵ These phases disrupt the structure, slow oxygen transport, and reduce surface reaction rates. Therefore, preventing Sr migration and secondary phase formation is essential for improving electrode durability.²⁵

Given these challenges, the high temperature energy conversion community continues to develop alternative SOFC electrode materials with improved catalytic performance and stability for oxygen reduction and fuel oxidation. An ideal electrode material should exhibit high

electronic conductivity and suitable ionic conductivity under reducing conditions at temperatures up to 800 °C. It must also possess strong electrocatalytic activity for fuel oxidation and maintain chemical and thermal compatibility with the electrolyte.^{16, 26-28} To overcome the limitations of traditional SOFC electrodes, a promising approach is to use a single-phase mixed ionic-electronic conductor (MIEC). Such materials combine the functions of a cermet into a single material that conducts ions and electrons and extends the triple phase boundary throughout the fuel electrode, thereby enhancing electrochemical reaction efficiency.²⁹

Mixed Ionic-Electronic Conductors

Mixed ionic-electronic conductors (MIECs) are materials that facilitate the simultaneous transportation of ionic (O^{2-} , H^+ , or Ag^+) and electronic charge carriers (electrons or holes). In a traditional SOFC, the electrode materials are usually pure electronic conductors with nickel being the most common anode material. Consequently, electrochemical reactions are only possible at the narrow TPB because the movement of ions is restricted to the electrolyte. In contrast, MIECs can transport oxide ions from the solid oxide electrolyte to the fuel-rich anode surface. Since ions move through the electrode material itself, electrochemical reactions such as oxygen reduction or fuel oxidation can occur across the entire MIEC-gas interface, rather than being limited to the 1-dimensional electrolyte-electrode-gas phase junction. By effectively extending the anode/electrolyte/cathode TPB, MIECs expand the number of active sites for fuel oxidation and improve electrode performance.³⁰ Single perovskite materials currently serve as MIECs in SOFC cathodes. Double perovskites are attractive alternatives to single perovskites given the double perovskite's improved conductivity and anticipated high tolerance to contaminants.

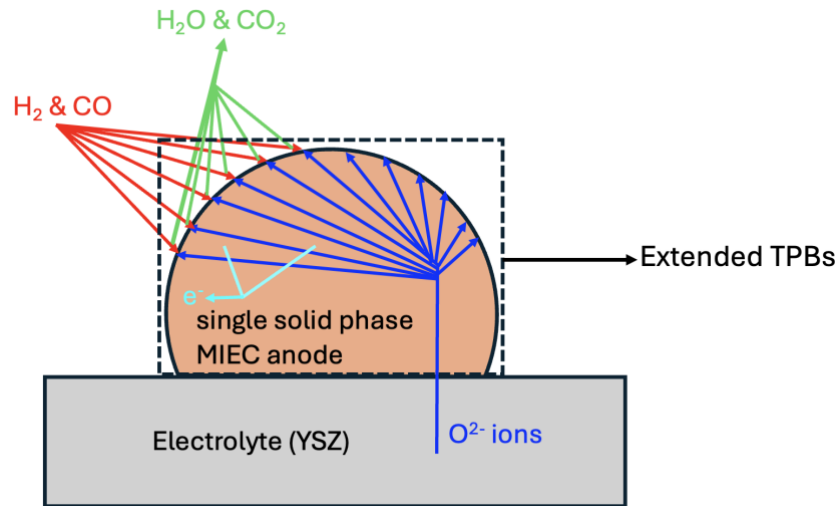


Figure 4.1. Schematic representation of the extended TPB in single solid phase MIEC anode

By expanding the TPB, MIECs can lower energy losses and enhance fuel utilization compared to traditional electrodes.³⁰ However, maintaining high conductivity and long-term stability under operating conditions remains an important design challenge for these materials.

Perovskite and Double Perovskite Materials for High Temperature Energy Conversion

Single Perovskites

Single perovskite materials have the general formula ABX_3 , where A and B are electropositive cations and X is an anion. The ideal single oxide perovskite, ABO_3 , adopts a cubic structure with the space group $Pm\bar{3}m$ (Figure 5.1). This structure consists of a flexible three-dimensional framework formed by corner-sharing $[BO_6]$ octahedral, with the A-site cations occupying the larger cuboctahedron cavities created by this network.³¹ Single perovskite oxides are commonly used as electrodes in SOFCs and SOECs, but their performance is often limited by

structural and chemical constraints. In these materials, the B-site cation is primarily responsible for electronic conductivity and catalytic behavior, while A-site substitution (for example, Sr^{2+} doping) is typically used to introduce oxygen vacancies and improve oxygen-ion transport. Although higher Sr content can enhance ionic mobility, it also increases the tendency for Sr to migrate to the surface and form secondary phases that reduce long-term stability. To address this issue, A-site deficiency has been explored as an alternative strategy to improving material performance and durability.^{25, 32-36} By deliberately reducing the A-site content, Sr segregation can be suppressed, defect chemistry can be modified, and structural stability can be improved. However, excessive A-site deficiency can also disturb phase stability and conductivity. Therefore, introducing A-site deficiency must be done in a carefully controlled manner.

Many single perovskites exhibit limited stability under strongly oxidizing or reducing conditions, particularly during reversible SOFC/SOEC operation. These materials may experience phase decomposition, cation migration, or changes in oxygen non-stoichiometry, all of which can lower conductivity and accelerate degradation. These compromises between conductivity, catalytic activity, and stability have been previously reported for materials such as LSCF and LSM.^{17, 18, 31, 37} Double perovskites offer greater flexibility and the opportunity for greater stability because two different cations can occupy the B-site in an ordered arrangement. This ordered structure makes it possible to better control the electronic properties, defect chemistry, and redox behavior of the material, which leads to improved catalytic activity and long-term stability.^{17, 31}

Double Perovskites

DPs are perovskite structures in which either the A-site or the B-site is occupied by two different cations. Their compositions are written as $A'A''B_2O_6$ for double A-site materials and $A_2B'B''O_6$ for double B-site materials.³⁸ A DP, for example, forms when exactly half of the B-site cations in a simple perovskite are replaced by another type of cation, B', and these two cations arrange themselves in a rock-salt structure.³⁹ As shown schematically in Figure 5, this ordering doubles the perovskite formula unit from ABO_3 to $A_2B_2O_6$.⁴⁰ In oxide perovskites, the A-site cations mainly donate electrons to the $[BO_6]$ framework, while the B-site cations largely determine the material's physical properties, such as electrical and ionic conductivity, catalytic activity, thermal expansion, and electrochemical performance. As a result, the term double perovskite most often refers to double B-site systems.³⁸ DPs provide greater structural flexibility than single perovskites because DPs can accommodate two different transition-metal ions at the B sites (B and B'), and in some cases two different rare-earth or alkaline-earth ions at the A sites.⁴¹ This wide range of possible cation combinations allows more degrees of freedom to tune DP structure and properties.³¹

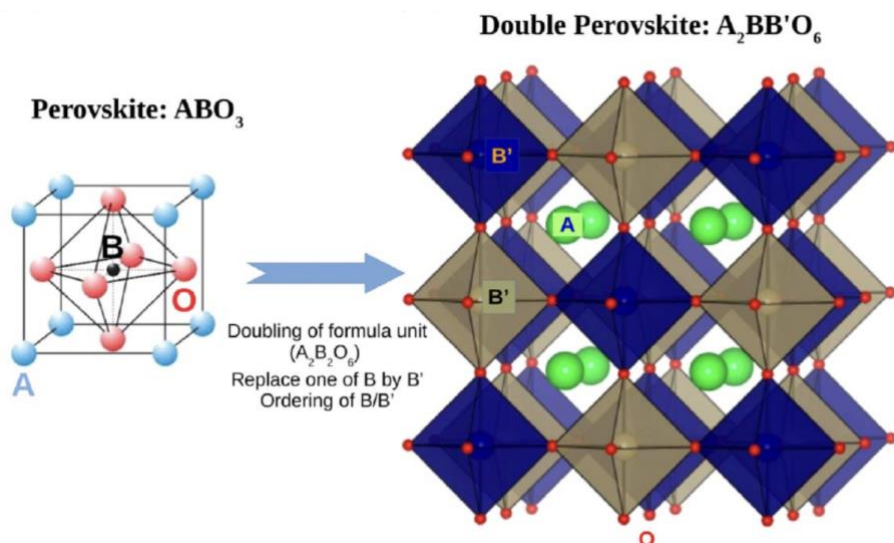


Figure 5.1. Schematic illustration of a double perovskite structure (right), shown as a derivative of the simple perovskite structure (left).⁴⁰

Table 1.1 summarizes the reported electrical (σ_e) and ionic (σ_i) conductivities of selected single and double perovskite materials that have been investigated for high-temperature electrochemical applications. These values are presented at different temperatures (900 °C, 800 °C, 700 °C, 600 °C, and 500 °C) to enable direct comparison of transport properties under relevant operating conditions. The table also includes the crystal structure (phase) and corresponding literature references for each composition. Ni and YSZ are not perovskites, but they are common SOFC/SOEC materials and are included in Table 1.1 for reference purposes.

Table 1.1. Comparison of reported conductivities of selected single and double perovskite materials

Composition	$\sigma_e/S\text{ cm}^{-1}$			$\sigma_i/S\text{ cm}^{-1}$			Phase	Ref.
Single perovskites/°C	900	800	600	900	800	600		

Table 1.1 continued

Ni-YSZ (15 vol.%)	0.103	-	-	-	-	-	Cubic	42
(30 vol.%)	40	-	-	-	-	-	Cubic	42
(50 vol.%)	989	-	-	-	-	-	Cubic	42
Ni-YSZ	-	495	-	-	-	-	Cubic	43
LaCoO _{3-δ}	1259	1122	1000	-	-	-	Cubic	44
La _{0.8} Sr _{0.2} CoO _{3-δ}	1125	1221	1375	-	-	-	-	45
La _{0.8} Sr _{0.2} FeO _{3-δ}	84	87	90	-	-	-	-	45
La _{0.6} Sr _{0.4} Co _{0.8} Fe _{0.2} O _{3-δ}	-	359	489	-	8.1×10^{-2}	1.2×10^{-2}	-	46
LaCo _{0.8} Fe _{0.2} O _{3-δ}	-	-	-	-	3.9×10^{-3}	3.5×10^{-4}	-	46
LaCo _{0.2} Fe _{0.8} O _{3-δ}	9	4.2	-	-	-	-	-	47
La _{0.6} Sr _{0.4} CoO _{3-δ}	-	-	-	-	0.393	4.8×10^{-2}	-	46
La _{0.8} Sr _{0.2} MnO ₃	300	-	-	5.9×10^{-7}	-	-	Cubic	48, 49
Double perovskites								
Sr _{2-x} MgMoO _{6-δ} (SMMO, x = 0-0.15)	-	15.7	-	-	-	-	Triclinic	50
Sr ₂ FeTiO _{6-δ} (SFT)	-	-	2.83	-	-	-	Cubic	51
Sr ₂ Fe _{1.5} Mo _{0.5} O _{6-δ} (SFMO) Co-doped	-	51.96 59.48	-	-	-	-	Cubic	52
Sr ₂ FeMoO _{6-δ} (SFMO)	-	25	-	-	-	-	Cubic	53
PrBa _{0.92} CoCuO _{6-δ}	-	134	-	-	-	-	Orthorhombic	54
Sr ₂ Fe _{1-x} Co _x NbO ₆ (SFCN, x = 0.9)	-	5.7	-	-	-	-	Tetragonal	55
Sr _{1.9} VMoO _{6-δ} (SVMO)	-	574 508	-	-	-	-	Cubic Cubic	43 43
Pd-impregnated SVMO								

Table 1.1 continued						
	100 – 850 °C					
Sr _{1.9} VMoO _{6-δ} (SVMO)	1364 – 499	-	-	-	Cubic	43
Pd-impregnated SVMO.	1267 – 458	-	-	-	Cubic	43

History of Double Perovskites Research

Double perovskites (A₂BB'O₆) began attracting scientific attention in the 1950s and early 1960s, when crystallographic studies showed that two different cations could share the B site of a perovskite structure in an ordered rock-salt arrangement.⁵⁶ This B-site ordering was found to depend mainly on differences in ionic size and charge between the two cations, and these differences strongly influence crystal symmetry, octahedral tilting, and overall structural stability.⁵⁶⁻⁵⁸ A clear and widely accepted classification of B-site ordering patterns was later provided by Anderson *et al.*³⁹ who defined the structural principles governing rock-salt, layered, and columnar cation arrangements. The broader structural chemistry and compositional flexibility of double perovskite oxides were comprehensively reviewed by Vasala and Karppinen,³¹ who summarized stability criteria, tolerance factor effects, and structure-property relationships across many compounds. These studies firmly established double perovskites as a structurally versatile and chemically tunable family of materials.

A major advance occurred in 1998 when Kobayashi *et al.*⁵⁹ reported large room-temperature magnetoresistance in Sr₂FeMoO₆. From the mid-2000s onward, double perovskites became important in energy-related applications; for example, Sr₂Mg_{1-x}Mn_xMoO_{6-δ} was shown to be a redox-stable and sulfur-tolerant anode material for SOFCs.⁶⁰ Overall, the development of

double perovskites has progressed from fundamental structural studies to advanced applications in magnetism, multiferroics, energy conversion, and semiconductor materials.^{31, 39, 59, 61, 62}

The first experimental work demonstrating DP oxides being used as SOFC electrodes was performed in the late 2000s. In 2006, Huang *et al.* reported high resistance to carbon deposition and excellent tolerance to sulfur in natural gas for the B-site ordered DP $\text{Sr}_2\text{MgMoO}_{6-\delta}$. This material was also shown to be stable with a variety of fuels and showed excellent performance as an SOFC anode.^{60, 63} Marrero-Lopez *et al.*⁶⁴ and Bernuy-Lopez *et al.*⁶⁵ performed stability tests on $\text{Sr}_2\text{MgMoO}_{6-\delta}$ DP oxides under reducing conditions. The results showed this material to be stable under 5% H_2/N_2 up to 1000 °C and 5% H_2/Ar up to 1200 °C respectively. In 2009, Huang *et al.* reported the SOFC anode performance for the Sr_2MMoO_6 series (M = Co, Ni). The results showed that an $\text{Sr}_2\text{CoMoO}_6$ anode produced a high cell output performance in H_2 and wet CH_4 while an $\text{Sr}_2\text{NiMoO}_6$ anode showed a high cell output performance only in dry CH_4 .⁶⁶

Throughout these early studies, a central theme has remained consistent: scientists have systematically varied the size, valence state, and electronic configuration of the ions within the DP structure and correlated how these changes affect material behavior.⁶⁷⁻⁷⁰ Such variations strongly influence magnetic ordering, electronic conductivity, charge transport mechanisms, and overall crystal chemistry. By adjusting these parameters, researchers have worked to uncover structure-property relationships that explain why certain DPs exhibit desirable behaviors - such as high electrical conductivity, magnetoresistance, or structural stability-while others do not.^{59,}

Overall, these studies show that the properties of double perovskites mainly come from their crystal structure, especially how the cations are arranged and how the oxygen octahedra are connected. It is important to understand where the A, B and B' ions sit in the lattice and how factors like cation ordering, ionic size, and charge affect this arrangement, because these directly control how the material behaves. For this reason, a clear understanding of the structure of double perovskites is essential for linking composition to properties and for designing better materials for energy and other applications.

Structure of Double Perovskites

The crystal structure and space group of DPs with the general formula $A_2B'B''O_6$ are largely controlled by how the two types of octahedra - $B'O_6$ and $B''O_6$ – are positioned within the lattice, especially the extent of their ordering and their tilting patterns. Depending on how the B-site cations are arranged, DPs can form three main structural configurations: random, rock-salt, and layered arrangements,³⁹ as illustrated in Figure 6 and summarized in Table 2.1.

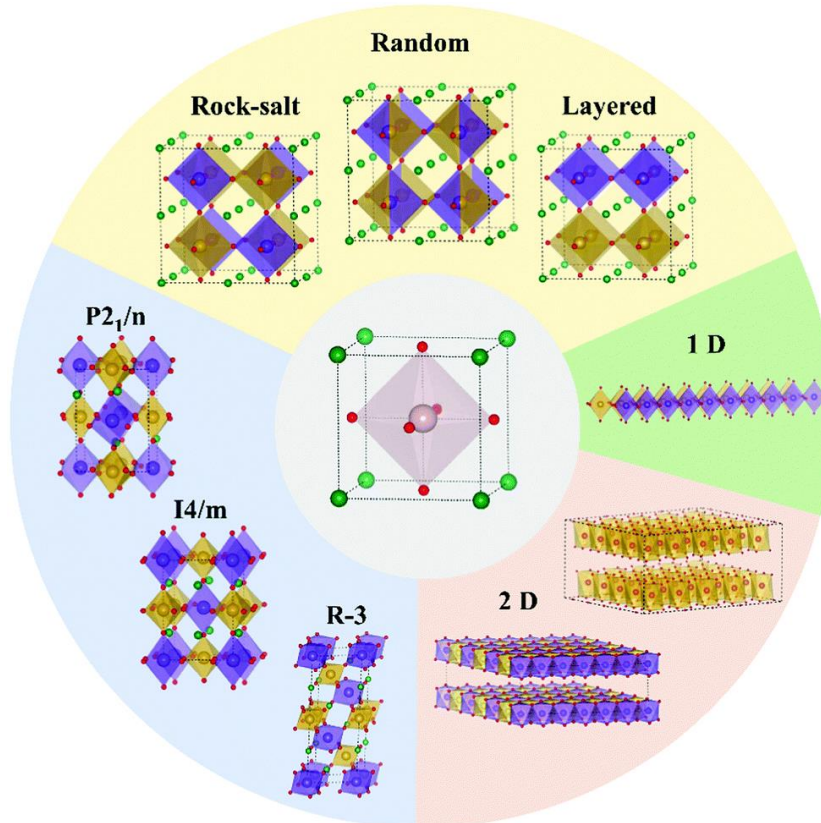


Figure 6.1. Structural flexibility of oxide perovskites. The central image shows the simple cubic perovskite structure, while the surrounding figures illustrate the formation of double perovskites with different types of B-site ordering, including rock-salt, random, and layered arrangements. Octahedral tilting within the $[\text{BO}_6]$ framework can transform the cubic structure into several lower-symmetry tilt systems, three of which are shown at the bottom left. Under large octahedral distortions, the three-dimensional connectivity of the $[\text{BO}_6]$ network can break down, giving rise to two-dimensional and one-dimensional perovskite-derived structures.³⁸

In summary, Figure 6.1 shows how flexible the perovskite structure can be. Starting from a simple cubic arrangement, small changes in how the B-site cations are ordered or how the oxygen octahedra tilt can lead to many different structures. These changes can lower the symmetry or even break the three-dimensional network into layered or chain-like forms. This structural flexibility is one of the key reasons why perovskite materials, including double

perovskites, can exhibit such a wide range of properties and can be tailored for different applications.

1. Random Compounds with a randomly arranged B-site sublattice usually form a cubic unit cell with lattice parameter a_p , as seen in materials such as BaLaFeMoO₆,⁷³ BaLaScMoO₆,⁷³ and BaLaScZrO₆.⁷³ In other cases, they adopt an orthorhombic unit cell with dimensions $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$, such as in SrLaCuRuO₆.⁷⁴ An orthorhombic structure typically appears when the A-O bond length is smaller than $\sqrt{2}$ times the B-O bond length. Compounds with a random B-site sublattice, show no evidence of B-cation ordering.

2. Rock Salt In contrast to materials with a random B-site sublattice, compounds that exhibit rock-salt B-site ordering typically form either a cubic unit cell with lattice parameter $2a_p$, as seen in Sr₂CuWO₆,⁷⁵ Ba₂PrPtO₆,⁷⁶ LaCaMnCoO₆,⁷⁷ and Ba₂CaOsO₆,⁷⁸ or a monoclinic unit cell with dimensions $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$. Examples of the latter include Sr₂LuRuO₆,⁷⁹ Ca₂YRuO₆,⁸⁰ Nd₂MgTiO₆,⁸¹ Ba₂LaRuO₆,⁸² and Ca₂LaRuO₆,⁸² NaLaMgWO₆,⁸³ Sr₂CaUO₆,⁸⁴ and Ca₃UO₆.⁸⁵ Compounds that have a rock-salt B-site sublattice show clear evidence of B-cation ordering. In a cubic cell, ordering is indicated by a doubling of the lattice parameter relative to a random B-site arrangement.^{79-82, 84, 86, 87} SVMO, the focus of this dissertation, adopts a rock-salt structure.

3. Layered The only known compound with a layered B-site arrangement, La₂CuSnO₆,⁸⁸ adopts a monoclinic unit cell with dimensions $2a_p \times 2a_p \times 2a_p$. This layered structure can be distinguished from a random B-site sublattice by its larger $2a_p \times 2a_p \times 2a_p$ cell, instead of the simple cubic $a_p \times a_p \times a_p$ unit cell. It can also be distinguished from rock-salt-ordered structures, which typically show a $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ cell.

Table 2.1. Crystallographic information for common double perovskites

Sublattice type	Cell size	Crystal system	Space group
Random	$1a_p \times 1a_p \times 1a_p$	Cubic	$Pm\bar{3}m$ ^{58, 75, 89}
	$\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$	Orthorhombic	$Pbnm$ ^{74, 86}
Rock salt	$2a_p \times 2a_p \times 2a_p$	Cubic	$Fm\bar{3}m$ ^{56, 75-77, 90-94}
	$\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$	Monoclinic	$P2_1/n$ ^{79-87, 91}
Layered	$2a_p \times 2a_p \times 2a_p$	Monoclinic	$P2_1/m$ ⁸⁸

Table 2.1 summarizes the main crystallographic structures found in common double perovskites by comparing their cation arrangement, unit cell size, crystal system, and space group. Random DPs typically have smaller unit cells ($1a_p \times 1a_p \times 1a_p$ or $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$) and adopt cubic or orthorhombic structures with space groups such as $Pm\bar{3}m$ and $Pbnm$. Rock-salt ordered DPs generally have a larger unit cell ($2a_p \times 2a_p \times 2a_p$ or $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$) and are commonly cubic ($Fm\bar{3}m$) or monoclinic ($P2_1/n$). Layered DPs also have a doubled unit cell ($2a_p \times 2a_p \times 2a_p$) but crystallize in a monoclinic system with space group $P2_1/m$. Overall, the table shows that the type of B-site cation ordering (random, rock-salt, or layered) strongly influences the symmetry, unit cell size, and space group of double perovskite structures.

Properties of Double Perovskites

Electrical Conductivity A suitable anode material for solid oxide fuel cells should combine several key properties. It must exhibit high electronic conductivity and sufficient ionic conductivity across a wide range of oxygen partial pressures. The anode should also show strong electrocatalytic activity for fuel oxidation. In addition, it must be chemically stable and thermally compatible with the electrolyte and interconnect materials under typical SOFC operating conditions.^{27, 28}

Double perovskite materials have attracted considerable interest because of their high electrical conductivity. To enhance and understand this property, several double perovskite series have been studied through isovalent and aliovalent cation substitutions at the A, B', and B'' lattice sites.^{95, 96} Among these materials, Mo-based double perovskites show particularly high electrical conductivity.⁹⁷ Compounds with the general formula Sr_2MMoO_6 (where M = Mg, Mn, Fe, Co, Ni, Zn, etc.) have therefore been widely investigated under different atmospheres, including air, H_2 , H_2 -Ar, and CH_4 , at intermediate temperatures.⁹⁸⁻¹⁰¹ As a result, several double perovskite systems have been explored as potential anode materials for solid oxide fuel cells (SOFCs).¹⁰²⁻¹⁰⁷ Among these, doped double perovskites are of particular interest because they show good chemical and thermal compatibility with commonly used electrolyte materials.^{95, 108} For example, Fe doping in the $\text{Sr}_2\text{MgMoO}_{6-\delta}$ system has been shown to increase electrical conductivity with increasing dopant concentration.⁹⁷ Similarly, Mn substitution at the Mg site in $\text{Sr}_2\text{Mg}_{1-x}\text{Mn}_x\text{MoO}_{6-\delta}$ enhances catalytic activity.¹⁰⁹

The $\text{Sr}_2\text{NiMoO}_{6-\delta}$ system has also emerged as a promising SOFC anode material due to its high electronic conductivity, good catalytic activity, and excellent thermal stability with other cell components.⁶⁶ Its electrical conductivity has been reported to lie in the range of 0.1-250 S

cm^{-1} under reducing atmospheres.¹¹⁰ Furthermore, $\text{Sr}_2\text{NiMoO}_{6-\delta}$ exhibits stable electrical conductivity and a thermal expansion coefficient well matched with that of the LSGM electrolyte.¹⁰⁸ In addition, rare-earth doping (such as La^{3+} and Sm^{3+}) at the Sr site in $\text{Sr}_2\text{MgMoO}_{6-\delta}$ has been reported to improve electrocatalytic activity by enhancing fuel oxidation and overall electrochemical performance.^{111, 112} However, the formation of secondary phases, such as SrMoO_4 , has been observed in some of these systems and may impact their structural and electrical properties.^{95, 113-115} Vasala *et al.*¹¹⁶ reported that the presence of SrMoO_4 impurity can increase electrical conductivity after its reduction to SrMoO_3 , while also helping to suppress Mo evaporation during high-temperature synthesis of $\text{Sr}_2\text{MgMoO}_{6-\delta}$.

Presto *et al.*¹¹⁷ studied the electrical properties of $\text{Sr}_2\text{NiMoO}_6$, $\text{Sr}_{1.96}\text{La}_{0.04}\text{NiMoO}_6$, and $\text{Sr}_{1.99}\text{Ce}_{0.01}\text{NiMoO}_6$ under reducing conditions relevant to solid oxide fuel cells. All three materials showed higher electrical conductivity and lower activation energy in a reducing atmosphere than in air, indicating improved charge transport under fuel-rich conditions. Among them, the La-doped composition exhibited the highest conductivity and remained chemically and structurally stable after high-temperature reduction. These results indicate that $\text{Sr}_{1.96}\text{La}_{0.04}\text{NiMoO}_6$ is a promising anode material for solid oxide fuel cells and warrants further study under operating conditions to assess its performance and long-term durability.

MIEC double perovskite oxides with the formula A_2FeMoO_6 ($\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$) have been investigated as potential anode materials for solid oxide fuel cells.¹¹⁸ These materials are attractive because they can efficiently transport charge under reducing conditions. In a hydrogen atmosphere, $\text{Ba}_2\text{FeMoO}_6$, $\text{Sr}_2\text{FeMoO}_6$, and $\text{Ca}_2\text{FeMoO}_6$ show high electrical conductivities of about 243, 302, and 561 S cm^{-1} , respectively, which are comparable to those of conventional

NiO-electrolyte anodes. This demonstrates that A_2FeMoO_6 compounds can deliver excellent electrical performance without using nickel, making them promising nickel-free anode materials for SOFC operation in fuel-rich environments.

Xie *et al.*¹¹⁹ reported that Al doping significantly enhances the electrical conductivity of Sr_2MgMoO_6 . The conductivity increases with increasing Al content and strongly depends on the reduction temperature, with samples reduced at higher temperatures showing higher conductivity due to increased molybdenum reduction. In addition, $Sr_2Mg_{0.95}Al_{0.05}MoO_6$ exhibits good structural recoverability and stable electrical conductivity, as well as good structural stability under different oxygen partial pressures. This composition also shows excellent chemical compatibility with GDC and LSGM electrolytes at temperatures below 1000 °C. Furthermore, Al substitution improves the electrochemical performance of $Sr_2Mg_{1-x}Al_xMoO_6$ anodes in hydrogen. These results indicate that $Sr_2Mg_{1-x}Al_xMoO_6$ is a promising anode material for SOFC applications.

Ionic Conductivity. For efficient operation of a solid oxide fuel cell (SOFC), the electrolyte must conduct oxide ions (O^{2-}) effectively while remaining electronically insulating. This strategy ensures that charge is transported by ions rather than electrons, preventing internal short-circuiting and maintaining high energy conversion efficiency. In practice, an ionic conductivity of at least 0.1 S cm^{-1} at the operating temperature is widely regarded as the minimum requirement for viable SOFC electrolytes.¹ Among single perovskite oxides, oxide ion transport occurs mainly through oxygen vacancies and is strongly influenced by defect chemistry and crystal structure. A notable example is $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGM), which exhibits conductivities of about $0.15 - 0.20 \text{ S cm}^{-1}$ at 800 °C, significantly higher than YSZ at the same

temperature.¹²⁰ However, many single perovskite materials show mixed ionic-electronic conduction. Although this property is beneficial for electrode applications, it is undesirable for electrolytes because electronic conduction lowers cell efficiency.¹²¹ Ceria-based materials, particularly gadolinium-doped ceria (GDC) and samarium-doped ceria (SDC), offer some of the highest oxide-ion conductivities in the intermediate-temperature range, reaching approximately $0.10 - 0.12 \text{ S cm}^{-1}$ at $700 - 800 \text{ }^{\circ}\text{C}$.¹²² Their main limitation is partial electronic conduction under reducing conditions due to the reduction of Ce^{4+} to Ce^{3+} . Despite this drawback, doped ceria remains one of the most widely used electrolyte materials for intermediate-temperature SOFCs.¹²³

Metal oxides that exhibit high oxide-ion conductivity at relatively low operating temperatures ($\sim 600 \text{ }^{\circ}\text{C}$) are of significant technological importance, as they enable the development of solid oxide fuel cells (SOFCs) that are more efficient, durable, and commercially viable.^{124, 125} Thangadurai *et al.*¹²⁶ studied the ionic conductivity of anion-deficient, ordered perovskite oxides with the general composition $\text{Ba}_2\text{BB}'\text{O}_{5.5}$ ($\text{B} = \text{Li}$ or Na ; $\text{B}' = \text{Mo}$, W , or Te). They found that these materials exhibit significant oxide-ion conductivity, on the order of $10^{-2} - 10^{-3} \text{ S cm}^{-1}$ at $700 \text{ }^{\circ}\text{C}$.

Xie *et al.*¹²⁷ examined the temperature-dependent electrical and ionic transport behavior of $\text{Sr}_2\text{Mg}_{1-x}\text{Co}_x\text{MoO}_{6-\delta}$ ($x = 0, 0.3$, and 0.7) and showed that replacing Mg with Co markedly improves both electronic and ionic conductivity relative to the undoped $\text{Sr}_2\text{MgMoO}_{6-\delta}$. They observed that charge transport increases systematically with increasing Co content over the investigated temperature range. Density-of-state (DOS) calculations indicated that Co substitution significantly reduces the electronic band gap, making electron hopping easier and

thereby enhancing electronic conductivity. In addition, the weaker Co-O bonds introduce greater lattice flexibility and promote the formation of oxygen vacancies. These defects lower the activation energy for oxygen-ion migration, leading to enhanced ionic conductivity of about $10^{-3} - 10^{-4} \text{ S cm}^{-1}$. The authors concluded that ionic conductivity increases systematically with Co substitution: $\text{Co (0.7)} > \text{Co (0.3)} > \text{Co (0)}$.

Catalysis. Catalysis is one of the most important parts of fuel oxidation in solid oxide fuel cells (SOFCs). At the anode, the fuel reacts with oxide ions coming from the electrolyte to produce electrons, and this only happens efficiently when the electrode has good catalytic activity. A good catalyst lowers the energy barrier for the reaction, speeds up fuel oxidation, and helps the cell deliver high power with lower losses. Catalysis is also important because SOFC anodes often do more than one job at once: they support the electrochemical oxidation step, assist fuel reforming and related surface reactions. For this reason, the catalytic properties of anode materials are directly linked to SOFC performance, fuel flexibility, resistance to carbon deposition and sulfur poisoning, and long-term stability.¹²⁸⁻¹³²

The double perovskite $\text{Sr}_2\text{FeNb}_{0.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ (SFNM20) has been identified as a promising ceramic electrode material for solid oxide fuel cells operating directly on hydrocarbon fuels.¹⁰³ It performs well under different fuel conditions and maintains high electrochemical activity. At 800 °C, the SFNM20 anode has an electrical conductivity of about 5.3 S cm^{-1} in an atmosphere containing 5% H_2 . Under these conditions, the fuel cell reaches a maximum power density of 520 mW cm^{-2} when hydrogen is used as the fuel, and 380 mW cm^{-2} when methane is used. When exposed to methane, the material resists carbon build-up, even in the absence of excess steam. The fuel cell also remains stable at different current levels, which is linked to the strong and

stable crystal structure of SFNM20 in reducing atmospheres. Furthermore, the material shows excellent redox stability and quickly regains its performance after oxidation-reduction cycles. These findings indicate that SFNM20 can serve as an efficient nickel-free anode with high catalytic activity for fuel oxidation.¹⁰³

$\text{Sr}_2\text{MgMoO}_{6-\delta}$ (SMMO) has also been reported to exhibit a high MIEC properties and strong catalytic activity for fuel oxidation.^{60, 63, 133} SOFC single cells incorporating SMMO anodes have achieved power densities of 838, 829, and 438 mW cm^{-2} at 800 °C when operated in H_2 , H_2 with 5 ppm H_2S , and CH_4 , respectively. These cells are durable, with only minor performance loss after 50 redox cycles. Moreover, no carbon or sulfur deposits are detected, indicating strong resistance to carbon coking and sulfur poisoning.⁶³ Double-perovskite oxides in the $\text{A}_2\text{FeMoO}_{6-\delta}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) family have attracted significant attention because of their excellent catalytic activity, particularly for methane oxidation,¹³⁴ while remaining structurally stable at temperatures up to 1200 °C under low oxygen partial pressures.¹³⁵ Their catalytic performance is closely linked to their high electronic conductivity, strong electron delocalization, and the oxidation states and ordering of the B-site cations.^{134, 136}

Stability. The redox stability of $\text{Sr}_2\text{MgMoO}_{6-\delta}$ has been widely investigated, but the reported findings are inconsistent.^{64, 65, 105, 137-140} Some studies have shown that $\text{Sr}_2\text{MgMoO}_{6-\delta}$ partially decomposes above 900 °C in a hydrogen atmosphere, forming a Ruddlesden-Popper phase with the composition $\text{Sr}_3\text{Mo}_2\text{O}_7$.^{65, 137} In contrast, other reports indicate that this material retains structural stability at temperatures up to 1200 °C.^{63, 64, 139} Furthermore, the $\text{Sr}_2\text{MgMoO}_6$ perovskite structure has been found to partially degrade when exposed to air and CH_4 – containing atmospheres, primarily due to the formation of carbonate species.^{105, 140} Chemical

interactions have been reported between $\text{Sr}_2\text{MgMoO}_{6-\delta}$ and commonly used SOFC electrolytes, particularly zirconia-based systems.¹⁰⁵ This reactivity limits the choice of compatible electrolytes for SOFC fabrication. Often, a protective interlayer, such as $\text{La}_{0.6}\text{Ce}_{0.4}\text{O}_{2-\delta}$ or $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$, is introduced between the anode and electrolyte to suppress unwanted interfacial reactions.^{60, 63, 105}

dos Santos-Gómez *et al.*¹⁴¹ studied the phase stability of $\text{Sr}_2\text{CoMoO}_6$ (SCMO), $\text{Sr}_2\text{NiMoO}_6$ (SNMO), and $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ (SFMO) anode under hydrogen and CO_2 atmospheres to assess their resistance to reduction and CO_2 -induced degradation. Both SCMO and SNMO were found to be *unstable* in these environments, undergoing partial decomposition. In hydrogen, these materials decomposed into SrMoO_3 , Sr_3MoO_6 , and metallic Co or Ni, while in CO_2 , they formed SrMoO_4 and Sr_3MoO_6 . In contrast, SFMO maintained its structural integrity under both hydrogen and CO_2 atmospheres, indicating superior phase stability. However, all these prospective anode materials react with YSZ electrolytes at temperatures as low as 800 °C, leading to the formation of secondary phases such as SrMoO_4 and SrZrO_3 . SrMoO_4 is particularly troublesome in these devices as it is both an electronic and ionic insulator. Reactions between SCMO and LSGM or CGO electrolytes have also been observed at 800 °C, resulting in SrMoO_4 formation.

Applications of Double Perovskite Oxides

Double perovskite oxides are structurally versatile and possess wide range of functional properties. Due to their mixed ionic-electronic conductivity, these materials are widely used in

energy conversion and storage applications, including solid oxide fuel cells (SOFCs), thermochemical water-splitting processes, and oxygen separation membranes.¹⁴²⁻¹⁴⁷ They also function as efficient catalysts in CO oxidation and methane reforming.^{60, 63, 133} These materials have been reported to exhibit magnetic and electronic tunability, which makes them valuable in memory technologies, magnetic sensors and spintronic devices.¹⁴⁸

Sr_{2-x}VMoO_{6-δ} Double Perovskite Oxides

The focus of this dissertation is the stability of Sr_{2-x}VMoO_{6-δ} (SVMO). SVMO is a rock-salt ordered DP that has attracted significant attention due to its versatile multivalent cation behavior and complex structural ordering. In this structure, the two B-site cations (V and Mo) are arranged in an ordered, alternating pattern within the BO₆ octahedral framework. Like Sr₂FeMoO₆ (SFMO), SVMO exhibits multiple oxidation states originating from both vanadium and molybdenum, that contribute to its diverse electronic and ionic transport properties.¹⁴⁹ The ordered arrangement of V and Mo ions at the B-sites promotes mixed ionic-electronic conduction, where the coexistence of multiple valencies (V^{3+/4+/5+} and Mo^{4+/5+/6+}) enables flexible charge transport through the lattice.¹⁴⁹ This multivalency allows SVMO to maintain high electrical conductivity even under reducing atmospheres, which is important for its application in SOFCs.¹⁵⁰ Furthermore, the interaction among these variable oxidation states enhances the formation and mobility of oxygen vacancies, improving ionic conductivity and promoting efficient fuel oxidation processes.¹⁵¹ These combined electronic and ionic properties enable SVMO to function efficiently as a mixed ionic-electronic conductor, making it well suited for catalysis and energy conversion applications.¹⁵²

All SVMO materials used in this work were synthesized and processed by members of Prof. Stephen Sofie's research team in the Mechanical and Industrial Engineering Department at Montana State University. Details about the sample synthesis can be found in Chapters 2 and 3 of this thesis. The Sofie Research Group first discovered that SVMO exhibits high electrical conductivity.¹⁵² The double perovskite structure of SVMO is believed to enable long-range ordering of single perovskite phases within its lattice, further promoting oxidation state variations that enhance the material's electrical conductivity. Its high electrical conductivity, especially under reducing conditions, makes SVMO a strong candidate for SOFC applications.¹⁵² As a mixed ionic-electronic conductor, SVMO supports both electron and ion transport, reducing the need for impregnating fuel electrodes with metal catalysts and minimizing metal coarsening that shortens the triple phase boundary (TPB) and limits SOFC durability.¹⁵⁰

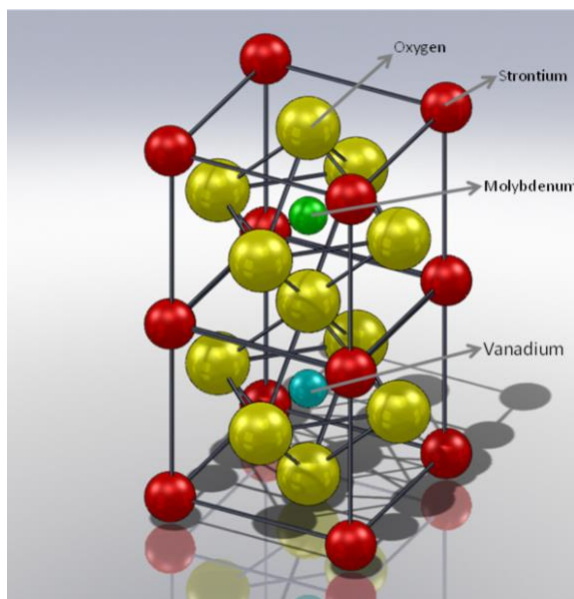


Figure 7.1. Schematic representation of the crystal structure of Sr_2VMoO_6 double perovskite.¹⁵²

Weisenstein *et al.*¹⁵³ and Childs *et al.*¹⁵² reported the synthesis and electrical characterization of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ ($x = 0, 0.1, 0.2$) double perovskites. These materials exhibited exceptional electrical conductivity under reducing conditions. Prominently, Sr_2VMoO_6 demonstrated a conductivity of $12,000 \text{ S cm}^{-1}$ at room temperature in a He-cryostat environment.¹⁵⁴ At 800°C , in a 2.9 % H_2O / 4.9 % H_2 / 92.2 % N_2 atmosphere, the conductivities were 1250, 3610, and 2530 S cm^{-1} for $x = 0, 0.1$, and 0.2 respectively. These values substantially exceed those of the conventional Ni/YSZ anode (50 vol. % Ni; 989 S cm^{-1} at 900°C)⁴² and are well above the reference value of 100 S cm^{-1} typically required for electronic conductivity in SOFC anode material. Among the series, $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ ($x = 0.1$)¹⁵² exhibited the highest electrical conductivity, representing one of the most conductive double perovskite anode materials reported to date. Table 3.1 presents a summary of the reported electrical conductivities for these and other related materials.¹⁵²

Table 3.1. Reported electrical conductivities of Sr_2MMoO_6 and other relevant materials

Composition	Conductivity (S/cm)	Temperature ($^\circ\text{C}$)	Environment	Ref.
Sr_2VMoO_6	12000	25	Air	154
Sr_2VMoO_6	280	900	10% H_2/N_2	155
Sr_2VMoO_6	256	800	vacuum after reduction	156
$\text{Sr}_2\text{FeMoO}_6$	222	800	H_2	157
$\text{Sr}_2\text{MnMoO}_6$	~ 10	800	H_2	63
$\text{Sr}_2\text{MgMoO}_6$	~ 10	800	H_2	63
$\text{Sr}_2\text{MgMoO}_6$	7.7	800	5% H_2/Ar	114
$\text{Sr}_2\text{CrMoO}_6$	2.54	800	5% H_2/Ar	158
$\text{Sr}_2\text{CoMoO}_6$	1.7	800	5% H_2/Ar	66

Sr ₂ CoMoO ₆	4.0	800	H ₂	66
Sr ₂ CoMoO ₆	0.013	800	5% H ₂ /N ₂	159
Sr ₂ CoMoO ₆	0.08	800	15% H ₂	159
Sr ₂ NiMoO ₆	0.07	800	5% H ₂ /Ar	66
Sr ₂ NiMoO ₆	0.45	800	H ₂	66
Ni-YSZ (15vol. % Ni)	0.103	900	H ₂	42
Ni-YSZ (30vol. % Ni)	40	900	H ₂	42
Table 3 continued				
Ni-YSZ (50vol. % Ni)	989	900	H ₂	42
SrVO ₃	100	577	H ₂ /Ar mixture	160
SrMoO ₃	10000	27	cryostat	161
SrMoO ₃ (single crystal)	196000	27	Not reported	162

Motivated by earlier studies showing SVMO to have exceptionally high electrical conductivity ($> 10^4 \text{ S cm}^{-1}$), this dissertation explores several critical aspects of SVMO's structural stability and speculates on the consequences of this stability for high-temperature energy conversion applications. The main objectives are to determine if SVMO remains stable under conditions relevant to SOFC anodes and cathodes, to identify any secondary phases that form during exposure to reducing and oxidizing atmospheres at high temperatures, and to understand the reaction kinetics and energy factors that control secondary phase formation. In addition, the work investigates whether SVMO degradation can be reversed and evaluates SVMO's potential as a high-performance electrode material for SOFCs.

Results reported in this dissertation examine how the double perovskites Sr_{2-x}VMoO_{6-δ} ($x = 0, 0.05, 0.1, 0.15, 0.2$) behave under conditions typically encountered in SOFCs and SOECs. All materials contain equal amounts of V and Mo in the DP B-sites. *In situ* Raman spectroscopy

is used to monitor material stability under inert, reducing, and oxidizing atmospheres at temperatures up to 1000 °C. Data show SVMO to be stable under inert, reducing, and weakly oxidizing atmospheres.¹⁶³ In air, however, SVMO phase separates into a dominant scheelite phase (SrMoO_4) and secondary Sr and V containing phases (SrVO_3 and $\text{Sr}_2\text{V}_2\text{O}_7$).¹⁶³ TGA data corroborate these findings and set a 400 °C minimum threshold for oxygen uptake.¹⁶³ Isothermal Raman and TGA kinetic analyses of SVMO degradation show clearly that scheelite formation is direct without intermediate steps and proceeds via a pair of first order rate processes with the faster process assigned to surface decomposition and the latter process describing secondary phase formation within the bulk material.¹⁶³

Techniques/Experimental Methods

Solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs) operate at high temperatures and in reactive gas environments. For this reason, it is important to study material stability under conditions that closely resemble real operating environments. My Ph.D. research used two primary experimental techniques to perform *in situ* characterization. Raman spectroscopy and thermal gravimetric analysis (TGA) were used to evaluate the thermal and atmospheric stability of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ (SVMO) under carefully controlled temperature and gas conditions. These techniques are described in detail below.

Raman spectroscopy

Raman spectroscopy is a vibrational spectroscopy used to study the structure and bonding of materials. It is based on the inelastic scattering of monochromatic light, usually from a laser source. When light strikes a sample, most photons are scattered without a change in energy (Rayleigh scattering), but a small fraction experience an energy shift. If the scattered photon has lower energy than the incident photon, it is called Stokes Raman scattering. If it has higher energy, it is called anti-Stokes Raman scattering.¹⁶⁴ Stokes scattering leaves the system in a higher vibrational state, while anti-Stokes scattering occurs when the molecule is already in an excited vibrational state and transfers energy to the scattered photon. In Raman spectroscopy, the measured quantity is the energy difference between the incident and scattered photons and is described using the equation $\Delta\bar{\nu} = 10^7 \times \left(\frac{1}{\lambda_i} - \frac{1}{\lambda_s} \right)$, where $\Delta\bar{\nu}$ is the Raman shift expressed in wavenumbers (cm^{-1}), λ_i is the wavelength of the incident light, and λ_s is the wavelength of the scattered light (both in nm). A typical Raman spectrum can extend from $\sim 50 \text{ cm}^{-1}$ to 4500 cm^{-1} . Each spectrum serves as a unique, material-specific fingerprint. The energy shift, $\Delta\bar{\nu}$ depends on the chemical composition and bonding within the material. The intensity of the Raman signal is directly related to the extent of change in molecular polarizability during vibration.¹⁶⁴⁻¹⁷¹

Figure 8 presents a schematic representation of the light-scattering process, illustrating how the interaction of incident radiation with a system can induce changes in its vibrational energy state.

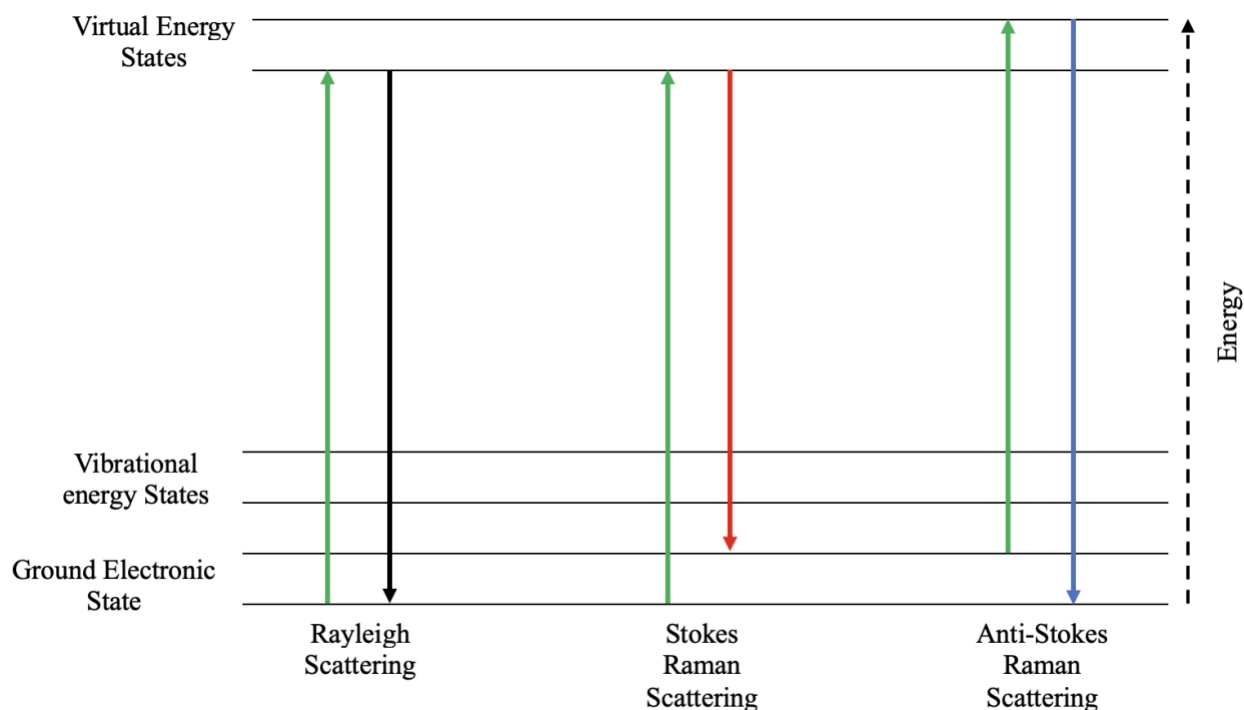


Figure 8.1. Schematic energy level diagram illustrating scattering and absorption processes in vibrational spectroscopy

A typical Raman instrument consists of a laser source, optical components to focus the beam onto the sample, a spectrometer to disperse the scattered light, and a detector, commonly a charge-coupled device CCD. Modern systems are often coupled with optical microscopes that allow measurements from micrometer-sized regions, thin films, or individual grains. Raman spectroscopy is non-destructive, non-contact, and requires minimal sample preparation, and it can be performed under controlled temperature and atmospheric conditions. However, the Raman signal is inherently weak, since only about one in $10^6 - 10^8$ photons undergo Raman scattering.¹⁷² Despite these limitations, Raman spectroscopy remains a powerful and versatile tool for probing structural stability, bonding characteristics, and defect behavior in solid-state materials.¹⁷²

Data acquisition using Raman spectroscopy

In this thesis, the thermal and atmospheric stability of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ (SVMO) was evaluated with *in situ* Raman spectroscopy using continuous wave 488 nm excitation coupled into a Renishaw inVia spectrometer and a Linkam CCR1000 heating stage. Measurements were made as samples were heated from room temperature to 1000 °C in a controlled atmosphere. Raman spectra were collected at intervals of 100 °C, with a heating rate of 10 °C/min between temperatures and a dwell time of 15 min at temperature to equilibrate. Most spectra shown in this work resulted from 3×30 -s accumulations. Incident laser powers were ~30 mW with a ~100 μm spot size using a $5\times$ objective. Incident power at the sample surface was 2.8 mW.

Isothermal Raman experiments were performed to monitor the kinetics of SVMO degradation. Isothermal Raman experiments consisted of heating SVMO to the intended temperature under forming gas. After reaching the target temperature and dwelling for 15 min with no change in the spectrum, the atmosphere was switched from forming gas to air, and spectra were acquired every 5 min. Raman spectra show that SVMO under air at 700 °C takes up O_2 to form SrMoO_4 . (Figure 9.1)

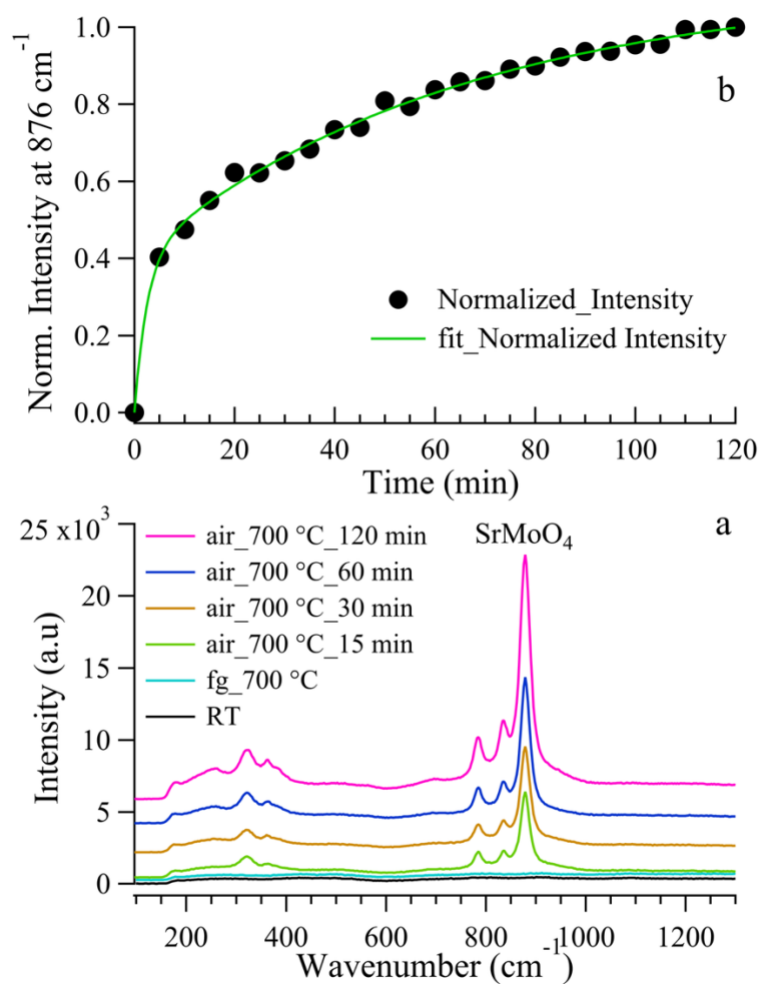


Figure 9.1. (a) In situ Raman spectra of SVMO in 5% H₂ and air from room temperature to 700 °C; (b) Kinetic trace showing the normalized intensity of the SrMoO₄ secondary phase after exposure to air at 700 °C.

The emergence and growth of SrMoO₄ at 876 cm⁻¹ provide direct evidence that SVMO is unstable under conditions commonly encountered as the oxygen electrode in solid oxide electrochemical cells.¹⁶³

Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a technique used to measure changes in a material's mass as a function of temperature or time under a controlled atmosphere. TGA uses sensitive balance combined with a precisely controlled furnace. In a typical experiment, a small quantity of sample is placed in a pan attached to a microbalance inside a programmable furnace. The sample is either heated at a constant rate or maintained at a fixed temperature (isothermal TGA), while the mass is continuously monitored. The TGA instrument used in this dissertation allows experiments to be performed under both inert and oxidizing atmospheres. The resulting TGA data provide information about processes such as decomposition, oxidation and overall thermal stability.¹⁷³

In this dissertation, TGA experiments characterized SVMO thermal and chemical stability. Experiments were performed using a TA-TGA 5500 instrument, measuring weight gain as a function of temperature in both inert (N₂) and oxidizing (air) atmospheres. The analysis covered a temperature range from room temperature to 900 °C, with a heating rate of 5 °C/min and a flow rate of 25 mL/min. Measurement reproducibility measured mass changes as small as ± 0.01 %.

Pseudo-isothermal TGA measurements were performed by ramping the temperature as quickly as possible (50 °C/min) to the target temperature and then maintaining a constant temperature for the duration of the experiment. Representative TGA data in Figure 10a show that SVMO is stable under N₂ at temperatures up to 900 °C. The slight gain in mass (0.1%) is associated with instrument drift. In contrast, SVMO being heated in air shows mass accumulation beginning at ~400 °C with sample mass growing steadily before asymptotically leveling off near 750 °C. Figure 10b shows pseudo-isothermal experiments where the TGA was ramped as quickly as possible (50 °C/min) to the target temperature in air and then the

temperature was held constant. Data from this experiment show that SVMO begins acquiring mass before reaching its target temperatures (500 °C, 600 °C and 700 °C), but the last ~40 % of the mass gain happens isothermally.

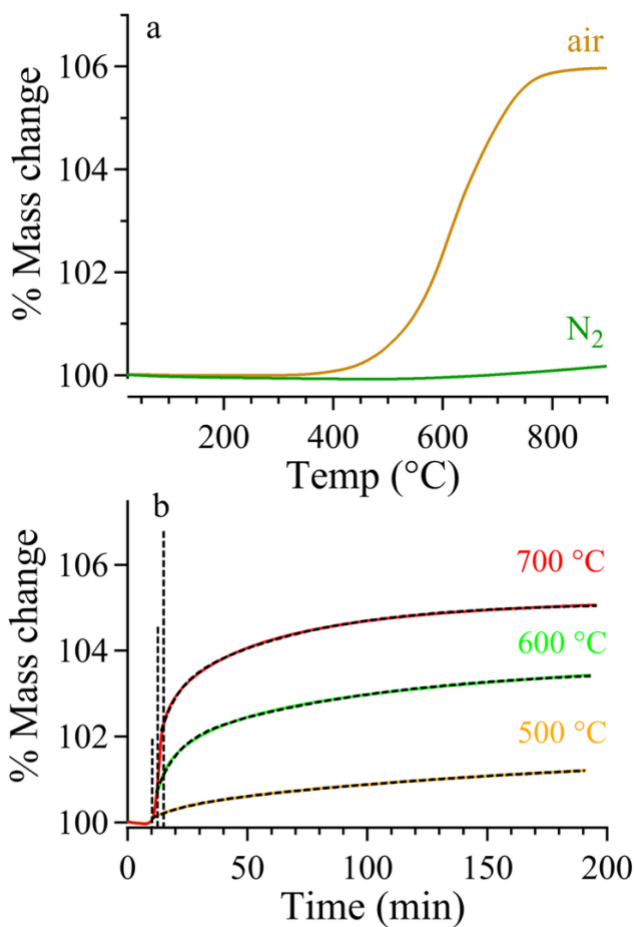


Figure 10.1. (a) TGA curves of SVMO in N_2 and air from 25 to 900 °C (b) Isothermal TGA curves of SVMO in air at 500 °C, 600 °C and 700 °C. The dashed vertical lines correspond to the time when the sample has reached its target temperature. The dashed lines superimposed on the data correspond to fits generated by the double exponential kinetic model.

From these data and the fitted curves in Figures 10b, we determine the temperature-dependent rate constants for SVMO oxidation using two approaches: a simple model with two

independent first-order processes and the Avrami model. Arrhenius analysis from both models gives an activation energy for SVMO degradation in the range of 0.48 – 0.65 eV.

X-ray Diffractometry

To characterize our materials, we also use X-ray diffraction to check for phase purity and to identify and quantify any secondary phase materials that form. XRD is a non-destructive technique used to study the crystal structure of materials. XRD experiments measure the constructive and destructive interference of X-rays scattered by the atomic planes within a crystal. Diffraction occurs at specific angles that satisfy Bragg's law:

$$n\lambda = 2d\sin\theta \quad (\text{Eq. 1.1})$$

where n is an integer representing the diffraction order, λ is the wavelength of the incident X-rays, d is the spacing between the crystallographic planes, and θ is the angle of incidence.¹⁷⁴

In a typical XRD measurement, the diffracted intensity is recorded as a function of 2θ . The positions of the diffraction peaks are determined by the crystal's lattice parameters, which vary with its symmetry. For a simple cubic crystal, the unit cell is defined by a single lattice constant a , which represents the length, width, and height of the cell, and all interaxial angles (α , β , γ) are 90° . In this case, the spacing d between adjacent lattice planes is directly related to a . In contrast, a monoclinic crystal has lower symmetry, with three independent lattice constants (a , b , c) and interaxial angles where $\beta \neq 90^\circ$. Therefore, the relationship between the interplanar spacing d and the lattice parameters is more complex and must be calculated using the general monoclinic lattice equation:

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta} \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} + \frac{2hlc\cos\beta}{ac} \right] \quad (\text{Eq. 1.2})$$

In this dissertation, X-ray powder diffraction (XRD) was used to confirm the double perovskite crystal structure in SVMO samples. Experiments were conducted using a Bruker D8 Advance powder X-ray diffractometer (PXRD) with Cu K α radiation, operating at 40 kV and 40 mA, equipped with a Ni filter. The analysis utilized an angle step size of 0.02° over a scanning range of 5 - 80° to identify phases and assess phase purity. Rietveld refinement provided data about each sample's phase purity.

Research in this dissertation is motivated by the need to establish a clear link between material composition and both, thermal and chemical stability in DP oxides. While many studies have explored DP oxide synthesis and functional performance, fewer have addressed the mechanisms governing secondary phase evolution and their impact on long-term material integrity. Studies described in Chapters 2 and 3 carefully investigate how composition, temperature, and pO₂ influence phase stability and transformational kinetics in sample DP systems. By identifying the thermodynamic and kinetic parameters that control secondary phase formation, this work provides a framework for designing chemically and structurally stable DP oxides optimized for use in solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs). Ultimately, the knowledge gained will contribute to the development of durable, high-performance oxide materials capable of supporting future sustainable energy technologies.

References

- (1) Minh, N. Q. Solid oxide fuel cell technology—features and applications. *Solid State Ionics* **2004**, 174 (1-4), 271-277.
- (2) Steele, B. C.; Heinzel, A. Materials for fuel-cell technologies. *Nature* **2001**, 414 (6861), 345-352.
- (3) Laguna-Bercero, M. A. Recent advances in high temperature electrolysis using solid oxide fuel cells: A review. *Journal of Power sources* **2012**, 203, 4-16.
- (4) Golkhatmi, S. Z.; Asghar, M. I.; Lund, P. D. A review on solid oxide fuel cell durability: Latest progress, mechanisms, and study tools. *Renewable and Sustainable Energy Reviews* **2022**, 161, 112339.
- (5) Singhal, S. C.; Kendall, K. Introduction to SOFCs. High temperature and solid oxide fuel cells **2003**, 1-22.
- (6) Klyndyuk, A. I.; Chizhova, E. A.; Kharytonau, D. S.; Medvedev, D. A. Layered oxygen-deficient double perovskites as promising cathode materials for solid oxide fuel cells. *Materials* **2021**, 15 (1), 141.
- (7) Skutina, L.; Filonova, E.; Medvedev, D.; Maignan, A. Undoped Sr₂MMoO₆ double perovskite molybdates (M= Ni, Mg, Fe) as promising anode materials for solid oxide fuel cells. *Materials* **2021**, 14 (7), 1715.
- (8) Zhang, B.; Zhang, S.; Han, H.; Tang, K.; Xia, C. Cobalt-free double perovskite oxide as a promising cathode for solid oxide fuel cells. *ACS Applied Materials & Interfaces* **2023**, 15 (6), 8253-8262.
- (9) Bode, G. L.; McIntyre, M. D.; Neuberger, D. M.; Walker, R. A.; Thorstensen, B. P.; Eigenbrodt, B. C. Electrochemical and Operando Spectroscopic Studies of Sr₂Fe₁₋₅Mo_{0.5}O_{6-δ} Anode Catalysts in Solid Oxide Fuel Cells Operating with Direct Alcohol Fuels. *ChemElectroChem* **2018**, 5 (21), 3162-3168.
- (10) Hussain, A. M.; Pan, K.-J.; Huang, Y.-L.; Robinson, I. A.; Gore, C.; Wachsman, E. D. Highly Performing Chromate-Based Ceramic Anodes (Y_{0.7}Ca_{0.3}Cr_{1-x}Cu_xO_{3-δ}) for Low-Temperature Solid Oxide Fuel Cells. *ACS Applied Materials & Interfaces* **2018**, 10 (42), 36075-36081.
- (11) Xu, J.; Zhou, X.; Dong, X.; Pan, L.; Sun, K. Catalytic activity improvement for efficient hydrogen oxidation of infiltrated La_{0.3}Sr_{0.7}Ti_{0.3}Fe_{0.7}O_{3-δ} anode for solid oxide fuel cell. *Ceramics International* **2017**, 43 (14), 10750-10756.

- (12) Ahmed, K.; Foger, K. Kinetics of internal steam reforming of methane on Ni/YSZ-based anodes for solid oxide fuel cells. *Catalysis today* **2000**, 63 (2-4), 479-487.
- (13) Fernández-González, R.; Ruiz-Morales, J. C.; Canales-Vázquez, J.; Jurado, J. R.; Makradi, A.; Núñez, P. Decreasing the polarisation resistance of a Ni-YSZ solid oxide fuel cell anode by infiltration of a ceria-based solution. *International Journal of Hydrogen Energy* **2016**, 41 (43), 19731-19736.
- (14) Lu, Y.; Gasper, P.; Pal, U. B.; Gopalan, S.; Basu, S. N. Improving intermediate temperature performance of Ni-YSZ cermet anodes for solid oxide fuel cells by liquid infiltration of nickel nanoparticles. *Journal of Power Sources* **2018**, 396, 257-264.
- (15) Yue, W.; Li, Y.; Zheng, Y.; Wu, T.; Zhao, C.; Zhao, J.; Geng, G.; Zhang, W.; Chen, J.; Zhu, J. Enhancing coking resistance of Ni/YSZ electrodes: In situ characterization, mechanism research, and surface engineering. *Nano Energy* **2019**, 62, 64-78.
- (16) Kan, W. H.; Samson, A. J.; Thangadurai, V. Trends in electrode development for next generation solid oxide fuel cells. *Journal of Materials Chemistry A* **2016**, 4 (46), 17913-17932.
- (17) Mogensen, M. B.; Chen, M.; Frandsen, H. L.; Graves, C.; Hansen, J. B.; Hansen, K. V.; Hauch, A.; Jacobsen, T.; Jensen, S. H.; Skaftø, T. L. Reversible solid-oxide cells for clean and sustainable energy. *Clean Energy* **2019**, 3 (3), 175-201.
- (18) Wang, Y.; Li, W.; Ma, L.; Li, W.; Liu, X. Degradation of solid oxide electrolysis cells: Phenomena, mechanisms, and emerging mitigation strategies—A review. *Journal of Materials Science & Technology* **2020**, 55, 35-55.
- (19) Gómez, S. Y.; Hotza, D. Current developments in reversible solid oxide fuel cells. *Renewable and Sustainable Energy Reviews* **2016**, 61, 155-174.
- (20) Yang, C.; Guo, R.; Jing, X.; Li, P.; Yuan, J.; Wu, Y. Degradation mechanism and modeling study on reversible solid oxide cell in dual-mode—A review. *International Journal of Hydrogen Energy* **2022**, 47 (89), 37895-37928.
- (21) Kong, X.; Tian, Y.; Zhou, X.; Wu, X.; Zhang, J. Surface tuned La_{0.9}Ca_{0.1}Fe_{0.9}Nb_{0.1}O_{3-δ} based anode for direct methane solid oxide fuel cells by infiltration method. *Electrochimica Acta* **2017**, 234, 71-81.
- (22) Kuramoto, K.; Hosokai, S.; Matsuoka, K.; Ishiyama, T.; Kishimoto, H.; Yamaji, K. Degradation behaviors of SOFC due to chemical interaction between Ni-YSZ anode and trace gaseous impurities in coal syngas. *Fuel Processing Technology* **2017**, 160, 8-18.

- (23) Chinda, P.; Chanchaona, S.; Brault, P.; Wechsato, W. Mathematical modeling of a solid oxide fuel cell with nearly spherical-shaped electrode particles. *Journal of sustainable energy and environment* **2010**, 1, 185-196.
- (24) Khan, M. Z.; Song, R.-H.; Mehran, M. T.; Lee, S.-B.; Lim, T.-H. Controlling cation migration and inter-diffusion across cathode/interlayer/electrolyte interfaces of solid oxide fuel cells: a review. *Ceramics International* **2021**, 47 (5), 5839-5869.
- (25) Koo, B.; Kim, K.; Kim, J. K.; Kwon, H.; Han, J. W.; Jung, W. Sr segregation in perovskite oxides: why it happens and how it exists. *Joule* **2018**, 2 (8), 1476-1499.
- (26) Jacobson, A. J. Materials for solid oxide fuel cells. *Chemistry of Materials* **2010**, 22 (3), 660-674.
- (27) Jiang, S. P.; Chan, S. H. A review of anode materials development in solid oxide fuel cells. *Journal of materials science* **2004**, 39 (14), 4405-4439.
- (28) Mahato, N.; Banerjee, A.; Gupta, A.; Omar, S.; Balani, K. Progress in material selection for solid oxide fuel cell technology: A review. *Progress in Materials Science* **2015**, 72, 141-337.
- (29) Tang, Y.; Zhang, Q.; Liang, J.; Yuan, R.; Gao, S.; Wang, X. Structure-electrochemical performance relationship in Sr₂(Fe_{1-x}V_x)MoO₆ anode. *International Journal of Hydrogen Energy* **2024**, 77, 1205-1216.
- (30) Gao, Z.; Mogni, L. V.; Miller, E. C.; Railsback, J. G.; Barnett, S. A. A perspective on low-temperature solid oxide fuel cells. *Energy & Environmental Science* **2016**, 9 (5), 1602-1644.
- (31) Vasala, S.; Karppinen, M. A₂B'B''O₆ perovskites: a review. *Progress in solid state chemistry* **2015**, 43 (1-2), 1-36.
- (32) Bai, J.; Zhou, D.; Zhu, X.; Wang, N.; Chen, R.; Wang, B.; Yan, W. In-situ segregation of A-site defect (La_{0.6}Sr_{0.4})_{0.90}Co_{0.2}Fe_{0.8}O_{3-δ} to form a high-performance solid oxide fuel cell cathode material with heterostructure. *Ceramics International* **2023**, 49 (4), 5687-5699.
- (33) Jung, W.; Tuller, H. L. Investigation of surface Sr segregation in model thin film solid oxide fuel cell perovskite electrodes. *Energy & Environmental Science* **2012**, 5 (1), 5370-5378.
- (34) Lei, Y.-Q.; Xu, Q.; Huang, D.-P.; Chen, M.; Zhao, K.; Zhang, F. A new look into the surface segregation problem of Fe–Cr based perovskite cathodes enabled by bond valence modeling: A viable solution strategy and the underlying mechanisms. *International Journal of Hydrogen Energy* **2025**, 157, 150350.

- (35) Salman, M.; Saleem, S.; Ling, Y.; Khan, M. Fe-based high-entropy perovskite oxide: A strategy to suppress Sr segregation and performance evaluation as an electrode material for SOFCs. *ACS Applied Energy Materials* **2024**, 7 (19), 8648-8657.
- (36) Yu, Y.; Ludwig, K. F.; Woicik, J. C.; Gopalan, S.; Pal, U. B.; Kaspar, T. C.; Basu, S. N. Effect of Sr Content and Strain on Sr Surface Segregation of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ as Cathode Material for Solid Oxide Fuel Cells. *ACS applied materials & interfaces* **2016**, 8 (40), 26704-26711.
- (37) Tsvetkov, N.; Lu, Q.; Sun, L.; Crumlin, E. J.; Yildiz, B. Improved chemical and electrochemical stability of perovskite oxides with less reducible cations at the surface. *Nature materials* **2016**, 15 (9), 1010-1016.
- (38) Yin, W.-J.; Weng, B.; Ge, J.; Sun, Q.; Li, Z.; Yan, Y. Oxide perovskites, double perovskites and derivatives for electrocatalysis, photocatalysis, and photovoltaics. *Energy & Environmental Science* **2019**, 12 (2), 442-462.
- (39) Anderson, M. T.; Greenwood, K. B.; Taylor, G. A.; Poeppelmeier, K. R. B-cation arrangements in double perovskites. *Progress in solid state chemistry* **1993**, 22 (3), 197-233.
- (40) Saha-Dasgupta, T. Double perovskites with 3d and 4d/5d transition metals: compounds with promises. *Materials Research Express* **2020**, 7 (1), 014003.
- (41) Bhalla, A. S.; Guo, R.; Roy, R. The perovskite structure—a review of its role in ceramic science and technology. *Materials research innovations* **2000**, 4 (1), 3-26.
- (42) Aruna, S.; Muthuraman, M.; Patil, K. Synthesis and properties of Ni-YSZ cermet: anode material for solid oxide fuel cells. *Solid State Ionics* **1998**, 111 (1-2), 45-51.
- (43) Niu, B.; Jin, F.; Fu, R.; Feng, T.; Shen, Y.; Liu, J.; He, T. Pd-impregnated $\text{Sr}_{1-x}\text{VMoO}_{6-\delta}$ double perovskite as an efficient and stable anode for solid-oxide fuel cells operating on sulfur-containing syngas. *Electrochimica Acta* **2018**, 274, 91-102.
- (44) Mizusaki, J.; Tabuchi, J.; Matsuura, T.; Yamauchi, S.; Fueki, K. Electrical conductivity and seebeck coefficient of nonstoichiometric $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$. *Journal of the Electrochemical Society* **1989**, 136 (7), 2082.
- (45) Tai, L.-W.; Nasrallah, M.; Anderson, H. U.; Sparlin, D. M.; Sehlin, S. Structure and electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$. Part 1. The system $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$. *Solid State Ionics* **1995**, 76 (3-4), 259-271.
- (46) Teraoka, Y.; Nobunaga, T.; Okamoto, K.; Miura, N.; Yamazoe, N. Influence of constituent metal cations in substituted LaCoO_3 on mixed conductivity and oxygen permeability. *Solid State Ionics* **1991**, 48 (3-4), 207-212.

- (47) Tai, L.-W.; Nasrallah, M.; Anderson, H. U.; Sparlin, D. M.; Sehlin, S. Structure and electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$. Part 2. The system $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$. *Solid State Ionics* **1995**, 76 (3-4), 273-283.
- (48) Li, Z.; Behruzi, M.; Fuerst, L.; Stöver, D. Crystalline Structure and Electrical Conductivity of Bulk-Sintered and Plasma-Sprayed $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ with $0 \leq x \leq 0.9$. *ECS Proceedings Volumes* **1993**, 1993 (1), 171.
- (49) Yasuda, I.; Ogasawara, K.; Hishinuma, M.; Kawada, T.; Dokiya, M. Oxygen tracer diffusion coefficient of (La, Sr) $\text{MnO}_{3\pm\delta}$. *Solid State Ionics* **1996**, 86, 1197-1201.
- (50) Jiang, L.; Liang, G.; Han, J.; Huang, Y. Effects of Sr-site deficiency on structure and electrochemical performance in $\text{Sr}_2\text{MgMoO}_6$ for solid-oxide fuel cell. *Journal of Power Sources* **2014**, 270, 441-448.
- (51) Li, W.; Cheng, Y.; Zhou, Q.; Wei, T.; Li, Z.; Yan, H.; Wang, Z.; Han, X. Evaluation of double perovskite $\text{Sr}_2\text{FeTiO}_{6-\delta}$ as potential cathode or anode materials for intermediate-temperature solid oxide fuel cells. *Ceramics International* **2015**, 41 (9), 12393-12400.
- (52) Song, Y.; Zhong, Q.; Tan, W.; Pan, C. Effect of cobalt-substitution $\text{Sr}_2\text{Fe}_{1.5-x}\text{Co}_x\text{Mo}_{0.5}\text{O}_{6-\delta}$ for intermediate temperature symmetrical solid oxide fuel cells fed with H_2 - H_2S . *Electrochimica Acta* **2014**, 139, 13-20.
- (53) Rath, M. K.; Lee, K.-T. Superior electrochemical performance of non-precious Co-Ni-Mo alloy catalyst-impregnated $\text{Sr}_2\text{FeMoO}_{6-\delta}$ as an electrode material for symmetric solid oxide fuel cells. *Electrochimica Acta* **2016**, 212, 678-685.
- (54) Jiang, X.; Wang, J.; Jia, G.; Qie, Z.; Shi, Y.; Idrees, A.; Zhang, Q.; Jiang, L. Characterization of $\text{PrBa}_{0.92}\text{CoCuO}_{6-\delta}$ as a potential cathode material of intermediate-temperature solid oxide fuel cell. *International Journal of Hydrogen Energy* **2017**, 42 (9), 6281-6289.
- (55) Xia, T.; Lin, N.; Zhao, H.; Huo, L.; Wang, J.; Grenier, J.-C. Co-doped $\text{Sr}_2\text{FeNbO}_6$ as cathode materials for intermediate-temperature solid oxide fuel cells. *Journal of Power Sources* **2009**, 192 (2), 291-296.
- (56) Galasso, F.; Darby, W. Ordering of the octahedrally coordinated cation position in the perovskite structure. *The Journal of Physical Chemistry* **1962**, 66 (1), 131-132.
- (57) Galasso, F.; Darby, W. Preparation of single crystals of complex perovskite ferroelectric and semiconducting compounds. *Inorganic Chemistry* **1965**, 4 (1), 71-73.

- (58) Galasso, F.; Katz, L.; Ward, R. Substitution in the octahedrally coordinated cation positions in compounds of the perovskite type 1, 2. *Journal of the American Chemical Society* **1959**, 81 (4), 820-823.
- (59) Kobayashi, K.-I.; Kimura, T.; Sawada, H.; Terakura, K.; Tokura, Y. Room-temperature magnetoresistance in an oxide material with an ordered double-perovskite structure. *Nature* **1998**, 395 (6703), 677-680.
- (60) Huang, Y.-H.; Dass, R. I.; Denyszyn, J. C.; Goodenough, J. B. Synthesis and characterization of $\text{Sr}_2\text{MgMoO}_6-\delta$: an anode material for the solid oxide fuel cell. *Journal of the Electrochemical Society* **2006**, 153 (7), A1266.
- (61) Grimaud, A.; May, K. J.; Carlton, C. E.; Lee, Y.-L.; Risch, M.; Hong, W. T.; Zhou, J.; Shao-Horn, Y. Double perovskites as a family of highly active catalysts for oxygen evolution in alkaline solution. *Nature communications* **2013**, 4 (1), 2439.
- (62) Sengodan, S.; Choi, S.; Jun, A.; Shin, T. H.; Ju, Y.-W.; Jeong, H. Y.; Shin, J.; Irvine, J. T.; Kim, G. Layered oxygen-deficient double perovskite as an efficient and stable anode for direct hydrocarbon solid oxide fuel cells. *Nature materials* **2015**, 14 (2), 205-209.
- (63) Huang, Y.-H.; Dass, R. I.; Xing, Z.-L.; Goodenough, J. B. Double perovskites as anode materials for solid-oxide fuel cells. *Science* **2006**, 312 (5771), 254-257.
- (64) Marrero-López, D.; Peña-Martínez, J.; Ruiz-Morales, J.; Pérez-Coll, D.; Aranda, M.; Núñez, P. Synthesis, phase stability and electrical conductivity of $\text{Sr}_2\text{MgMoO}_6-\delta$ anode. *Materials Research Bulletin* **2008**, 43 (8-9), 2441-2450.
- (65) Bernuy-Lopez, C.; Allix, M.; Bridges, C. A.; Claridge, J. B.; Rosseinsky, M. J. $\text{Sr}_2\text{MgMoO}_6-\delta$: structure, phase stability, and cation site order control of reduction. *Chemistry of materials* **2007**, 19 (5), 1035-1043.
- (66) Huang, Y.-H.; Liang, G.; Croft, M.; Lehtimäki, M.; Karppinen, M.; Goodenough, J. B. Double-perovskite anode materials Sr_2MMoO_6 (M= Co, Ni) for solid oxide fuel cells. *Chemistry of materials* **2009**, 21 (11), 2319-2326.
- (67) Bock, O.; Müller, U. Symmetry in perovskite variants. *Acta crystallographica. Section B, Structural Science* **2002**, 58 (Pt 4), 594-606.
- (68) Flerov, I.; Gorev, M.; Aleksandrov, K.; Tressaud, A.; Granec, J.; Couzi, M. Phase transitions in elpasolites (ordered perovskites). *Materials Science and Engineering: R: Reports* **1998**, 24 (3), 81-151.
- (69) Howard, C. J.; Kennedy, B. J.; Woodward, P. M. Ordered double perovskites—a group-theoretical analysis. *Structural Science* **2003**, 59 (4), 463-471.

- (70) Ortega-San Martin, L.; Chapman, J.; Hernández-Bocanegra, E.; Insausti, M.; Arriortua, M.; Rojo, T. Structural phase transitions in the ordered double perovskite $\text{Sr}_2\text{MnTeO}_6$. *Journal of Physics: Condensed Matter* **2004**, 16 (23), 3879.
- (71) Blackstead, H. A.; Dow, J. D.; Harshman, D. R.; Yelon, W.; Chen, M. X.; Wu, M.; Chen, D.; Chien, F.; Pulling, D. Magnetically ordered Cu and Ru in $\text{Ba}_2\text{GdRu}_{1-u}\text{Cu}_u\text{O}_6$ and in $\text{Sr}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$. *Physical Review B* **2001**, 63 (21), 214412.
- (72) Spinicci, R.; Delmastro, A.; Ronchetti, S.; Tofanari, A. Catalytic behaviour of stoichiometric and non-stoichiometric LaMnO_3 perovskite towards methane combustion. *Materials Chemistry and Physics* **2003**, 78 (2), 393-399.
- (73) Nakamura, T.; Choy, J.-H. Determination of ionic valency pairs via lattice constants in ordered perovskites $(\text{ALa})(\text{Mn}^{2+}\text{Mo}^{5+})\text{O}_6$ (A= Ba, Sr, Ca) with applications to $(\text{ALa})(\text{Fe}^{3+}\text{Mo}^{4+})\text{O}_6$, $\text{Ba}_2(\text{Bi}^{3+}\text{Bi}^{5+})\text{O}_6$ and $\text{Ba}_2(\text{Bi}^{3+}\text{Sb}^{5+})\text{O}_6$. *Journal of Solid State Chemistry* **1977**, 20 (3), 233-244.
- (74) Attfield, M.; Battle, P.; Bollen, S.; Kim, S.; Powell, A.; Workman, M. Structural and electrical studies of mixed copper/ruthenium oxides and related compounds of zinc and antimony. *Journal of Solid State Chemistry* **1992**, 96 (2), 344-359.
- (75) Blasse, G. New compounds with perovskite-like structures. *Journal of Inorganic and Nuclear Chemistry* **1965**, 27 (5), 993-1003.
- (76) Amador, U.; Hetherington, C.; Moran, E.; Alario-Franco, M. $\text{Ba}_2\text{PrPtO}_6$: A novel double perovskite. *Journal of Solid State Chemistry France* **1992**, 96 (1), 132-140.
- (77) Vallet-Regí, M.; García, E.; González-Calbet, J. M. Synthesis and characterization of a new double perovskite: LaCaMnCoO_6 . *Journal of the Chemical Society, Dalton Transactions* **1988**, (3), 775-779.
- (78) Sleight, A. W.; Longo, J.; Ward, R. Compounds of osmium and rhenium with the ordered perovskite structure. *Inorganic Chemistry* **1962**, 1 (2), 245-250.
- (79) Battle, P.; Jones, C. The crystal and magnetic structures of $\text{Sr}_2\text{LuRuO}_6$, Ba_2YRuO_6 , and $\text{Ba}_2\text{LuRuO}_6$. *Journal of Solid State Chemistry* **1989**, 78 (1), 108-116.
- (80) Battle, P.; Macklin, W. The crystal and magnetic structures of Ca_2YRuO_6 and the electronic properties of the series $\text{M}_2\text{X}_3\text{RuO}_6$ (M= Ca, Sr, Ba; X= La, Y). *Journal of Solid State Chemistry* **1984**, 54 (2), 245-250.

- (81) Groen, W.; Van Berkel, F.; Ijdo, D. Dineodymium magnesium titanate (IV). A Rietveld refinement of neutron powder diffraction data. *Crystal Structure Communications* **1986**, 42 (11), 1472-1475.
- (82) Battle, P.; Goodenough, J.; Price, R. The crystal structures and magnetic properties of Ba₂LaRuO₆ and Ca₂LaRuO₆. *Journal of solid state chemistry* **1983**, 46 (2), 234-244.
- (83) Sekiya, T.; Yamamoto, T.; Torii, Y. Cation ordering in (NaLa)(MgW) O₆ with the perovskite structure. *Bulletin of the Chemical Society of Japan* **1984**, 57 (7), 1859-1862.
- (84) Groen, W.; Ijdo, D. The monoclinic perovskites Sr₂CaUO₆ and Ba₂SrUO₆. A Rietveld refinement of neutron powder diffraction data. *Crystal Structure Communications* **1987**, 43 (6), 1033-1036.
- (85) Van Duivenboden, H.; Ijdo, D. Redetermination of tricalcium uranate (VI). A Rietveld refinement of neutron powder diffraction data. *Crystal Structure Communications* **1986**, 42 (5), 523-525.
- (86) Attfield, M.; Battle, P.; Bollen, S.; Gibb, T.; Whitehead, R. The crystal structure and magnetic properties of SrLaFeSnO₆ and SrLaNiSbO₆. *Journal of Solid State Chemistry* **1992**, 100 (1), 37-48.
- (87) Battle, P.; Macklin, W. The crystal and magnetic structures of Sr₂YRuO₆. *Journal of Solid State Chemistry* **1984**, 52 (2), 138-145.
- (88) Anderson, M. T.; Poeppelmeier, K. R. Lanthanum copper tin oxide (La₂CuSnO₆): a new perovskite-related compound with an unusual arrangement of B cations. *Chemistry of Materials* **1991**, 3 (3), 476-482.
- (89) Roy, R. Multiple ion substitution in the perovskite lattice. *Journal of the American Ceramic Society* **1954**, 37 (12), 581-588.
- (90) Choy, J.-H.; Hong, S.-T. Preparation of the ordered perovskite (SrLa)(MgMo) O₆ and its physico-chemical characterization. *Journal of the Chemical Society, Dalton Transactions* **1989**, (11), 2335-2337.
- (91) Filipev, V.; Fesenko, E. Symmetry and lattice parameters of some composite perovskites. *Sov. Phys. Crystallogr.* **1966**, 10, 532-540.
- (92) Longo, J.; Ward, R. Magnetic compounds of hexavalent rhenium with the perovskite-type structure. *Journal of the American Chemical Society* **1961**, 83 (13), 2816-2818.
- (93) Sleight, A. W.; Ward, R. Compounds of hexavalent and pentavalent uranium with the ordered perovskite structure. *Inorganic Chemistry* **1962**, 1 (4), 790-793.

- (94) Steward, E.; Rooksby, H. Pseudo-cubic alkaline-earth tungstates and molybdates of the R3MX6 type. *Acta Crystallographica* **1951**, 4 (6), 503-507.
- (95) Filonova, E.; Dmitriev, A.; Pikalov, P.; Medvedev, D.; Pikalova, E. Y. The structural and electrical properties of Sr2Ni0.75Mg0.25MoO6 and its compatibility with solid state electrolytes. *Solid State Ionics* **2014**, 262, 365-369.
- (96) Kumar, P.; Singh, N. K.; Sinha, A.; Singh, P. Structural and electrical characterizations of cerium (Ce3+)-doped double perovskite system Sr2NiMoO6- δ . *Applied Physics A* **2016**, 122 (9), 828.
- (97) Dorai, A. K.; Masuda, Y.; Joo, J.-H.; Woo, S.-K.; Kim, S.-D. Influence of Fe doping on the electrical properties of Sr2MgMoO6- δ . *Materials Chemistry and Physics* **2013**, 139 (2-3), 360-363.
- (98) Cowin, P. I.; Petit, C. T.; Lan, R.; Irvine, J. T.; Tao, S. Recent progress in the development of anode materials for solid oxide fuel cells. *Advanced Energy Materials* **2011**, 1 (3), 314-332.
- (99) Ge, X. M.; Chan, S. H.; Liu, Q. L.; Sun, Q. Solid oxide fuel cell anode materials for direct hydrocarbon utilization. *Advanced Energy Materials* **2012**, 2 (10), 1156-1181.
- (100) Kong, L.; Liu, B.; Zhao, J.; Gu, Y.; Zhang, Y. Synthesis of nano-crystalline Sr2MgMoO6- δ anode material by a sol-gel thermolysis method. *Journal of Power Sources* **2009**, 188 (1), 114-117.
- (101) Zheng, K.; Świerczek, K.; Bratek, J.; Klimkowicz, A. Cation-ordered perovskite-type anode and cathode materials for solid oxide fuel cells. *Solid State Ionics* **2014**, 262, 354-358.
- (102) Aguadero, A.; Alonso, J.; Martínez-Coronado, R.; Martínez-Lope, M.; Fernández-Díaz, M. Evaluation of Sr2CoMoO6- δ as anode material in solid-oxide fuel cells: A neutron diffraction study. *Journal of Applied Physics* **2011**, 109 (3).
- (103) Ding, H.; Tao, Z.; Liu, S.; Yang, Y. A redox-stable direct-methane solid oxide fuel cell (SOFC) with Sr2FeNb0.2Mo0.8O6- δ double perovskite as anode material. *Journal of Power Sources* **2016**, 327, 573-579.
- (104) Huang, Y. H.; Dass, R. I.; Xing, Z. L.; Goodenough, J. B. Double perovskites as anode materials for solid-oxide fuel cells. *Science* **2006**, 312 (5771), 254.
- (105) Marrero-López, D.; Peña-Martínez, J.; Ruiz-Morales, J.; Gabás, M.; Núñez, P.; Aranda, M.; Ramos-Barrado, J. Redox behaviour, chemical compatibility and electrochemical performance of Sr2MgMoO6- δ as SOFC anode. *Solid State Ionics* **2010**, 180 (40), 1672-1682.

- (106) Troncoso, L.; Martínez-Lope, M.; Alonso, J.; Fernández-Díaz, M. Evaluation of Sr_2MMoO_6 (M= Mg, Mn) as anode materials in solid-oxide fuel cells: A neutron diffraction study. *Journal of Applied Physics* **2013**, 113 (2).
- (107) Wang, Z.; Tian, Y.; Li, Y. Direct CH_4 fuel cell using $\text{Sr}_2\text{FeMoO}_6$ as an anode material. *Journal of Power Sources* **2011**, 196 (15), 6104-6109.
- (108) Wei, T.; Ji, Y.; Meng, X.; Zhang, Y. $\text{Sr}_2\text{NiMoO}_6-\delta$ as anode material for LaGaO_3 -based solid oxide fuel cell. *Electrochemistry communications* **2008**, 10 (9), 1369-1372.
- (109) Li, C.; Wang, W.; Zhao, N.; Liu, Y.; He, B.; Hu, F.; Chen, C. Structure properties and catalytic performance in methane combustion of double perovskites $\text{Sr}_2\text{Mg}_{1-x}\text{Mn}_x\text{MoO}_6-\delta$. *Applied Catalysis B: Environmental* **2011**, 102 (1-2), 78-84.
- (110) Zuev, A.; Singheiser, L.; Hilpert, K. Defect structure and isothermal expansion of A-site and B-site substituted lanthanum chromites. *Solid State Ionics* **2002**, 147 (1-2), 1-11.
- (111) Ji, Y.; Huang, Y.-H.; Ying, J.-R.; Goodenough, J. B. Electrochemical performance of La-doped $\text{Sr}_2\text{MgMoO}_6-\delta$ in natural gas. *Electrochemistry communications* **2007**, 9 (8), 1881-1885.
- (112) Zhang, L.; He, T. Performance of double-perovskite $\text{Sr}_{2-x}\text{Sm}_x\text{MgMoO}_6-\delta$ as solid-oxide fuel-cell anodes. *Journal of Power Sources* **2011**, 196 (20), 8352-8359.
- (113) Kumar, P.; Singh, N. K.; Gupta, G.; Singh, P. Effect of lanthanum (La^{3+}) doping on the structural and electrical properties of double perovskite $\text{Sr}_2\text{NiMoO}_6$. *RSC Advances* **2016**, 6 (26), 22094-22102.
- (114) Vasala, S.; Lehtimäki, M.; Haw, S.; Chen, J.; Liu, R.; Yamauchi, H.; Karppinen, M. Isovalent and aliovalent substitution effects on redox chemistry of $\text{Sr}_2\text{MgMoO}_6-\delta$ SOFC-anode material. *Solid State Ionics* **2010**, 181 (15-16), 754-759.
- (115) Vasala, S.; Lehtimäki, M.; Huang, Y.-H.; Yamauchi, H.; Goodenough, J. B.; Karppinen, M. Degree of order and redox balance in B-site ordered double-perovskite oxides, $\text{Sr}_2\text{MMoO}_6-\delta$ (M= Mg, Mn, Fe, Co, Ni, Zn). *Journal of Solid State Chemistry* **2010**, 183 (5), 1007-1012.
- (116) Vasala, S.; Yamauchi, H.; Karppinen, M. Role of SrMoO_4 in $\text{Sr}_2\text{MgMoO}_6$ synthesis. *Journal of Solid State Chemistry* **2011**, 184 (5), 1312-1317.
- (117) Presto, S.; Kumar, P.; Varma, S.; Viviani, M.; Singh, P. Electrical conductivity of NiMo-based double perovskites under SOFC anodic conditions. *International Journal of Hydrogen Energy* **2018**, 43 (9), 4528-4533.

- (118) Huan, Y.; Li, Y.; Yin, B.; Ding, D.; Wei, T. High conductive and long-term phase stable anode materials for SOFCs: A_2FeMoO_6 ($A = Ca, Sr, Ba$). *Journal of Power Sources* **2017**, 359, 384-390.
- (119) Xie, Z.; Zhao, H.; Chen, T.; Zhou, X.; Du, Z. Synthesis and electrical properties of Al-doped $Sr_2MgMoO_{6-\delta}$ as an anode material for solid oxide fuel cells. *international journal of hydrogen energy* **2011**, 36 (12), 7257-7264.
- (120) Huang, K.; Goodenough, J. B. A solid oxide fuel cell based on Sr-and Mg-doped $LaGaO_3$ electrolyte: the role of a rare-earth oxide buffer. *Journal of Alloys and Compounds* **2000**, 303, 454-464.
- (121) Goodenough, J. B. Electronic and ionic transport properties and other physical aspects of perovskites. *Reports on Progress in Physics* **2004**, 67 (11), 1915-1993.
- (122) Steele, B. C. Appraisal of $Ce_{1-y}Gd_yO_{2-y/2}$ electrolytes for IT-SOFC operation at 500° C. *Solid state ionics* **2000**, 129 (1-4), 95-110.
- (123) Kilner, J. A.; Burriel, M. Materials for intermediate-temperature solid-oxide fuel cells. *Annual Review of Materials Research* **2014**, 44 (1), 365-393.
- (124) Hamnett, A. Fuel cells and their development. *Philos Trans A Math Phys Eng Sci* **1996**, 354 (1712), 1653-1669
- (125) Steele, B. C. H., & Dell, R. M. . Materials for High-Temperature Fuel Cells [and Discussion]. *Philosophical Transactions: Mathematical, Physical and Engineering Sciences* **1996**, 354 (1712), 1695-1710.
- (126) Thangadurai, V.; Shukla, A.; Gopalakrishnan, J. Oxide-ion conduction in anion-deficient double perovskites, $Ba_2BB'O_5$. 5 ($B = Li, Na$; $B' = Mo, W, Te$). *Solid State Ionics* **1997**, 104 (3-4), 277-283.
- (127) Xie, Z.; Zhao, H.; Du, Z.; Chen, T.; Chen, N.; Liu, X.; Skinner, S. J. Effects of Co doping on the electrochemical performance of double perovskite oxide $Sr_2MgMoO_{6-\delta}$ as an anode material for solid oxide fuel cells. *The Journal of Physical Chemistry C* **2012**, 116 (17), 9734-9743.
- (128) Boldrin, P.; Ruiz-Trejo, E.; Mermelstein, J.; Bermúdez Menéndez, J. M.; Ramírez Reina, T.; Brandon, N. P. Strategies for carbon and sulfur tolerant solid oxide fuel cell materials, incorporating lessons from heterogeneous catalysis. *Chemical reviews* **2016**, 116 (22), 13633-13684.
- (129) Hussain, S.; Yangping, L. Review of solid oxide fuel cell materials: cathode, anode, and electrolyte. *Energy Transitions* **2020**, 4 (2), 113-126.

- (130) Jang, I.; SA Carneiro, J.; Crawford, J. O.; Cho, Y. J.; Parvin, S.; Gonzalez-Casamachin, D. A.; Baltrusaitis, J.; Lively, R. P.; Nikolla, E. Electrocatalysis in solid oxide fuel cells and electrolyzers. *Chemical Reviews* **2024**, 124 (13), 8233-8306.
- (131) Shi, N.; Xie, Y.; Yang, Y.; Xue, S.; Li, X.; Zhu, K.; Huan, D.; Peng, R.; Xia, C.; Lu, Y. Review of anodic reactions in hydrocarbon fueled solid oxide fuel cells and strategies to improve anode performance and stability. *Materials for Renewable and Sustainable Energy* **2020**, 9 (1), 6.
- (132) Zhu, W.; Deevi, S. A review on the status of anode materials for solid oxide fuel cells. *Materials Science and Engineering: A* **2003**, 362 (1-2), 228-239.
- (133) Goodenough, J. B.; Huang, Y.-H. Alternative anode materials for solid oxide fuel cells. *Journal of Power Sources* **2007**, 173 (1), 1-10.
- (134) Falcón, H. B., J.A; Araujo, G; Casais, M.T; Martínez-Lope, M.J; Alonso, J.A; Fierro, J.L.G. Double perovskite oxides $A_2\text{FeMoO}_{6-\delta}$ ($A=\text{Ca}$, Sr and Ba) as catalysts for methane combustion. *Applied Catalysis B: Environmental* **2004**, 53 (1), 37-45. DOI: <https://doi.org/10.1016/j.apcatb.2004.05.004>.
- (135) Nakamura, T. K., K.; Hirose, Y. . Stable Po_2 -region of ordered perovskites $\text{Ca}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{FeMoO}_6$ at 1200°C . *Materials Research Bulletin* **1981**, 16 (3), 321-326. DOI: [https://doi.org/10.1016/0025-5408\(81\)90048-9](https://doi.org/10.1016/0025-5408(81)90048-9).
- (136) Yamazoe, N. T., Y. . Oxidation catalysis of perovskites --- relationships to bulk structure and composition (valency, defect, etc.). *Catalysis Today* **1990**, 8 (2), 175-199. DOI: [https://doi.org/10.1016/0920-5861\(90\)87017-W](https://doi.org/10.1016/0920-5861(90)87017-W).
- (137) Bernuy-Lopez, C.; Pelloquin, D.; Raveau, B.; Allix, M.; Claridge, J. B.; Rosseinsky, M. J.; Wang, P.; Bleloch, A. Phasoid intergrowth between the double perovskite $\text{Sr}_2\text{MgMoO}_6$ and the $n=2$ RP phase $\text{Sr}_3\text{Mo}_2\text{O}_7$. *Solid State Ionics* **2010**, 181 (19-20), 889-893.
- (138) Marrero-López, D.; Peña-Martínez, J.; Ruiz-Morales, J.; Martín-Sedeño, M.; Núñez, P. High temperature phase transition in SOFC anodes based on $\text{Sr}_2\text{MgMoO}_{6-\delta}$. *Journal of Solid State Chemistry* **2009**, 182 (5), 1027-1034.
- (139) Matsuda, Y.; Karppinen, M.; Yamazaki, Y.; Yamauchi, H. Oxygen-vacancy concentration in $\text{A}_2\text{MgMoO}_{6-\delta}$ double-perovskite oxides. *Journal of Solid State Chemistry* **2009**, 182 (7), 1713-1716.
- (140) van den Bossche, M.; McIntosh, S. On the methane oxidation activity of $\text{Sr}_2(\text{MgMo})_2\text{O}_{6-\delta}$: a potential anode material for direct hydrocarbon solid oxide fuel cells. *Journal of Materials Chemistry* **2011**, 21 (20), 7443-7451.

- (141) dos Santos-Gómez, L.; León-Reina, L.; Porras-Vázquez, J.; Losilla, E.; Marrero-López, D. Chemical stability and compatibility of double perovskite anode materials for SOFCs. *Solid State Ionics* **2013**, 239, 1-7.
- (142) Aoki, Y.; Wiemann, C.; Feyer, V.; Kim, H.-S.; Schneider, C. M.; Ill-Yoo, H.; Martin, M. Bulk mixed ion electron conduction in amorphous gallium oxide causes memristive behaviour. *Nature communications* **2014**, 5 (1), 3473.
- (143) Ding, D.; Li, X.; Lai, S. Y.; Gerdes, K.; Liu, M. Enhancing SOFC cathode performance by surface modification through infiltration. *Energy & Environmental Science* **2014**, 7 (2), 552-575.
- (144) Lin, Y.; Fang, S.; Su, D.; Brinkman, K. S.; Chen, F. Enhancing grain boundary ionic conductivity in mixed ionic–electronic conductors. *Nature communications* **2015**, 6 (1), 6824.
- (145) Luo, H.; Efimov, K.; Jiang, H.; Feldhoff, A.; Wang, H.; Caro, J. CO₂-stable and cobalt-free dual-phase membrane for oxygen separation. *Angewandte Chemie International Edition* **2011**, 50 (3), 759-763.
- (146) Miao, F.; Yi, W.; Goldfarb, I.; Yang, J. J.; Zhang, M.-X.; Pickett, M. D.; Strachan, J. P.; Medeiros-Ribeiro, G.; Williams, R. S. Continuous electrical tuning of the chemical composition of TaO x-based memristors. *ACS nano* **2012**, 6 (3), 2312-2318.
- (147) Tarascon, J.; Delacourt, C.; Prakash, A.; Morcrette, M.; Hegde, M.; Wurm, C.; Masquelier, C. Various strategies to tune the ionic/electronic properties of electrode materials. *Dalton Transactions* **2004**, (19), 2988-2994.
- (148) Mahmood, Q. Study of half metallic ferromagnetism, Curie temperature, and thermoelectric aspects of double perovskite oxides Ba₂XMoO₆ (X= Cr, Mn, Fe, Co) for spintronic applications. *Materials Science in Semiconductor Processing* **2025**, 193, 109519.
- (149) Shimada, T.; Nakamura, J.; Motohashi, T.; Yamauchi, H.; Karppinen, M. Kinetics and thermodynamics of the degree of order of the B cations in double-perovskite Sr₂FeMoO₆. *Chemistry of materials* **2003**, 15 (23), 4494-4497.
- (150) Niu, B.; Jin, F.; Liu, J.; Zhang, Y.; Jiang, P.; Feng, T.; Xu, B.; He, T. Highly carbon–and sulfur–tolerant Sr₂TiMoO_{6–δ} double perovskite anode for solid oxide fuel cells. *International Journal of Hydrogen Energy* **2019**, 44 (36), 20404-20415.
- (151) Bartel, C. J.; Sutton, C.; Goldsmith, B. R.; Ouyang, R.; Musgrave, C. B.; Ghiringhelli, L. M.; Scheffler, M. New tolerance factor to predict the stability of perovskite oxides and halides. *Science advances* **2019**, 5 (2), eaav0693.
- (152) Childs, N. B.; Weisenstein, A.; Smith, R.; Sofie, S.; Key, C. Electrical conductivity of Sr_{2–x}VMoO_{6–y} (x= 0.0, 0.1, 0.2) double perovskites. *J. Appl. Phys.* **2013**, 113 (24), 243506.

- (153) Weisentein, A.; Childs, N.; Amendola, R.; Driscoll, D.; Sofie, S.; Gannon, P.; Smith, R. Processing and characterization of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ double perovskites. *Materials Chemistry and Physics* **2013**, 139 (2-3), 706-718.
- (154) Karen, P.; Moodenbaugh, A.; Goldberger, J.; Santhosh, P.; Woodward, P. Electronic, magnetic and structural properties of A_2VMoO_6 perovskites (A= Ca, Sr). *Journal of Solid State Chemistry* **2006**, 179 (7), 2120-2125.
- (155) Aguadero, A.; De La Calle, C.; Pérez-Coll, D.; Alonso, J. Study of the crystal structure, thermal stability and conductivity of $\text{Sr}(\text{V}_{0.5}\text{Mo}_{0.5})\text{O}_{3+\delta}$ as SOFC material. *Fuel Cells* **2011**, 11 (1), 44-50.
- (156) Fotiev, V.; Bazuev, G.; Zubkov, V. Synthesis and electric properties of the solid solutions $\text{SrV}_{1-x}\text{Mo}_x\text{O}_3$ with the perovskite structure. *Inorg. Mater. (Engl. Transl.) (United States)* **1987**, 23 (6).
- (157) Zhang, L.; Zhou, Q.; He, Q.; He, T. Double-perovskites $\text{A}_2\text{FeMoO}_{6-\delta}$ (A= Ca, Sr, Ba) as anodes for solid oxide fuel cells. *Journal of Power sources* **2010**, 195 (19), 6356-6366.
- (158) Yin, Y.-M.; Xiong, M.-W.; Yang, N.-T.; Tong, Z.; Guo, Y.-Q.; Ma, Z.-F.; Sun, E.; Yamanis, J.; Jing, B.-Y. Investigation on thermal, electrical, and electrochemical properties of scandium-doped $\text{Pr}_{0.6}\text{Sr}_{0.4}(\text{Co}_{0.2}\text{Fe}_{0.8})_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ as cathode for IT-SOFC. *international journal of hydrogen energy* **2011**, 36 (6), 3989-3996.
- (159) Viola, M. d. C.; Martínez-Lope, M.; Alonso, J.; Velasco, P.; Martínez, J.; Pedregosa, J.; Carbonio, R.; Fernández-Díaz, M. Induction of colossal magnetoresistance in the double perovskite $\text{Sr}_2\text{CoMoO}_6$. *Chemistry of materials* **2002**, 14 (2), 812-818.
- (160) Giannakopoulou, V.; Odier, P.; Bassat, J.; Loup, J. SrVO_3 and Sr_2VO_4 , electrical properties below and above room T. *Solid state communications* **1995**, 93 (7), 579-583.
- (161) Hayashi, S.; Aoki, R.; Nakamura, T. Metallic conductivity in perovskite-type compounds AMoO_3 (A= Ba, Sr, Ca) down to 2.5 K. *Materials Research Bulletin* **1979**, 14 (3), 409-413.
- (162) Nagai, I.; Shirakawa, N.; Ikeda, S.-i.; Iwasaki, R.; Nishimura, H.; Kosaka, M. Highest conductivity oxide SrMoO_3 grown by a floating-zone method under ultralow oxygen partial pressure. *Applied Physics Letters* **2005**, 87 (2).
- (163) Samuel, B. J.; Esakoff, J. A.; Heywood, S. K.; Sofie, S. W.; Walker, R. A. Chemical and Thermal Stability of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$: Implications for High Temperature Energy Conversion Applications. *ACS Omega* **2026**. DOI: 10.1021/acsomega.5c06796.

- (164) Asher, S. A. UV resonance Raman spectroscopy for analytical, physical, and biophysical chemistry. Part 2. *Analytical chemistry* **1993**, 65 (4), 201A-210A.
- (165) Clark, R.; Long, D. Raman spectroscopy; *McGraw-Hill*, New York, **1977**.
- (166) Das, R. S.; Agrawal, Y. Raman spectroscopy: Recent advancements, techniques and applications. *Vibrational spectroscopy* **2011**, 57 (2), 163-176.
- (167) Efremov, E. V.; Ariese, F.; Gooijer, C. Achievements in resonance Raman spectroscopy: Review of a technique with a distinct analytical chemistry potential. *Analytica chimica acta* **2008**, 606 (2), 119-134.
- (168) Kudelski, A. Analytical applications of Raman spectroscopy. *Talanta* **2008**, 76 (1), 1-8.
- (169) Kudelski, A. Raman spectroscopy of surfaces. *Surface Science* **2009**, 603 (10-12), 1328-1334.
- (170) Li-Chan, E. C. The applications of Raman spectroscopy in food science. *Trends in Food Science & Technology* **1996**, 7 (11), 361-370.
- (171) Raman, C.; Krishnan, K. Polarisation of scattered light-quanta. *Nature* **1928**, 122 (3066), 169-169.
- (172) Smith, E.; Dent, G. Modern Raman spectroscopy: a practical approach; *John Wiley & Sons*, **2019**.
- (173) Tanzi, M. C.; Farè, S.; Candiani, G. Techniques of analysis. thermogravimetric analysis. *Academic* **2019**, 393-469.
- (174) Yoshio, W. X-ray diffraction crystallography; *Springer*, **2011**.

CHAPTER TWO

CHEMICAL AND THERMAL STABILITY OF $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$:

IMPLICATIONS FOR HIGH TEMPERATURE ENERGY

CONVERSION APPLICATIONS

Contributions of Authors and Co-Authors

Manuscript in Chapter 2:

Author: Bamidele J. Samuel

Contributions: Collected and analyzed all data, generated figures, planned experimental protocols and wrote manuscript in preparation for publication, addressed reviewers' comments.

Co-Author: Julia A. Esakoff

Contributions: Prepared materials, reviewed and edited successive versions of the manuscript.

Co-Author: Stephen K. Heywood

Contributions: Prepared materials, reviewed and edited successive versions of the manuscript.

Co-Author: Stephen W. Sofie

Contributions: Reviewed and edited successive versions of the manuscript.

Co-Author: Robert A. Walker

Contributions: Helped plan experimental protocols and cowrote the first version of the manuscript. Reviewed and edited successive versions of the manuscript.

Manuscript Information

Bamidele J. Samuel, Julia A. Esakoff, Stephen K. Heywood, Stephen W. Sofie and Robert A.

Walker

ACS Omega

Status of Manuscript:

- ☐ Prepared for submission to a peer-reviewed journal
- ☐ Officially submitted to a peer-reviewed journal
- ☐ Accepted by a peer-reviewed journal
- ☒ Published in a peer-reviewed journal

Publisher: American Chemical Society – Omega

Date of Submission: July 12, 2025

Date Accepted: January 21, 2026

Volume 11, Issue 6 February 2026, 9050 - 9058

DOI: 10.1021/acsomega.5c06796

Abstract. Raman spectroscopy and thermal gravimetric analysis (TGA) were used to evaluate the thermal and atmosphere stability of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ (SVMO-19), an A-site deficient double perovskite. Motivated by previous reports describing SVMO-19's unprecedented electrical conductivity under reducing atmospheres, studies described in this work determine SVMO-19's stability under conditions commonly encountered in high temperature solid oxide electrolysis and fuel cell applications. Vibrational Raman data show that SVMO-19 is stable up to 1000 °C under reducing, inert, and CO_2 containing atmospheres. Under air, however, *in situ* Raman data show that SVMO-19 phase separates at temperatures ≥ 600 °C. The primary degradation products include a scheelite phase (SrMoO_4) as well as a vanadium containing single perovskite, SrVO_3 , and a vanadium containing pyrochlore $\text{Sr}_2\text{V}_2\text{O}_7$. TGA measurements suggest that SVMO decomposition in air begins at even lower temperatures (400 °C). TGA data show that SVMO is stable under N_2 at temperatures as high as 900 °C, consistent with Raman data. SVMO oxidation kinetics are analyzed using both a simple kinetic model consisting of two independent first-order processes and an Avrami model. The data are better described by the pair of first order processes, but an Arrhenius analysis using both models result in an activation energy (E_a) for SVMO degradation between 0.48 and 0.65 eV. Taken together, these findings are considered in the context of properties required by electrode materials used in reversible solid oxide electrochemical cells.

Introduction.

High temperature energy conversion devices such as solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs) require electron and ion conducting materials that are stable under chemically aggressive conditions including oxidizing/reducing atmospheres, applied overpotentials, and temperatures approaching 1000 °C. Given these limitations, most traditional SOFCs and SOECs rely on oxide-conducting yttria stabilized zirconia (YSZ) as an electrolyte with a nickel-YSZ cermet serving as a fuel electrode and a mixed ion-electron conducting (MIEC) perovskite as an oxygen electrode.^{1, 2} Some variants to this design include ceria-based electrodes and electrolytes as well as porous, electron-conducting ceramics as fuel electrodes.³

Fuel electrodes face major challenges to stable, long-term operation in SOFCs and SOECs.

Ni-based electrodes, in particular, are susceptible to coking, metal dusting, and sulfur poisoning that can yield irreversible degradation to the anode.⁴⁻¹⁰ If used as an electrode in reversible SOFC/SOEC applications, a Ni-based electrode can be subject to strong oxidizing conditions that lead to NiO formation and significant mechanical stress on device components.^{11, 12} To address these issues, efforts have focused on improving resistance to carbon accumulation and sulfur tolerance employing new anode materials such as alloys and conducting ceramics whose catalytic activity is enhanced through infiltration or nanoparticle exsolution.¹³ These improvements, however, often come at the cost of other key properties, such as electrocatalytic activity, conversion efficiency, long-term stability, and cost.

Perovskite oxides ($\text{ABO}_{3-\delta}$) are promising candidates for general fuel electrode applications, due to their ability to serve as mixed electronic and ionic conductors (MIECs). By replacing

conventional nickel (Ni) and yttria-stabilized zirconia (YSZ) with a perovskite MIEC, the electrode's electrochemically active region is no longer confined to a narrow triple-phase boundary (TPB) making the electrode less susceptible to contamination and degradation. Furthermore, certain perovskite compounds have proven robust in extreme conditions including high temperature reducing and oxidizing atmospheres,¹⁴ while also showing exceptional catalytic activity for hydrogen and methane oxidation,^{15, 16} sulfur tolerance,¹⁷ and resistance to carbon deposition.¹⁸

Double perovskites have the general formula $A'A''B'B''O_{6-\delta}$ and afford even greater flexibility over average B-site oxidation state(s) and oxide vacancy concentrations. These materials have shown more promise than single perovskites in terms of their ionic conductivity and resistance to common SOFC/SOEC contaminants.¹⁹⁻²³ By integrating two different metal cations into the material's B-sites, double perovskites can accommodate one transition metal in a high oxidation state (e.g. Mo^{6+} , Ta^{5+}) to enable a higher number of oxide vacancies and a second metal that suppresses A-site species mobility, a common source of perovskite instability.

Double perovskite oxides such as $Sr_2Fe_{1.5}Mo_{0.5}O_6$ exhibit high oxide ion conductivity, reaching 0.13 S/cm at 800 °C, and have demonstrated promising performance as cathode materials in intermediate-temperature electrochemical devices.²⁴ In addition to their ion conducting capabilities, double perovskites can also have appreciable electronic conductivities. Previous studies have reported that certain double perovskite oxides exhibit moderate electronic conductivities under reducing conditions at 800 °C, with values such as 5.3 S/cm for $(Sr_2FeNb_{0.2}Mo_{0.8}O_{6-\delta})$ ²⁵ and approximately 1 S/cm for $(La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3)$.²⁶ However, significantly higher conductivities have been achieved through targeted B-site doping, as

demonstrated by $\text{Sr}_2\text{FeMo}_{0.6}\text{Mg}_{0.25}\text{Ga}_{0.15}\text{O}_{6-\delta}$ (36 S/cm)²⁷ and $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (~17 S/cm).²⁸

Notably, the introduction of A-site deficiency has led to a dramatic enhancement in conductivity, with values reaching 1250 S/cm for $\text{Sr}_2\text{VMoO}_{6-y}$, 2530 S/cm for $\text{Sr}_{1.8}\text{VMoO}_{6-y}$, and up to 3610 S/cm for $\text{Sr}_{1.9}\text{VMoO}_{6-y}$ all at 800 °C in 5% H_2 /95% N_2 .²⁹

Despite these attractive performance metrics, double perovskite electrodes suffer from material decomposition into secondary phases including single perovskites (e.g. SrMO_3) and a scheelite phase (e.g. SrMO_4).³⁰ (Here, M corresponds to B-site constituents in the parent material). The scheelite phase is particularly problematic, given that these materials are often both electronically and ionically insulating. Son *et al.*³¹ used a host of methods including x-ray diffraction (XRD), thermogravimetric analysis (TGA), thermomagnetization (TM) and Raman spectroscopy to show that the double perovskite $\text{Sr}_2\text{FeMoO}_6$ (SFMO) remained stable in N_2 at temperatures up to 900 °C, but in air this material began to degrade above 400 °C. *Post-mortem* analyses showed SrFeO_3 and SrMoO_4 to be the dominant secondary phases, but SFMO's degradation kinetics and the mechanisms responsible for decomposition into these secondary phases remained unresolved.

Results reported in this work examine how the double perovskite SVMO-19 behaves under conditions typically encountered in SOFCs and SOECs. This material has been cited as having unusually high electronic conductivities and has shown resilience to sulfur poisoning.³² *In situ* Raman spectroscopy is used to monitor material stability under inert, reducing, and oxidizing atmospheres at temperatures up to 1000 °C. Data show SVMO-19 to be stable under inert, reducing, and weakly oxidizing atmospheres. In air, however, SVMO-19 phase separates into a dominant scheelite phase (SrMoO_4) and secondary Sr and V containing phases (SrVO_3 and

$\text{Sr}_2\text{V}_2\text{O}_7$). TGA data corroborate these findings and set a 400 °C threshold for oxygen uptake.

Isothermal Raman and TGA kinetic analyses of SVMO-19 degradation show clearly that scheelite formation is direct without intermediate steps and proceeds via 2 first order rate processes with the faster process describing surface decomposition and the latter reaction describing conversion of the bulk material.

Materials and Methods.

$\text{Sr}_{1.9}\text{VMoO}_{6.8}$ (SVMO-19) synthesis. Solid state synthesis techniques were developed to mimic previously reported procedures²⁹ These solid-state methods combined SrCO_3 , VO_2 , and MoO_2 powder precursors in distilled water. The solution was then mixed with an ultrasonic probe at a power output of 60%. To avoid separation of the precursors and water, liquid nitrogen was immediately introduced to flash freeze the aqueous mixture. The solidified mixture was lyophilized for 48 h with the results being a homogenized fine particulate powder. The powder was processed by hand using a mortar and pestle and placed in a Thermolyne 4800 box furnace to be calcined for 6 h at 1000 °C with a ramp to temperature of 5 °C/min and a return ramp to 25 °C of 10 °C/min. This calcination step removes carbonates and residual moisture from the freeze-dried powder and forms a mixture of SrMoO_4 (Scheelite) and $\text{Sr}_2\text{V}_2\text{O}_7$ phases. As the Mo^{6+} and V^{5+} oxidation states are immiscible and unable to form an oxidized solid-state perovskite, this calcination step serves as an intermediate solid cation mixing step towards perovskite formation via reduction.

Subsequent hand processing using a mortar and pestle was performed before forming $\frac{3}{4}$ " diameter pellets through uniaxial pressing at 250 MPa. The pellets were reduced at 1100 °C in a forming gas atmosphere of 5% H_2 /95%Ar to produce SVMO and single perovskite secondary phases (SrVO_3 and SrMoO_3). Post reduction, the pellets were again processed by hand before being dispersed in ethanol and wet ball-milled for 48 h. The perovskite solvent mixture was air-dried and uniaxially pressed into $\frac{1}{2}$ " pellets at 250 MPa and then sintered under N_2 at 1200 °C to convert remaining perovskites to fully formed SVMO. In the final processing stage, the material (already at 1200°C under N_2) was then placed under a forming gas environment before having the temperature ramped to 1500 °C and then maintained at 1400°C dwell for 12 h before cooling.

Chemical Stability Testing. The synthesized SVMO was tested to evaluate its phase and chemical stability under reducing atmospheres (5% H_2 in N_2), inert atmospheres, weakly oxidizing atmospheres (20% CO_2 in Ar and humidified (3% H_2O) argon, and an oxidizing atmosphere (air). All experiments were carried out at controlled-atmospheric conditions. Several analytical techniques were employed to characterize SVMO stability including XRD, Raman spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

Characterization – X-ray diffraction. X-ray powder diffraction (XRD) was utilized to confirm the double perovskite crystal structure in SVMO-19 samples. This was conducted using a Bruker D8 Advance powder X-ray diffractometer (PXRD) with $\text{Cu K}\alpha$ radiation, operating at 40 kV and 40 mA, equipped with a Ni filter. The analysis utilized an angle step size of 0.02° over a scanning range of 5 - 80° to identify phases and assess phase purity. Rietveld refinement provided data about each sample's phase purity.

Characterization – Raman spectroscopy. *In situ* Raman spectroscopy, performed using continuous wave 488 nm excitation coupled into a Renishaw inVia spectrometer and a Linkam CCR1000 heating stage. Measurements were made as samples were heated from room temperature to 1000 °C in a controlled atmospheric environment. Raman spectra were collected at intervals of 100 °C, with a heating rate of 10 °C/min between temperatures and a dwell time of 15 minutes at temperature to equilibrate. Most spectra shown in this work resulted from 3 x 30-second accumulations. Incident laser powers were ~30 mW with a ~100 µm spot size using a 5x objective. Incident power at the sample surface was 2.8 mW.

Characterization – Thermogravimetric analysis. Thermogravimetric analysis (TGA) was employed to characterize SVMO-19 thermal and chemical stability. Experiments were performed using a TA-TGA 5500 instrument, measuring weight loss/gain as a function of temperature in both inert (N₂) and oxidizing (air) atmospheres. The analysis covered a temperature range from room temperature to 900 °C, with a heating rate of 5 °C/min and a flow rate of 25 mL/min. Measurements reproducibly measured mass changes as small as ±0.01%. Pseudo-isothermal TGA measurements were performed by ramping the temperature as quickly as possible (50 °C/min) to the target temperature and then maintaining a constant temperature for the duration of the experiment.

Results

Phase composition and crystal structure of SVMO-19. Figure 1.2 shows the room-temperature X-ray diffraction pattern for the as-fabricated SVMO-19. The diffraction pattern exhibits sharp and well-defined peaks that are consistent with previous reports.²⁹ These results confirm that the solid-state synthesis method described above can produce high purity, double perovskite materials.

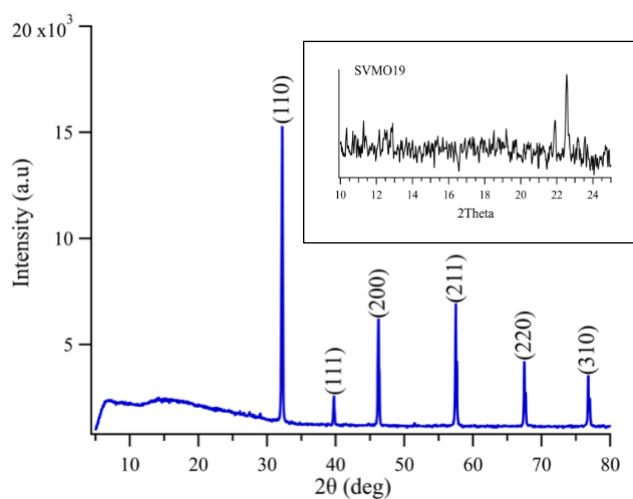


Figure 1.2. XRD patterns of SVMO-19 double-perovskite as-fabricated. Inset: XRD patterns of the SVMO-19 showing the expanded view of $2\theta = 10 - 24^\circ$ with features assigned to secondary phases.

Rietveld refinement shows near-single phase purity with cubic SVMO content consistently $\geq 94\%$. (Residual materials include SrMoO_4 ($\sim 3\%$), lesser amounts of a tetragonal and hexagonal an isotropic lattice constant of $3.192 \text{ \AA}$, again consistent with previous reports showing the presence of the Pm-3m primitive perovskite structure. Examining the SVMO-19 diffraction patterns more closely, very weak features are observed at low 2θ (Figure 1.2, inset). These features, located approximately at 13° , 22° , 23° , have been cited as evidence of long-range single perovskite domain ordering.^{29, 33, 34} Features at these scattering angles could also arise from the small amount of secondary phases cataloged in the Rietveld refined structure.

SVMO-19 stability in inert, reducing and oxidizing atmospheres. Secondary phases that form in double perovskites can compromise the material's MIEC properties. Often, these secondary phases are crucial for understanding the material's performance given that many are electronic and ionic insulating. To address SVMO's susceptibility to secondary phase formation at the surface, we employed *in-situ* Raman spectroscopy to monitor and characterize material stability under conditions common to SOFC and SOEC conditions.

Figure 2.2a shows Raman spectra of SVMO-19 over a temperature range from room temperature to 1000°C in a $5\% \text{ H}_2/\text{N}_2$ (forming gas) atmosphere. When exposed to forming gas, the Raman spectrum remains featureless, with the only noticeable change being a significant rise in the baseline at temperatures exceeding 800°C . Similar behavior is observed when the material is subjected to argon and humidified argon ($3\% \text{ steam}$).

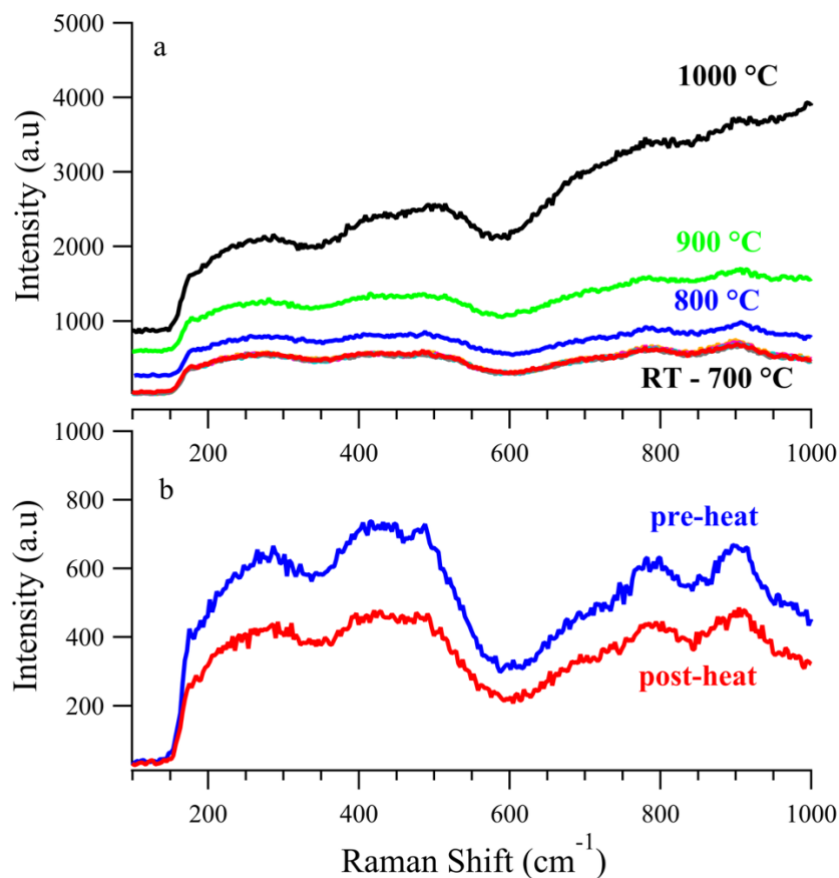


Figure 2.2. (a) Raman spectra of SVMO-19 in 5% H₂ from room temperature to 1000 °C; (b) Raman spectra of SVMO-19 in 5% H₂ pre-and post-heat

The spectra in 2.2a are virtually identical except for a baseline that begins to rise at temperatures above 700 °C. However, even at 1000 °C, the spectrum remains largely featureless. Possible explanations for the rising baseline include background blackbody radiation from the heated sample and a change in the material's reflectivity. These effects, however, are reversible as evidenced by the 'before' and 'after' spectra shown in Figure 2.2b. To within a small scaling factor, the pre- and post-heating spectra of SVMO-19 are almost identical, demonstrating that SVMO-19 is thermally stable in reducing atmospheres. (Similar results were observed for

experiments conducted in inert atmospheres (N_2) as well as weakly oxidizing atmospheres (3% steam in N_2 .) Importantly, SVMO-19 in a 20% CO_2 atmosphere (in N_2) showed behavior equivalent to that under 5% H_2 . This result is significant because both CO_2 and H_2O are known to be weakly oxidizing at elevated temperatures, showing that SVMO-19 has some resistance to oxidation. (Results from the SVMO-19 thermal stability studies under N_2 and N_2 with 3% steam, and N_2 are reported in Appendix A.)

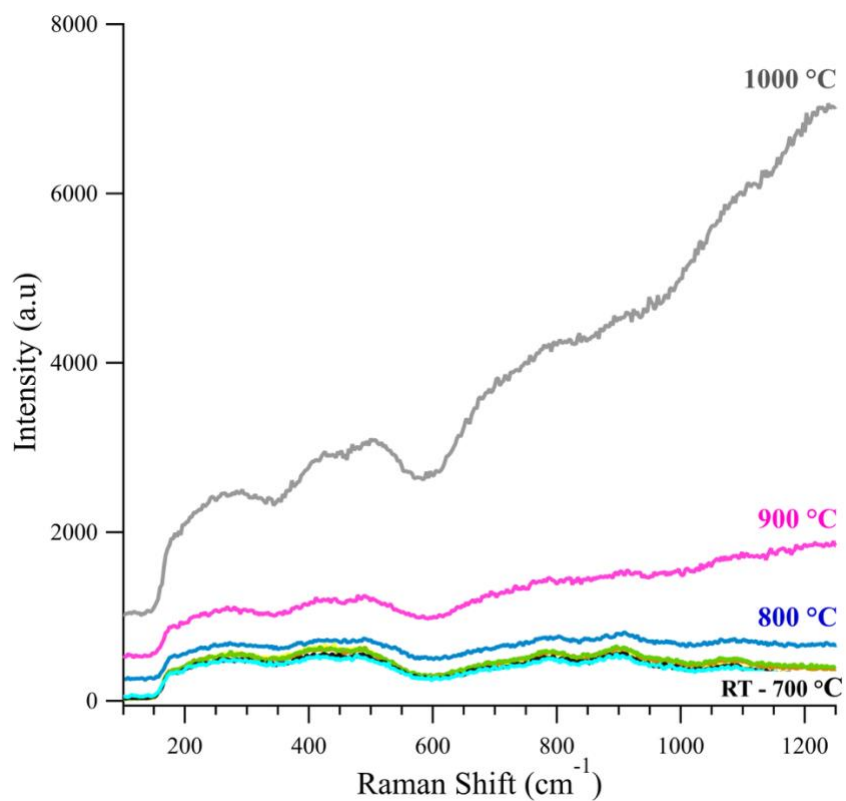


Figure 3.2. *In Situ* Raman spectra of SVMO-19 in 20 % CO_2 from room temperature to 1000 °C

Unlike behavior observed in reducing, inert, and weakly oxidizing atmospheres, SVMO-19 is distinctly unstable in air at elevated temperatures. Figure 4.2a shows the evolution of

SVMO-19 as the sample temperature is raised in 100° increments to 1000 °C. At temperatures above 600 °C in air, a prominent Raman peak is observed near 876 cm⁻¹. Additionally, the Raman spectrum of SVMO19 shows several other peaks appearing at approximately 825 cm⁻¹, 776 cm⁻¹, 358 cm⁻¹, and 322 cm⁻¹. Based on findings reported by Son *et al.*³¹, these features are assigned to the scheelite phase, SrMoO₄. A consequence of SVMO's decomposition in air at elevated temperatures implies that this material will not be effective as the oxygen electrode in SOFCs and SOECs.

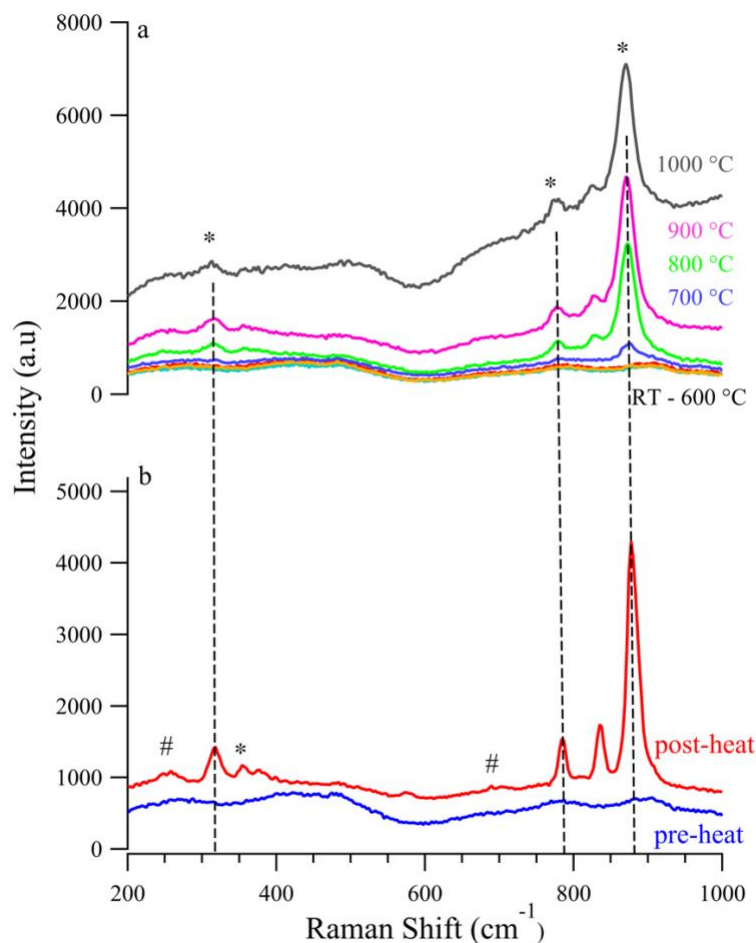


Figure 4.2. (a) *In situ* Raman spectra of SVMO-19 in air from room temperature to 1000 °C; (b) Raman spectra of SVMO-19 in air pre- and post-heat (* = SrMoO₄; # = SrVO₃)

Earlier studies by Porto and Scott³⁵ provided a detailed analysis of the Raman modes associated with the scheelite-type structure of SrMoO₄ and their results indicated that the most intense Raman peak, occurring at 888 cm⁻¹, corresponds to the totally symmetric stretching motion of the tetrahedral MoO₄ group. In Figure 4.2a the observed peak at 876 cm⁻¹ is assigned to SrMoO₄, and its growth signifies secondary phase formation in SVMO-19. A Raman spectrum of this sample after cooling back to room temperature shows the SrMoO₄ vibrational

features clearly. Additional small features at 685 cm^{-1} and 259 cm^{-1} are assigned tentatively to the bending vibrations of VO_3 groups associated with the single perovskite SrVO_3 .³⁶

To assess how fast SrMoO_4 forms, we performed an isothermal Raman experiment. In this experiment, SVMO-19 was heated to $700\text{ }^\circ\text{C}$ under forming gas. After reaching the target temperature and dwelling for 15 minutes with no change in the spectrum, the atmosphere was switched from forming gas to air (assigned as $t_0 = 0$), and spectra were acquired every 5 minutes. (Residence times in the gas manifold are $\leq 20\text{ sec.}$) Results from this experiment are shown in Figure 5.2. Figure 5.2a shows selected spectra acquired at different times after t_0 . Figure 5.2b plots the intensity of the primary SrMoO_4 feature at 876 cm^{-1} as a function of time.

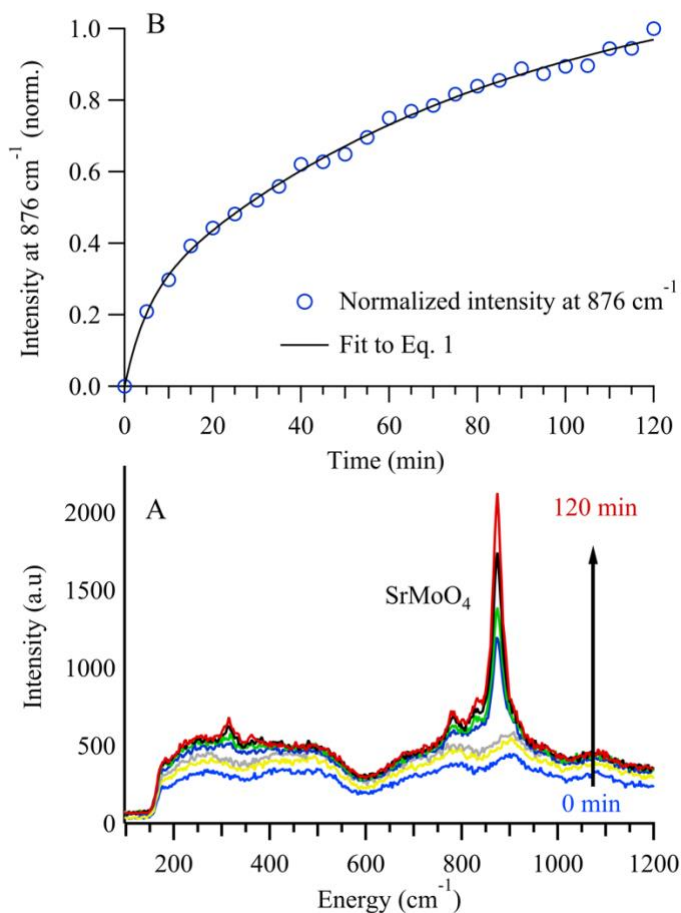


Figure 5.2. (a) *In Situ* Raman spectra of SVMO-19 in 5% H₂ and air from room temperature to 700 °C; (b) Kinetic trace showing the normalized intensity of the SrMoO₄ secondary phase after exposure to air at 700°C.

Raman spectroscopy reveals that SVMO-19 under air at 700°C takes up O₂ to form SrMoO₄. The emergence and growth of SrMoO₄ provide direct evidence that SVMO-19 is unstable under conditions commonly encountered as the oxygen electrode in solid oxide electrochemical cells. The data in Figure 5.2b can fit to a sum of two single exponential functions having characteristic rate constants, k_1 and k_2 :

$$Int(t) = A_0 + A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \quad (\text{Eq. 1.2})$$

Equation 1.2 suggests that SrMoO₄ forms via two first-order (or pseudo first order) processes with one rate measurably faster than the other. This hypothesis will be examined in the Discussion section below.

Thermal analysis. Thermal gravimetric analysis (TGA) was used to independently test the thermal stability of SVMO-19 in inert and air atmospheres. Figure 6.2 shows TGA traces of SVMO-19 in both N₂ and air as the sample temperature was raised to 900 °C at 5°C/min.

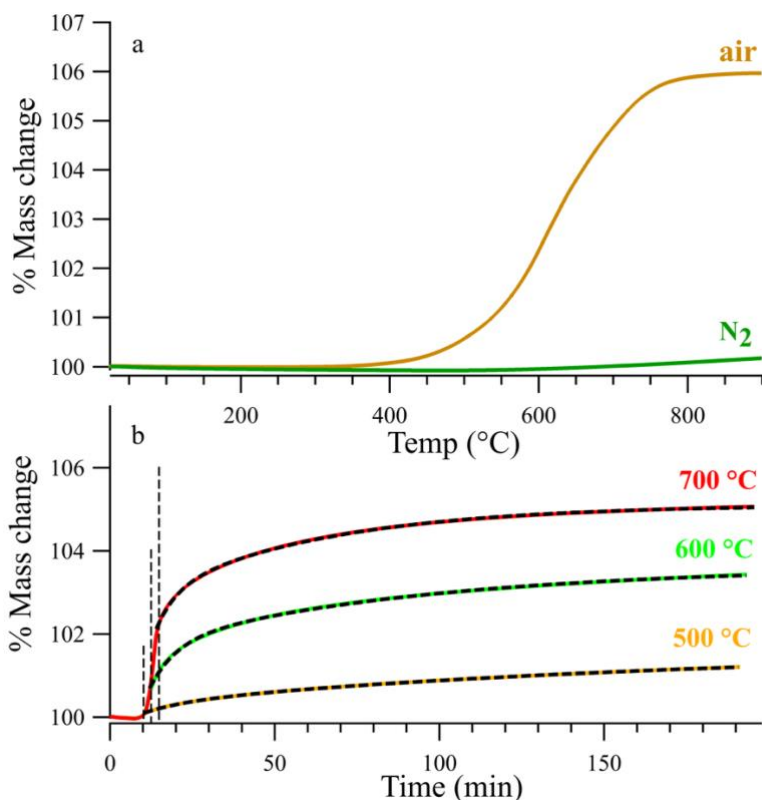


Figure 6.2. (a) TGA curves of SVMO-19 in N_2 and air from 25 to 900 °C (b) Isothermal TGA curves of SVMO-19 in air at 500 °C, 600 °C and 700 °C. The dashed vertical lines correspond to the time when the sample has reached its target temperature. The dashed lines superimposed on the data correspond to fits generated by Eq. 1.2.

Figure 6.2a shows that SVMO-19 is stable under N_2 at temperatures up to 900 °C. The slight gain in mass (0.1%) is associated with instrument drift and post-mortem Raman analysis of the sample showed that it remained SVMO-19. In contrast, SVMO-19 being heated in air shows mass accumulation beginning at ~400 °C with sample mass growing steadily before asymptotically leveling off near 750 °C.

To test if the rate of mass gain observed in the TGA experiment mirrored that in the isothermal Raman experiment (Figure 5.2b), we performed a ‘pseudo’-isothermal experiment

using TGA. In this experiment, the TGA was ramped as quickly as possible (50 °C/min) to 700 °C in air and then the temperature was held constant. Results from this experiment are shown in Figure 6.2b. The 700 °C trace shows that the sample begins acquiring mass before reaching its target temperature, but the last ~40% of the mass gain happens isothermally. Superimposed on the isothermal TGA data is a fit to the same double exponential function shown in Eq. 1.2. Again, the data fit exceptionally well to this functional form, implying that the mass gain corresponds directly to SrMoO_4 formation. This same method was repeated for a T_{max} of 600 °C and 500 °C and the data are included in Figure 6.2b. Again, the lower temperature data also follow the sum of two exponential decays.

Several questions emerge from the data presented above:

- How does oxygen uptake lead to SVMO-19 degradation?
- Do the kinetic rates observed in the isothermal Raman and TGA experiments correspond to the same processes?
- In both experiments, what physical phenomena do the two kinetic processes describe?

The first of these questions is easiest to answer. Raman data show that a major product formed from SVMO-19 degradation is SrMoO_4 . Raman data also show SrVO_3 in the sample post-heating. (SrVO_3 has a very small Raman scattering cross section. Even considerable quantities of this material would only provide a weak Raman signature). Finally, XRD patterns from the sample after it has been heated in air show an abundant pyrochlore phase, $\text{Sr}_2\text{V}_2\text{O}_7$. (Figure 7.2)

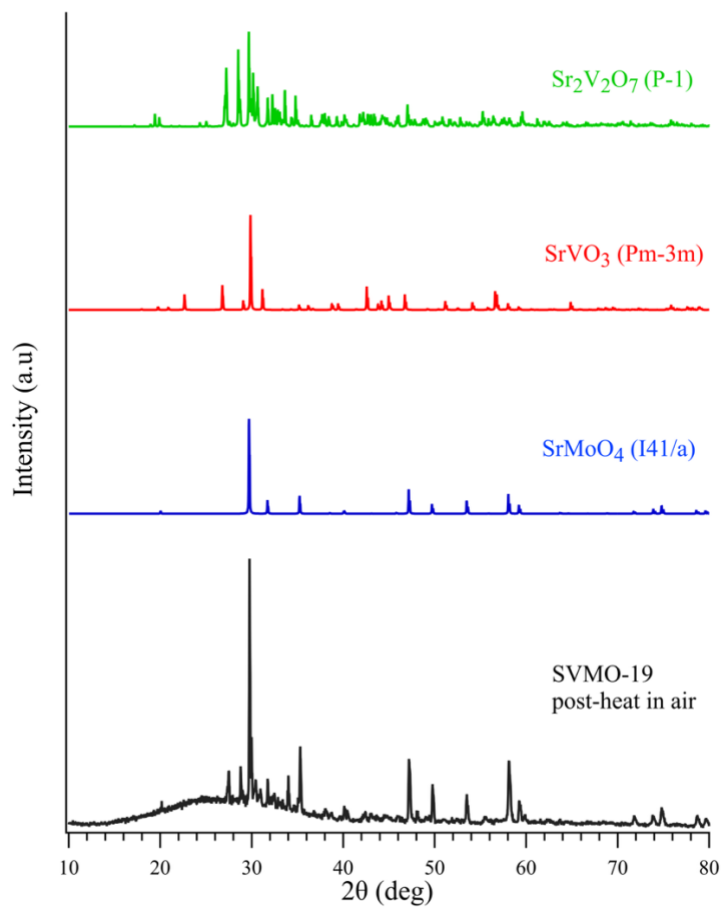
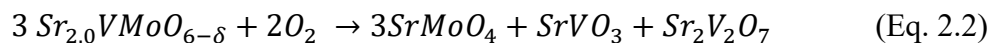


Figure 7.2. XRD pattern from SVMO-19 sample after being heated to 800°C in air. Rietveld refinement identifies 3 distinct secondary phases.

The XRD data in Figure 7.2 show definitively that SVMO-19 converts completely to SrMoO_4 , SrVO_3 , and $\text{Sr}_2\text{V}_2\text{O}_7$ with no measurable SVMO remaining in the sample.

Simple stoichiometric considerations require:



For A-site deficient SVMO-19, we propose that the perovskite is oxygen deficient ($\text{Sr}_{1-x}\text{VO}_{3-\delta}$) given that a perfect perovskite structure does not have any Raman active modes and instead requires defects or grain boundaries to induce a nonzero polarizability. These results are consistent with those reported by Son, *et al.*³¹ who reported scheelite, and perovskite phases formed during $\text{Sr}_2\text{FeMoO}_{6-\delta}$ oxidation in air.

The second question – do the isothermal Raman measurements tracking SrMoO_4 growth and the TGA measurements recording mass uptake report the same processes? – is an interesting one. TGA data contain no material specificity. Raman data, on the other hand, measure the real-time growth of SrMoO_4 . After reconciling units, we calculated rate constants (k_i) for the isothermal Raman intensity plot at 700°C shown in Figure 5.2b and the double exponential rate constants for the three isothermal TGA plots shown in Figure 6.2b. The results are reported in Table 1.2.

Table 1.2. Rate constants determined from fitting data in Figures 5.2b and 6.2b to Eq. 1. Typical uncertainties in k_1 are $\pm 20\%$; typical uncertainties in k_2 are $\pm 5\%$.

Method	Temp ($^\circ\text{C}$)	k_1 (s^{-1})	k_2 (s^{-1})	A_0	A_1	A_2
Raman	700	3.4×10^{-3}	2.1×10^{-4}	1.18	-0.96	-0.22
TGA	700	2.3×10^{-3}	3.4×10^{-4}	1.01	-0.53	-1.73
TGA	600	2.1×10^{-3}	2.0×10^{-4}	1.05	-0.61	-1.43
TGA	500	1.3×10^{-3}	9.5×10^{-5}	1.38	-1.14	-0.45

This analysis assumed that the rates were described by pseudo-first order rate constants where the O_2 partial pressure is taken as a constant. Given similarities in rate constants for the 700°C Raman and TGA data, we propose that the observables measured in each experiment describe the same physical processes. This conclusion is important because it implies oxygen uptake is rate

limiting when SVMO-19 oxidizes in air and that SrMoO_4 forms at the same rate that O_2 is being absorbed.

To address the third question posed above – to what physical processes do these rates correspond? – we first considered other possible models that might be applied to analyze phase transformations in solid state samples. The Avrami model, widely used for phase transformations in materials systems, predicts sigmoidal kinetics and is represented as follows:

$$f(t) = 1 - \exp(-kt^n) \quad (\text{Eq. 3.2})$$

where $f(t)$ is the fraction transformed at time t , and k and n are kinetic parameters.³⁷ The Avrami exponent n provides mechanistic insight: values near 1 suggest surface-controlled reactions or instantaneous nucleation with one-dimensional growth, while $0 < n < 1$ indicates diffusion-limited or constrained kinetics. In this regime, the rate is limited by the slow movement of O^{2-} ions through the lattice rather than by surface reaction or nucleation. The rate constant k reflects the combined effects of nucleation and growth processes.³⁷

Empirically, we found that the double exponential function (Eq. 1.2) representing two independent first order kinetic processes fit the data better than the Avrami function (Eq. 3.2), especially at the lowest temperature (500°C). We rationalize this observation in terms of the role played by oxide vacancies in facilitating O^{2-} diffusion in A-site deficient materials. Additionally, we note that for SVMO-19 to oxidize, excess oxygen must be present, meaning that the interior of the samples used in this work cannot oxidize to form secondary phases until O^{2-} ions diffuse into the material's bulk.

Removing Sr^{2+} ions from the A-site produces Sr vacancies (V_{Sr}'') and charge-compensating O^{2-} vacancies ($V_{\text{O}}^{\bullet\bullet}$) according to:



These vacancies provide pathways that promote O^{2-} diffusion. Under oxidizing conditions, molecular oxygen reacts rapidly at the surface of to fill these pre-existing vacancies:



Because these defect sites are already present, we expect that SVMO-19 oxidation forms SrMoO_4 and other secondary phases rapidly. In the double exponential model, secondary phases will form in the bulk after the oxides diffuse into the bulk with a similar activation energy. In the Avrami model, oxide diffusion then becomes rate limiting and the material transformation (from SVMO-19 to SrMoO_4 and $\text{Sr}_2\text{V}_2\text{O}_7$) in the bulk happens as soon as oxides arrive.

When the Avrami constant, n , approaches unity as is the case when fitting the isothermal TGA data at 500°C to an Avrami model, oxidation is assumed to happen spontaneously at multiple sites throughout the material rather than with a single diffusion front.³⁸⁻⁴⁰ Such a situation requires that the oxide responsible for driving the phase transition already be present in the material. This situation does not describe conditions relevant for SVMO-19, where the oxides must first diffuse into the interior before the SVMO-19 oxidation can occur.

Given the similarity in activation energies determined from the double exponential fit and the inability of an Avrami model to fit the low temperature data, we choose to use the former model to describe the isothermal TGA and Raman data. The two first order processes are

tentatively assigned to transformation of the surface (and near-surface) of SVMO-19 into its oxidized secondary phases and followed by the slower transformation of the bulk material after the diffusing oxides have arrived. This model implicitly assumes that oxidation in the bulk material is slower than oxidation of the surface. We acknowledge that this description is speculative, *but* it suggests several testable hypotheses that we will explore in subsequent work that examines SVMO-19 stability as a function of A-site deficiency (and B-site composition).

The double exponential kinetic model provides significantly better fits (Figure 8.2a) across all temperatures, accurately capturing both the initial and long-term kinetics of the transformation. In contrast, superimposed on the isothermal TGA data at 500 °C, 600 °C, and 700 °C (Figure 8.2b) are fits to the Avrami kinetic model (Eq. 3.2). We note that to fit the isothermal TGA data to an Avrami model, data needed to be scaled and normalized to 1.0 before Equation 3.2 could be applied. While the Avrami model captures the general sigmoidal behavior of the mass uptake, the agreement with the experimental data is limited. Discrepancies between the two different models suggest that mass uptake and phase transformation is better described by two distinct rate-limiting steps rather than a single, unified transformation mechanism assumed in the Avrami approach.

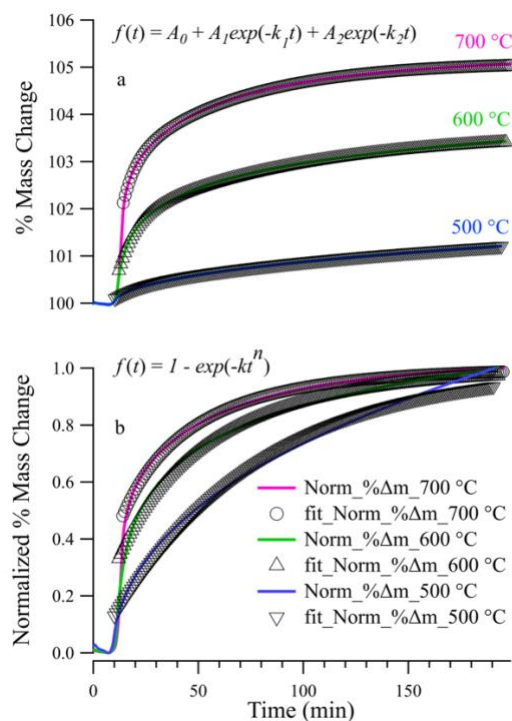


Figure 8.2. Isothermal TGA curves of SVMO-19 in air at 500 °C, 600 °C and 700 °C with fits to (a) the double exponential kinetic, and (b) the Avrami kinetic models

Following unit reconciliation, the Avrami rate constants (k) and exponents (n) were determined for the isothermal Raman intensity data at 700 °C (Figure 5.2b) and for the isothermal TGA data at 500 °C, 600 °C, and 700 °C (Figure 8b). Calculated kinetic parameters are reported in Table 2.2.

Table 2.2. Rate constant and exponent determined from fitting data in Figure 8.2b to Eq. 3.2. Typical uncertainties in rate constants are less than $\pm 25\%$.

Method	Temp ($^{\circ}\text{C}$)	k (s^{-1})	n
Raman	700	4.5×10^{-2}	0.84
TGA	700	9.9×10^{-2}	0.72
TGA	600	5.6×10^{-2}	0.79
TGA	500	1.4×10^{-2}	1.01

Several observations from Table 2.2 stand out. First, the Avrami rate constants are an order of magnitude larger than the rate constants determined from the double exponential fit. Importantly, the difference between the Raman and TGA rate constants at 700 $^{\circ}\text{C}$ is more than a factor of 2, compared to the $\sim 50\%$ differences found from the double exponential model. Second, the Avrami exponent, n , is less than unity for kinetic data at 600 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$ and equal to unity for the isothermal TGA data taken at 500 $^{\circ}\text{C}$. According to the conventional interpretation of the Avrami exponent, values less than unity correspond to diffusion-limited processes, while the 1.0 value at 500 $^{\circ}\text{C}$ would indicate a change in SVM0-19 decomposition to a surface-controlled mechanism.

With temperature dependent rate constants for both models – double exponential and Avrami – we performed Arrhenius analyses for both data sets. For the double exponential model, plotting $\ln(k_i)$ versus $1/T_i$ for k_1 and k_2 yielded two linear trends with similar slopes corresponding to activation energies $E_{a,1} = 0.65 \pm 0.19$ eV and $E_{a,2} = 0.48 \pm 0.01$ eV, respectively (Figure 9.2).

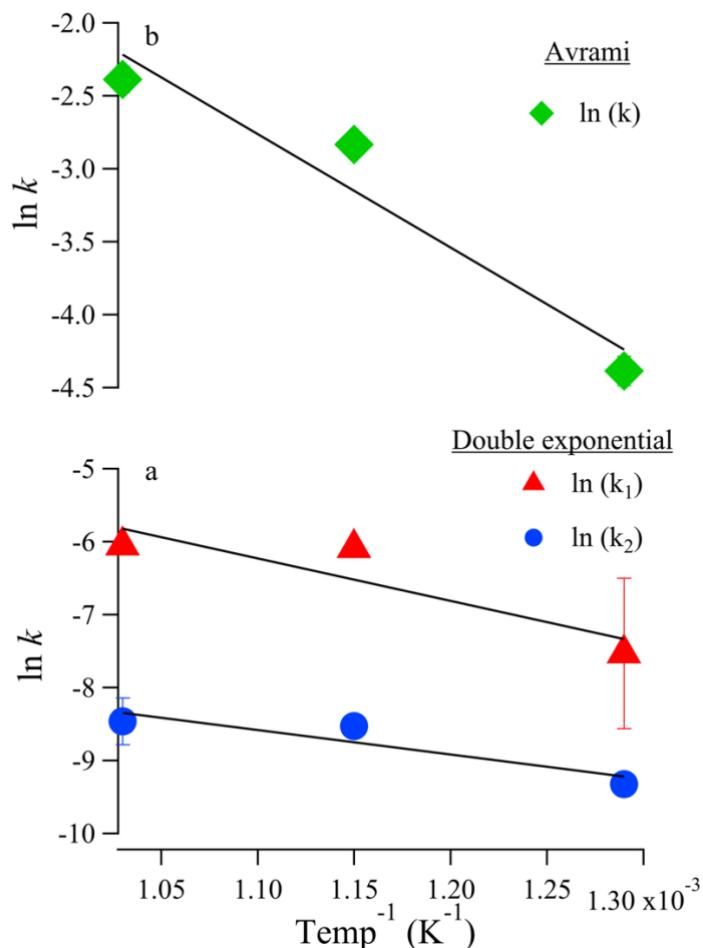


Figure 9.2. Arrhenius plots for SVMO-19 kinetic data from isothermal TGA measurements shown in Figure 6.2. Data in panel (a) correspond to a double exponential function describing two independent first order kinetic processes. (See Equation 1.) Data in panel (b) correspond to rate constants derived from an Avrami model. (See equation 3.) Experiments at each temperature were carried out a minimum of 4 times and the uncertainties represent two standard deviations. Note the break in scale between panels (a) and (b).

A similar analysis of the Avrami rate constants produced a single linear fit, yielding an activation energy of $E_a = 0.62 \pm 0.12$ eV (Figure 9.2). We note that the activation energies calculated from all three sets of rate constants (double exponential fast, double exponential slow, Avrami) are quite similar. This observation shows that the energetics of SVMO-19

decomposition are largely insensitive to the model used to describe the process. Based on the goodness of fits shown in Figure 8.2, we propose that the double exponential model is more appropriate to describe the processes. Furthermore, similarities between $E_{a,1}$ and $E_{a,2}$ to within experimental uncertainty suggest that the two kinetic processes are, themselves, also similar. Our hypothesis is that the faster rate constant, k_1 , corresponds to SVMO-19 decomposition and secondary phase formation at the material surface where reaction with ambient O_2 happens quickly, albeit with a higher activation energy. In this scenario, k_2 corresponds to SVMO-19 decomposition and secondary phase formation in the bulk. This second process should be slower given that it requires atomic restructuring that is more restricted than on the sample surface. Additionally, the pre-exponential factors A_1 and A_2 provide insight into the respective temperature ranges over which SVMO decomposition takes place. At elevated temperatures, the coefficient corresponding to the faster rate (A_1) is less than the slower rate coefficient (A_2). These numbers are consistent with more decomposition taking place in the bulk although the rate of reaction is slower. At 500 °C, the relative magnitudes reverse with A_1 being greater than A_2 . We propose that at lower temperatures, mass transport into the bulk is simply too slow and measurements are sensitive primarily to surface transformations. In the case of the isothermal Raman measurements at 700 °C, A_1 is again greater than A_2 , but Raman measurements are necessarily more sensitive to changes in a material's surface and near surface composition than to changes occurring in the bulk.

Summary

Double perovskite materials are attractive candidates to serve as electrodes in high temperature solid oxide electrochemical devices. Before they can be integrated into this

technology, however, individual materials must be evaluated in terms of their electrocatalytic potential, their resilience to contamination, and their stability to changes in ambient atmosphere. These assessments need to happen at relevant operating temperatures and in atmospheres representative of those the materials will encounter under operational conditions. SVMO holds promise given earlier reports of high conductivities.²⁹ In the current work, we used a combination of independent methods to assess SVMO-19's stability under a variety of thermal and atmospheric conditions. In doing so, we have identified conditions that support SVMO-19's sustained stability and conditions that lead to irreversible degradation. *In situ* Raman measurements demonstrate that SVMO-19 is stable up to 1000 °C under reducing atmospheres as well as weakly oxidizing atmospheres containing CO₂ and H₂O. This latter condition implies that SVMO-19 should be suitable for CO₂ electrolysis and CO₂/H₂O co-electrolysis. SVMO, even as a fuel electrode could be resilient to fuel flow disruptions. Under strongly oxidizing atmospheres, SVMO rapidly separates into secondary phases including SrMoO₄, SrVO₃, and Sr₂V₂O₇. A detailed examination of this decomposition process shows that it most closely follows a kinetic mechanism containing two independent first order (or pseudo first order) processes. The activation energies for these two processes are 0.53 and 0.70 eV. The similarity between these two values implies that the two processes describe similar transformations, ones that we tentatively assign to surface and bulk material reactions. More importantly, these findings demonstrated clearly that while SVMO-19 may be suitable for use as a fuel electrode in solid oxide cells (including under weakly oxidizing conditions), its utility as an oxygen electrode is limited given the material's propensity to form secondary phases at high temperature in air.

References

- (1) Vafaeenezhad, S.; Hanifi, A. R.; Laguna-Bercero, M. A.; Etsell, T. H.; Sarkar, P. Microstructure and long-term stability of Ni–YSZ anode supported fuel cells: a review. *Materials Futures* **2022**, 1 (4), 042101.
- (2) Zhang, J.; Barreau, M.; Dintzer, T.; Haevecker, M.; Teschner, D.; Efimenko, A.; Luo, W.; Zafeiratos, S. Unveiling Key Interface Characteristics of Ni/Yttria-Stabilized Zirconia Solid Oxide Cell Electrodes in H₂O Electroreduction Using Operando X-ray Photoelectron Spectroscopy. *ACS Applied Materials & Interfaces* **2024**, 16 (29), 37915-37926.
- (3) Kullmann, F.; Schwiers, A.; Juckel, M.; Menzler, N.; Weber, A. Enhancement of Performance and Sulfur Tolerance of Ceria-Based Fuel Electrodes in Low Temperature SOFC. *Journal of The Electrochemical Society* **2024**, 171 (4), 044511.
- (4) Calkins, W. H. Investigation of organic sulfur-containing structures in coal by flash pyrolysis experiments. *Energy & Fuels* **1987**, 1 (1), 59-64.
- (5) Cheng, Z.; Wang, J.-H.; Choi, Y.; Yang, L.; Lin, M.-C.; Liu, M. From Ni-YSZ to sulfur-tolerant anode materials for SOFCs: electrochemical behavior, in situ characterization, modeling, and future perspectives. *Energy & Environmental Science* **2011**, 4 (11), 4380-4409.
- (6) Gong, M.; Liu, X.; Trembly, J.; Johnson, C. Sulfur-tolerant anode materials for solid oxide fuel cell application. *Journal of Power Sources* **2007**, 168 (2), 289-298.
- (7) Hua, B.; Li, M.; Chi, B.; Jian, L. Enhanced electrochemical performance and carbon deposition resistance of Ni–YSZ anode of solid oxide fuel cells by in situ formed Ni–MnO layer for CH₄ on-cell reforming. *Journal of Materials Chemistry A* **2014**, 2 (4), 1150-1158.
- (8) Koh, J.-H.; Yoo, Y.-S.; Park, J.-W.; Lim, H. C. Carbon deposition and cell performance of Ni-YSZ anode support SOFC with methane fuel. *Solid State Ionics* **2002**, 149 (3-4), 157-166.
- (9) Niakolas, D. K. Sulfur poisoning of Ni-based anodes for Solid Oxide Fuel Cells in H/C-based fuels. *Applied Catalysis A: General* **2014**, 486, 123-142.
- (10) Zhan, Z.; Barnett, S. A. An octane-fueled solid oxide fuel cell. *Science* **2005**, 308 (5723), 844-847.

- (11) Song, Y.; Zhou, Z.; Zhang, X.; Zhou, Y.; Gong, H.; Lv, H.; Liu, Q.; Wang, G.; Bao, X. Pure CO₂ electrolysis over an Ni/YSZ cathode in a solid oxide electrolysis cell. *Journal of Materials Chemistry A* **2018**, 6 (28), 13661-13667.
- (12) Ebbesen, S. D.; Graves, C.; Hauch, A.; Jensen, S. H.; Mogensen, M. Poisoning of solid oxide electrolysis cells by impurities. *Journal of the Electrochemical Society* **2010**, 157 (10), B1419.
- (13) Lv, H.; Lin, L.; Zhang, X.; Gao, D.; Song, Y.; Zhou, Y.; Liu, Q.; Wang, G.; Bao, X. In situ exsolved FeNi₃ nanoparticles on nickel doped Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ} perovskite for efficient electrochemical CO₂ reduction reaction. *Journal of Materials Chemistry A* **2019**, 7 (19), 11967-11975.
- (14) Fagg, D.; Kharton, V.; Frade, J.; Ferreira, A. Stability and mixed ionic–electronic conductivity of (Sr, La)(Ti, Fe)O_{3-δ} perovskites. *Solid State Ionics* **2003**, 156 (1-2), 45-57.
- (15) Chen, X.; Liu, Q.; Chan, S.; Brandon, N.; Khor, K. A. High-performance cathode-supported SOFC with perovskite anode operating in weakly humidified hydrogen and methane. *Fuel Cells Bulletin* **2007**, 2007 (6), 12-16.
- (16) Tao, S.; Irvine, J. T.; Kilner, J. A. An efficient solid oxide fuel cell based upon single-phase perovskites. *Advanced Materials* **2005**, 17 (14), 1734-1737.
- (17) Mukundan, R.; Brosha, E. L.; Garzon, F. H. Sulfur tolerant anodes for SOFCs. *Electrochemical and Solid-State Letters* **2003**, 7 (1), A5.
- (18) Fu, X.-Z.; Melnik, J.; Low, Q.-X.; Luo, J.-L.; Chuang, K. T.; Sanger, A. R.; Yang, Q.-M. Surface modified Ni foam as current collector for syngas solid oxide fuel cells with perovskite anode catalyst. *International journal of hydrogen energy* **2010**, 35 (20), 11180-11187.
- (19) Huang, Y.-H.; Dass, R. I.; Denyszyn, J. C.; Goodenough, J. B. Synthesis and characterization of Sr₂MgMoO_{6-δ}: an anode material for the solid oxide fuel cell. *Journal of the Electrochemical Society* **2006**, 153 (7), A1266.
- (20) Huang, Y.-H.; Dass, R. I.; Xing, Z.-L.; Goodenough, J. B. Double perovskites as anode materials for solid-oxide fuel cells. *Science* **2006**, 312 (5771), 254-257.
- (21) Marina, O. A.; Canfield, N. L.; Stevenson, J. W. Thermal, electrical, and electrocatalytical properties of lanthanum-doped strontium titanate. *Solid State Ionics* **2002**, 149 (1-2), 21-28.

- (22) Qiu, P.; Yang, X.; Wang, W.; Wei, T.; Lu, Y.; Lin, J.; Yuan, Z.; Jia, L.; Li, J.; Chen, F. Redox-reversible electrode material for direct hydrocarbon solid oxide fuel cells. *ACS applied materials & interfaces* **2020**, 12 (12), 13988-13995.
- (23) Song, Y.; Zhong, Q.; Tan, W.; Pan, C. Effect of cobalt-substitution $\text{Sr}_2\text{Fe}_{1.5-x}\text{Co}_x\text{Mo}_{0.5}\text{O}_{6-\delta}$ for intermediate temperature symmetrical solid oxide fuel cells fed with H_2 - H_2S . *Electrochimica Acta* **2014**, 139, 13-20.
- (24) Xiao, G. L., Q.; Zhao, F.; Zhang, L.; Xia, C.; Chen, F. $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ as cathodes for intermediate-temperature solid oxide fuel cells with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.87}\text{Mg}_{0.13}\text{O}_3$ electrolyte. *Journal of The Electrochemical Society* **2011**, 158 (5), B455-B460. DOI: 10.1149/1.3556085.
- (25) Ding, H.; Tao, Z.; Liu, S.; Yang, Y. A redox-stable direct-methane solid oxide fuel cell (SOFC) with $\text{Sr}_2\text{FeNb}_{0.2}\text{Mo}_{0.8}\text{O}_{6-\delta}$ double perovskite as anode material. *Journal of Power Sources* **2016**, 327, 573-579.
- (26) Tao, S.; Irvine, J. T. A redox-stable efficient anode for solid-oxide fuel cells. *Nature materials* **2003**, 2 (5), 320-323.
- (27) Zhang, M.; Li, Y.; Du, Z.; Zhang, Y.; Zhao, H. Double perovskite $\text{Sr}_2\text{FeMo}_{0.6}\text{Mg}_{0.25}\text{Ga}_{0.15}\text{O}_{6-\delta}$ as high-performance fuel electrode for reversible solid oxide cell. *Journal of Power Sources* **2024**, 594, 234031.
- (28) Gou, M.; Ren, R.; Sun, W.; Xu, C.; Meng, X.; Wang, Z.; Qiao, J.; Sun, K. Nb-doped $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ electrode with enhanced stability and electrochemical performance for symmetrical solid oxide fuel cells. *Ceramics International* **2019**, 45 (12), 15696-15704.
- (29) Childs, N. B.; Weisenstein, A.; Smith, R.; Sofie, S.; Key, C. Electrical conductivity of $\text{Sr}_{2-x}\text{V}_x\text{Mo}_{0.6-y}\text{O}_{6-y}$ ($x=0.0, 0.1, 0.2$) double perovskites. *Journal of Applied Physics* **2013**, 113 (24).
- (30) Huang, Y.-H.; Liang, G.; Croft, M.; Lehtimäki, M.; Karppinen, M.; Goodenough, J. B. Double-perovskite anode materials Sr_2MMoO_6 ($M=\text{Co}, \text{Ni}$) for solid oxide fuel cells. *Chemistry of materials* **2009**, 21 (11), 2319-2326.
- (31) Son, L. H.; Phuc, N. X.; Phuc, P. V.; Hong, N. M.; Hong, L. V. Observation of phase decomposition of $\text{Sr}_2\text{FeMoO}_6$ by Raman spectroscopy. *Journal of Raman Spectroscopy* **2001**, 32 (10), 817-820.

- (32) Niu, B.; Jin, F.; Fu, R.; Feng, T.; Shen, Y.; Liu, J.; He, T. Pd-impregnated Sr_{1-x}9VMoO_{6-δ} double perovskite as an efficient and stable anode for solid-oxide fuel cells operating on sulfur-containing syngas. *Electrochimica Acta* **2018**, 274, 91-102.
- (33) Shimada, T.; Nakamura, J.; Motohashi, T.; Yamauchi, H.; Karppinen, M. Kinetics and thermodynamics of the degree of order of the B cations in double-perovskite Sr₂FeMoO₆. *Chemistry of materials* **2003**, 15 (23), 4494-4497.
- (34) Woodward, P. M. Octahedral tilting in perovskites. I. Geometrical considerations. *Acta Crystallographica Section B: Structural Science* **1997**, 53 (1), 32-43.
- (35) Porto, S.; Scott, J. Raman Spectra of CaWO₄, SrWO₄, CaMoO₄, and SrMoO₄. *Physical Review* **1967**, 157 (3), 716.
- (36) Botto, I. L.; Baran, E. J.; Pedregosa, J. C.; Aymonino, P. J. The vibrational spectrum of barium divanadate. *Monatshefte für Chemie-Chemical Monthly* **1979**, 110, 895-898.
- (37) Fanfoni, M.; Tomellini, M. The johnson-mehl-avrami-kohnogorov model: a brief review. II *Nuovo Cimento D* **1998**, 20, 1171-1182.
- (38) Avrami, M. Granulation, phase change, and microstructure kinetics of phase change. III. The *Journal of chemical physics* **1941**, 9 (2), 177-184.
- (39) Avrami, M. Kinetics of phase change. II transformation-time relations for random distribution of nuclei. *The Journal of chemical physics* **1940**, 8 (2), 212-224.
- (40) Avrami, M. Kinetics of phase change. I General theory. *The Journal of chemical physics* **1939**, 7 (12), 1103-1112.

CHAPTER THREE

THE ROLE OF A-SITE DEFICIENCY IN $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$

STABILITY

Contributions of Authors and Co-Authors

Manuscript in Chapter 3:

Author: Bamidele J. Samuel

Contributions: Collected and analyzed all data, generated figures, planned experimental protocols and wrote manuscript in preparation for publication.

Co-Author: Stephen K. Heywood

Contributions: Prepared materials reviewed and edited successive versions of the manuscript.

Co-Author: Julia A. Esakoff

Contributions: Prepared materials reviewed and edited successive versions of the manuscript.

Co-Author: Stephen W. Sofie

Contributions: Reviewed and edited successive versions of the manuscript.

Co-Author: Robert A. Walker

Contributions: Helped plan experimental protocols and cowrote the first version of the manuscript. Reviewed and edited successive versions of the manuscript.

Manuscript Information

Bamidele J. Samuel, Stephen K. Heywood, Julia A. Esakoff, Stephen W. Sofie and Robert A.

Walker

Chemistry of Materials

Status of Manuscript:

- ☒ Prepared for submission to a peer-reviewed journal
- ☐ Officially submitted to a peer-reviewed journal
- ☐ Accepted by a peer-reviewed journal
- ☐ Published in a peer-reviewed journal

Abstract

Studies in this chapter investigate the high-temperature stability of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ (SVMO) double perovskites in air for different A-site deficiencies with $x = 0, 0.05, 0.1, 0.15$ and 0.2 . The goal of these studies was to determine if A-site deficiency affected SVMO stability under conditions commonly encountered in high-temperature energy conversion devices. Material stability was evaluated using thermogravimetric analysis (TGA) and vibrational Raman spectroscopy, providing complementary insights into mass changes and compositional evolution during exposure to air at elevated temperatures. Among all five compositions, $x = 0.05$ (SVMO-195) was identified as the most stable, exhibiting the lowest mass gain and the highest onset temperature for oxidation-related mass accumulation. These results indicate a significant improvement in resistance to degradation compared to both the stoichiometric ($x = 0$, SVMO-20) and more deficient compositions. Raman spectroscopy further revealed that A-site deficiency plays a critical role in governing phase stability. In particular, the A-site deficient formulation $x = 0.1$ (SVMO-19) showed reduced formation of secondary phases compared to both the fully stoichiometric SVMO-20 and the more deficient $x = 0.2$ (SVMO-18), suggesting the existence of an optimal range of Sr deficiency for enhanced stability. A detailed kinetic analysis of degradation in air was carried out using isothermal TGA and isothermal Raman data. The results show that the degradation process can be described by two first-order reactions, indicating the presence of multiple underlying mechanisms. Temperature-dependent studies enabled the determination of effective activation energies for degradation using both experimental techniques. While the trends obtained from isothermal TGA and isothermal Raman experiments were in qualitative agreement, differences in the absolute activation energy values suggest that the two methods probe different, unassigned aspects of the degradation process. Overall, this work demonstrates that controlled A-site deficiency can significantly improve the air stability of SVMO materials in air at elevated temperatures, with $\text{Sr}_{1.95}\text{VMoO}_{6-\delta}$ emerging as a particularly promising composition.

The Role of A-site Deficiency in $\text{Sr}_{2.0-x}\text{VMoO}_{6-\delta}$ Stability

Introduction

Perovskite oxides have emerged as essential materials in a host of high temperature energy conversion applications.¹⁻⁷ With the general formula ABO_3 , perovskite oxides have expansive versatility in their ability to substitute elements at different sites and include stoichiometric deficiencies (typically on the A-site) to optimize specific functional behaviors.^{8,9} A-site and B-site deficiencies reduce a material's overall oxygen content, creating oxide vacancies and promoting ionic conductivity. As promising electrocatalysts for the oxygen reduction reaction (ORR),^{10,11} perovskite oxides are attractive high temperature electrodes given the material's compositional flexibility that allows for fine-tuning of the electronic structure and, consequently, conductivity and catalytic activity.¹²

One effective strategy for enhancing ORR performance involves the deliberate introduction of oxygen vacancies by creating A-site deficient materials.¹³ These vacancies play a dual role in catalysis: they facilitate the adsorption and activation of oxygen molecules on the catalyst surface and enhance the mobility of oxide ions throughout the material.¹⁴⁻¹⁷ Additionally, oxygen vacancies can serve as active sites for the ORR,⁸ promoting more efficient charge transfer and intermediate stabilization. Various synthetic and post-treatment methods have been developed to increase the oxygen vacancy concentrations, thereby improving ORR kinetics.^{18,19} Understanding and controlling these defect structures is essential for the directed design of high-performance perovskite-based electrocatalysts. This approach offers a cost-effective and scalable pathway to developing alternatives to noble metal catalysts, that are limited by high cost and material scarcity.^{2,3,20-22} As such, the study of oxygen vacancies in perovskite oxides represents

a necessary step toward the advancement of efficient, durable, and economically viable ORR catalysts for next-generation energy technologies.

With a stoichiometry $A_{1-x}BO_{3-\delta}$ (with x typically between 0.0 and 0.2), A-site deficient perovskites have intrinsic oxide vacancies making these materials efficient oxide ion conductors. Merkulov et al.⁹ investigated the influence of A-site cation deficiency in $La_{0.5-x}Sr_{0.5}FeO_{3-\delta}$ (LSF) perovskite oxides on their structural, thermomechanical, and transport properties, with a focus on their potential application as solid oxide fuel cell (SOFC) cathode materials and oxygen-permeable membranes. Systematic variation of the A-site deficiency (x) from 0-0.02 revealed a nonlinear relationship between composition and material properties. Specifically, increasing x from 0 to 0.01 expands the unit cell volume and improves electrical conductivity. However, further increasing x beyond 0.01 leads to the formation of a secondary phase impurity, (La, Sr) $Fe_{12}O_{19}$ that, even in trace amounts, reduces the concentration of A-site vacancies and reverses the observed conductivity improvements. Based on these findings, compositions between $x = 0$ and $x = 0.01$ were identified as particularly promising and were subjected to more detailed investigation.

An emerging class of perovskite oxides are double perovskites, typically represented by the formula $A_2BB'O_6$. These materials often extend and enhance the attractive properties of single perovskite oxides in high temperature electrochemical applications.²³ Compared to conventional single perovskites (ABO_3), double perovskites exhibit improved mixed ionic and electronic conductivity (MIEC), greater resistance to cation segregation and phase degradation, and increased tolerance to CO_2 and sulfur containing atmospheres.^{24,25} These properties collectively contribute to superior durability and performance, making double perovskites

particularly attractive for use as cathode or anode materials in next-generation SOFCs with extended operational lifetimes and enhanced efficiencies under harsh conditions. Furthermore, with expanded elemental flexibility, double perovskites offer opportunities to optimize properties with careful tuning of stoichiometries and vacancy concentrations. These materials have demonstrated remarkable performance in facilitating ORR kinetics,²⁶⁻²⁸ underscoring their potential for advanced electrochemical applications.

Lanthanide-based and strontium-based double perovskite oxides are widely studied because they are chemically stable, and their composition can be carefully adjusted to control their properties.²⁹⁻³⁵ The double perovskite $\text{La}_2\text{CoMnO}_6$ is a common example and has shown good potential as a catalyst for oxidation reactions.³⁶ In their work, Moradkhani *et al.*³⁶ prepared the stoichiometric compound $\text{La}_2\text{CoMnO}_6$ and a series of lanthanum-deficient materials, $\text{La}_{2-x}\text{CoMnO}_6$ ($x = 0.02, 0.05, 0.10, \text{ and } 0.15$), using a sol-gel method. These materials were tested for propane catalytic oxidation, a reaction commonly used to measure total oxidation activity. The stoichiometric material kept a well-ordered crystal structure and showed good structural stability during propane oxidation, but its catalytic activity was modest. When a small amount of lanthanum was removed, both activity and stability changed significantly.³⁶ The authors discovered that controlled lanthanum deficiency creates oxygen vacancies and lowers the barrier to oxygen reduction. More oxide vacancies increase oxygen mobility and raise the amount of reactive oxygen species on the surface, that then facilitates further propane oxidation.³⁶ As a result, the non-stoichiometric samples proved to be more active than the stoichiometric ones. Double perovskites having a composition with $x = 0.05$ typically show the best performance,

achieving 90% propane conversion at 423 °C and maintaining stable activity over long reaction times.³⁶

However, if too much lanthanum is removed, the crystal structure becomes distorted and may weaken, compromising long-term durability, even if redox properties continue to improve. Overall, the stoichiometric composition provides strong structural stability, while a carefully controlled lanthanum deficiency improves catalytic activity without greatly reducing stability. These results show that precise control of composition is essential for designing efficient and durable perovskite oxide catalysts for oxidation reactions.³⁶

Jiang et al.³⁷ examined how strontium (Sr) deficiency affects $\text{Sr}_{2-x}\text{MgMoO}_{6-\delta}$ SOFC anodes. The effects of Sr-site deficiency on the stability of $\text{Sr}_{2-x}\text{MgMoO}_{6-\delta}$ (SMMO, $x = 0-0.15$) was studied after reduction in a forming gas atmosphere (5% H_2/Ar) at 1200 °C for 48 h. X-ray diffraction results indicated that all compositions, including those with A-site deficiency, retain diffraction patterns very similar to stoichiometric $\text{Sr}_2\text{MgMoO}_6$. This behavior confirms that the double perovskite structure remains stable under reducing conditions and is primarily sustained by the robustness of the $[\text{BO}_6]$ octahedral network. Thermogravimetric analysis carried out in the same atmosphere (5% H_2/Ar) showed two clear weight-loss steps at around 300 °C and 700 °C. The first weight loss was assigned to lattice oxygen removal by the reducing atmosphere, while the second was linked to increased oxygen vacancy formation that accompanied the reduction of Mo^{6+} to Mo^{5+} , which typically occurs above 500 °C.³⁸ At 900 °C, the remaining mass percentages are 99.63%, 99.03%, 97.98%, and 98.41% for $x = 0, 0.05, 0.10$, and 0.15 , respectively, corresponding to oxygen vacancy values (δ) of 0.09, 0.18, 0.38, and 0.23. Among all four samples, the composition with $x = 0.10$ shows the highest concentration of oxygen

vacancies. A significant increase in electrical conductivity was observed with increasing Sr deficiency, with the highest conductivity achieved at $x = 0.10$.³⁷ Single-cell tests performed at 800 °C using a 280 μm thick LSGM electrolyte yielded maximum power densities of 527, 551, 659, and 573 mW cm^{-2} for $x = 0.00, 0.05, 0.10$, and 0.15 , respectively.³⁷ Among these compositions, the $x = 0.10$ sample demonstrated the most favorable overall performance. These findings suggest that Sr-deficient double perovskite oxides are promising candidates for high-performance solid oxide fuel cell anodes.

Feng et al.³⁹ studied how reducing strontium (Sr) content affects the properties of $\text{Sr}_{2-x}\text{Fe}_{1.4}\text{Ni}_{0.1}\text{Mo}_{0.5}\text{O}_{6-\delta}$ ($x = 0 - 0.1$, abbreviated as $\text{Sr}_{2-x}\text{FNM}$) perovskites used as anode materials in solid oxide fuel cells (SOFCs). The $\text{Sr}_{2-x}\text{FNM}$ oxides remain thermally stable in a reducing atmosphere at 750 °C, although some nickel particles exsolve at 800 °C when x is between 0 and 0.075.³⁹ Among the different A-site deficient species, $\text{Sr}_{1.95}\text{FNM}$ showed high electrical conductivity of 26.6 S cm^{-1} at 800 °C. The performance of electrolyte-supported SOFCS with $\text{Sr}_{2-x}\text{FNM}$ anodes and LSCF cathodes were tested. The cells achieved peak power densities of 326, 438, 606, 407, and 348 mW cm^{-2} at 800 °C using humidified H_2 for $x = 0, 0.025, 0.05, 0.075$, and 0.1 , respectively.³⁹ Sr deficiency improved the thermal stability of $\text{Sr}_{2-x}\text{FNM}$ and enhanced its electrical performance, showing that $\text{Sr}_{2-x}\text{FNM}$ is another promising anode material for SOFC applications.

Childs et al.⁴⁰ investigated the electrical conductivity of A-site cation deficient $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ ($x = 0.0, 0.1, 0.2$) (SVMO) double perovskites under reducing atmospheres at temperatures up to 800 °C, highlighting their potential as mixed ionic-electronic conductors (MIECs) for SOFC anodes. The materials exhibited surprising metallic-like conduction behavior,

with electrical conductivity values as high as 1250 S/cm for $\text{Sr}_2\text{VMoO}_{6-\delta}$, 2530 S/cm for $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$, and an exceptional 3610 S/cm for $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$ at 800 °C in a 5% H_2 /95% N_2 environment.

Missing in these characterizations of double perovskite oxide materials is their stability under the range of conditions commonly encountered in SOFCs and potential solid oxide electrolysis applications. Specifically, double perovskite resilience to oxidation and secondary phase formation is critical if these materials are to be considered for use in high temperature energy conversion devices including reversible solid oxide electrochemical cells where the materials must be able to tolerate both reducing and oxidizing atmospheres at elevated temperatures. Furthermore, even when materials are intended for use in an individual application such as SOFC anodes, these materials often encounter oxidizing or weakly oxidizing atmospheres that can drive secondary phase formation due to gas handling errors, gas leaks between anode and cathode chambers, and the addition of oxidizing agents such as steam or CO_2 to the anode gas stream.

Recently published work focused on a single SVMO material, $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ (SVMO-19) and reported that this material is stable up to 1000°C under atmospheres consisting of N_2 , forming gas, 3% H_2O in N_2 , and 20% CO_2 in N_2 .⁴¹ The latter two of these atmospheres have been shown to oxidize traditional Ni-based electrodes,⁴² meaning that SVMO-19 may be suitable as an anode material in SOFCs and the fuel electrode in SOECs. These same studies also showed that under air, SVMO-19 rapidly decomposed at elevated temperatures to form secondary phases, and these secondary phases appear to form through two independent first

order processes. What this study did not address was whether other SVMO formulations are more resistant to material degradation and secondary phase formation.

To clarify the influence of A-site deficiency on double perovskite stability, experiments described in this work examine the high temperature stability in air of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ (SVMO) with x values ranging from 0.00 to 0.20 in increments of 0.05. Controlled strontium vacancies were introduced at the A-site to enhance structural stability, and the resulting materials were characterized by thermogravimetric analysis (TGA) and Raman spectroscopy under isothermal conditions in air. The isothermal TGA data show that introducing a small amount of strontium deficiency ($x = 0.05$) consistently lowers the asymptotic mass gain in air at 500, 600, and 700 °C relative to all other compositions. This reduced oxygen uptake implies a higher resistance to atmospheric oxidation and greater inherent stability. The rates of oxygen uptake are mirrored by the growth of secondary phases in SVMO materials, as monitored with high temperature Raman spectroscopy. These results were supported by ambient temperature XPS measurements that showed SVMO with $x = 0.05$ having anomalously high V/Mo ratios on the material surface. Several different models were tested to describe this behavior including first and second order kinetic mechanisms as well as an Avrami mechanism often used to characterize secondary phase nucleation in materials. The model that best described both TGA and vibrational Raman data was a combination of two independent first order kinetic processes, although we note that SVMO degradation kinetics monitored by isothermal TGA and isothermal Raman experiments show subtle differences in their temperature dependences. These differences suggest that data from the TGA experiments may represent a more complicated mechanism describing mass-uptake than simple secondary phase formation.

EXPERIMENTAL

Sr_{2-x}VMoO_{6-δ} synthesis. Solid state synthesis techniques were developed by the Sofie Research Group and adapted from previously reported procedures.⁴⁰ These solid-state methods combined SrCO₃, VO₂, and MoO₂ powder precursors in distilled water. For the materials studied in this work, VO₂ and MoO₂ were included in equimolar amounts. The solution was then mixed with an ultrasonic probe at a power output of 60%. To avoid separation of the precursors and water, liquid nitrogen was immediately introduced to flash freeze the aqueous mixture. The solidified mixture was lyophilized for 48 h with the results being a homogenized fine particulate powder. The powder was processed by hand using a mortar and pestle and placed in a Thermolyne 4800 box furnace to be calcined for 6 h at 1000 °C with a ramp to temperature of 5 °C/min and a return ramp to 25 °C of 10 °C/min. This calcination step removes carbonates and residual moisture from the freeze-dried powder and forms a mixture of SrMoO₄ (Scheelite) and Sr₂V₂O₇ phases. As the Mo⁶⁺ and V⁵⁺ oxidation states are immiscible and unable to form an oxidized solid-state perovskite, this calcination step also serves as an intermediate solid cation mixing step toward perovskite formation via reduction.

Subsequent hand processing using a mortar and pestle was performed before forming 0.75" diameter pellets through uniaxial pressing at 250 MPa. The pellets were reduced at 1100 °C in a forming gas atmosphere of 5% H₂/95% Ar to produce SVMO and single perovskite secondary phases (SrVO₃ and SrMoO₃). Post reduction, the pellets were again processed by hand before being dispersed in ethanol and wet ball-milled for 48 h. The perovskite solvent mixture was air-

dried and uniaxially pressed into 0.5" pellets at 250 MPa and then sintered under N₂ at 1200 °C to convert remaining perovskites to fully formed SVMO. In the final processing stage, the material (already at 1200 °C under N₂) was then placed under forming gas before having the temperature ramped to 1500 °C and then maintained at 1400 °C dwell for 12 h before cooling.

In the studies described below SVMO having different A-site deficiencies are identified by the Sr stoichiometry. For example, stoichiometric SVMO having no A-site deficiencies, Sr₂VMoO_{6-δ}, is identified as SVMO-20. The smallest A-site deficiency corresponds to x = 0.05 to form Sr_{1.95}VMoO_{6-δ}. This material is identified as SVMO-195. Similar notation is used for x = 0.1 (Sr_{1.9}VMoO_{6-δ} or SVMO-19), x = 0.15 (Sr_{1.85}VMoO_{6-δ} or SVMO-185), and x = 0.2 (Sr_{1.8}VMoO_{6-δ} or SVMO-18). We note here that a previous report characterized the phase stability of SVMO-19 using many of the methods described below.

X-ray diffraction. X-ray powder diffraction (XRD) was used to confirm the double perovskite structure in SVMO samples. XRD patterns, as shown in Figure 1.3, were collected using a Bruker D8 Advance powder X-ray diffractometer (PXRD) with Cu Kα radiation, operating at 40 kV and 40 mA, equipped with a Ni filter. The analysis utilized an angle step size of 0.02° over a scanning range of 5-80° to identify phases and assess phase purity. Rietveld refinement provided data about each sample's phase purity and identified primary contaminant phases.

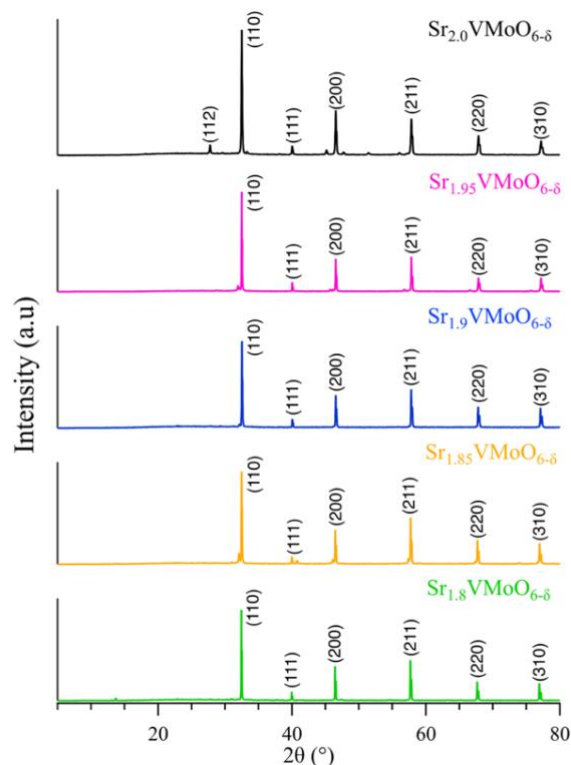


Figure 1.3 XRD patterns of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ (SVMO: $x = 0.0, 0.05, 0.1, 0.15, 0.2$) double perovskites as-fabricated.

The lattice constants obtained for the different $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ compositions ($x = 0.00, 0.05, 0.10, 0.15$, and 0.20) are respectively, $3.910 \text{ \AA}$, $3.912 \text{ \AA}$, $3.919 \text{ \AA}$, $3.924 \text{ \AA}$, and $3.924 \text{ \AA}$ as reported in Appendix B. The phase purity of each sample was 92.3% (SVMO-20), 95.4% (SVMO-195), 99.4% (SVMO-19), 93.5% (SVMO-185), and 99.7% (SVMO-18).

Chemical Stability Testing. All experiments were carried out at controlled-atmospheric conditions. Several analytical techniques were employed to characterize SVMO stability including XRD, Raman spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

Raman spectroscopy. *In situ* Raman spectroscopy was performed using continuous wave 488 nm excitation coupled into a Renishaw inVia spectrometer and a Linkam CCR1000 heating stage. Measurements were made as samples were heated from room temperature to 1000 °C in a controlled atmosphere. Raman spectra were collected at intervals of 100 °C, with a heating rate of 10 °C/min between temperatures with a dwell time of 15 minutes at temperature. Most spectra shown in this work resulted from 3 x 30-second accumulations. Incident laser powers were ~30 mW with a ~100 µm spot size using a 5x objective. Incident power at the sample surface was 2.8 mW. Isothermal Raman measurements testing material stability were conducted by raising the temperature of a sample to the desired target temperature under forming gas and then switching the atmosphere to air. SVMO decomposition was monitored by recording Raman spectra every 30 seconds.

Thermogravimetric analysis. Thermogravimetric analysis (TGA) was employed to characterize SVMO's thermal and chemical stability as a function of for all A-site deficiencies $x = 0 - 0.2$. Experiments were performed using a TA-TGA 5500 instrument, measuring weight loss/gain as a function of temperature in both inert (N₂) and oxidizing (air) atmospheres. The analysis covered a temperature range from room temperature to 900 °C, with a heating rate of 5 °C/min and a flow rate of 25 mL/min. Measurements reproducibly measured mass changes as small as ±0.01%. Pseudo-isothermal TGA measurements were performed by ramping the temperature as quickly as possible (50 °C/min) to the target temperature and then maintaining a constant temperature for the duration of the experiment.

The oxygen non-stoichiometry, δ in $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$, was determined from pseudo-isothermal thermogravimetric analysis (TGA) measurements. The value of δ was estimated from the mass change observed during isothermal oxidation (at 500 °C) according to the following expression:

$$\delta = \frac{m_T - m_0}{m_0} \times \frac{M_{mw}}{M_O} \quad (\text{Eq. 1.3})$$

where m_T is the sample weight post isothermal oxidation, m_0 is the original sample weight. M_O and M_{mw} are the molecular weights of oxygen and $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$, respectively. The mass increase measured during oxidation is attributed to oxygen uptake by the material. We note that this expression is valid provided that the material itself is stable. Once a material begins forming secondary phases (and accommodating more oxygen), calculating oxygen deficiency is no longer possible.

X-ray Photoelectron Spectroscopy (XPS). XPS was used to study the surface elemental and oxidative states of the SVMO samples. X-ray photoelectron spectroscopy (XPS) measurements were performed by Dr. Jayson Foster at the Colorado School of Mines using a custom Scienta-Omicron HiPP-3 system equipped with a R4000 hemispherical analyzer operating in swift acceleration mode, calibrated to the Au 4f region (83.95 eV) of a sputter cleaned Au foil. A focused Al K_{α} X-ray source (1486.6 eV) was operated with a 900 μm spot size at 300W. The X-ray beam was incident normal to the sample, and emitted photoelectrons were collected at an emission angle of 45° to the direction of the incident X-ray beam. Surface and high-resolution spectra (C 1s, Sr 3d, Mo 3d, O 1s, V 2p) were acquired at pass energies of 200 and 100 eV, respectively. A 0.8 mm $\times$ 30 mm slit size was used, resulting in an estimated energy resolution of approximately 0.59 eV. The analysis chamber pressure was maintained at a level below $5.0 \times$

10^{-8} mbar, while analyzer pressure remained below 1×10^{-8} mbar. SVMO samples were mounted on conductive carbon tape and therefore no charge neutralization was necessary. Additional details can be found in previous reports.^{43, 44}

Individual elemental line shapes were fit to available oxidation states based on earlier studies. Specifically, the Sr 3d line was fit to contributions from Sr (0), Sr (II) according to methods described by Wagner *et al.*⁴⁵ and Moulder *et al.*⁴⁶ The V 2p line was fit to allow for contributions from V (0), V (II), V (III), V (IV) and V (V) as previously reported.^{45, 47-50} The Mo 3d line was fit to allow for contributions from Mo (0), Mo (II), Mo (IV), Mo (V) and Mo (VI).^{45, 51-54}

3. RESULTS AND DISCUSSION

3.1. SVMOs stability in inert and oxidizing atmospheres

The independent methods used to examine SVMO's behavior as a function of temperature and atmospheric composition were focused on a global question: will A-site deficiency affect SVMO's high temperature stability? A second, related question is how secondary phases form if (or when) SVMO begins to decompose. Previously referenced studies of SVMO-19 showed that this material begins forming secondary phases between 600°C and 700°C, with the dominant secondary phase being SrMoO₄ or Scheelite.⁴¹ Temperature dependent kinetic studies led to calculated activation energies for Scheelite formation of ~0.5 – 0.6 eV, although the kinetics did not show traditional, Avrami-style growth.

3.1.1 Thermal analysis

To address the two questions above, thermal gravimetric analysis (TGA) was used to evaluate the thermal stability of different SVMO materials under different atmospheres. Figure 2.3 presents the representative TGA curves for SVMO-20 obtained as the temperature was increased to 900 °C at a rate of 5 °C/min in nitrogen and air. The data show that SVMO-20 remains stable in N₂ up to 900 °C, with no significant change in mass. In contrast, when heated in air, the material begins gaining mass at approximately 400 °C, and mass gain continues to increase steadily before asymptotically leveling off near 750 °C. Similar behavior was observed for non-stoichiometric compositions ($x = 0.05, 0.1, 0.15,$ and 0.2), as detailed in Appendix B.

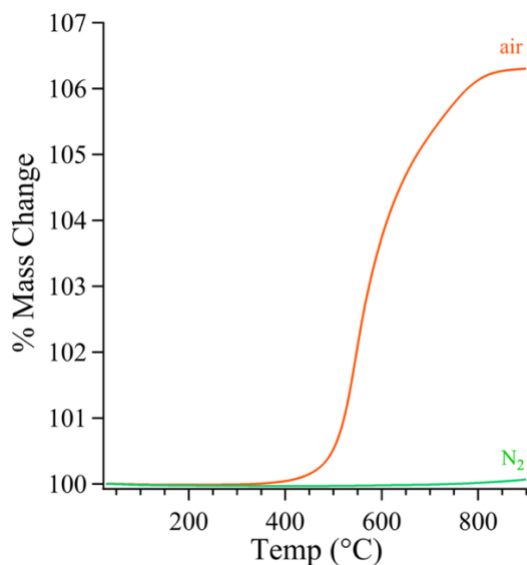


Figure 2.3 TGA curves of SVMO-20 in N₂ and air from 25 to 900 °C.

If we choose 100.05% as a benchmark denoting the onset of mass accumulation, SVMO-20 reaches this threshold at a temperature at 405.4°C. For the other compositions this threshold

temperature changes is rises significantly for SVMO-195 (456.1 °C) before dropping for SVMO-19 (381.5 °C), SVMO-185 (423.5 °C), and SVMO-18 (406.7 °C). These observations are the first indication that SVMO stability depends on A-site deficiency with SVMO-195 being the most stable formulation having the highest onset for mass accumulation.

3.1.1 Raman analysis

To explore the origin of SVMO-20's mass gain in air, we employed *in-situ* Raman spectroscopy to monitor its stability under conditions where the TGA data showed mass gain. Figure 3.3 shows Raman spectra collected in air as the temperature was raised from room temperature to 1000 °C. At temperatures ≥ 600 °C in air, a strong Raman peak appears near 876 cm^{-1} and this peak continues to grow in intensity at higher temperatures. The spectrum of SVMO-20 also shows additional peaks at about 825, 776, 358, and 322 cm^{-1} , along with weaker features at lower wavenumbers. Based on previous work by Son *et al.*⁵⁵, these peaks are assigned to the tetragonal Scheelite phase of SrMoO_4 .

Earlier studies by Porto and Scott⁵⁶ showed that the most intense room-temperature Raman peak of Scheelite SrMoO_4 , near 888 cm^{-1} , corresponds to the symmetric stretching of the MoO_4 tetrahedra. In Figure 3.3, the peak observed at 876 cm^{-1} is slightly red shifted but within experimental tolerance to be assigned to SrMoO_4 , and this feature's increasing intensity confirms the formation of this secondary phase in SVMO-20. Smaller peaks around 685 and 259 cm^{-1} are tentatively assigned to bending modes of VO_3 groups, possibly associated with the single perovskite phase SrVO_3 .⁵⁷ Similar results were obtained for the non-stoichiometric compositions ($x = 0.1$, and 0.2). See Appendix B.

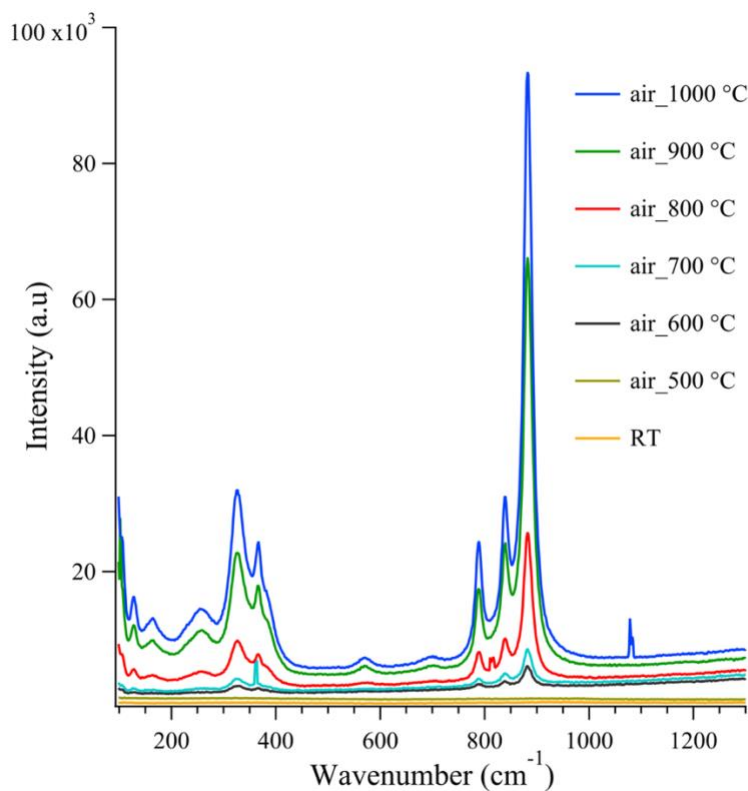


Figure 3.3 *In situ* Raman spectra of SVMO-20 in air from room temperature to 1000 °C.

SVMO-20's stability in air at 500°C is a promising result, given that intermediate temperature SOFCs can operate at temperatures this low.^{58, 59} Earlier work studying SVMO-19 also showed stability in air at 500°C. Interestingly, SVMO-19 was also stable at 600°C whereas SVMO-20 shows a clear onset of secondary phase formation at this temperature. Raman studies with SVMO-18 show this formulate to be even less stable than SVMO-20, as SVMO-18 begins forming scheelite at 500°C in air. (Figure 4.3).

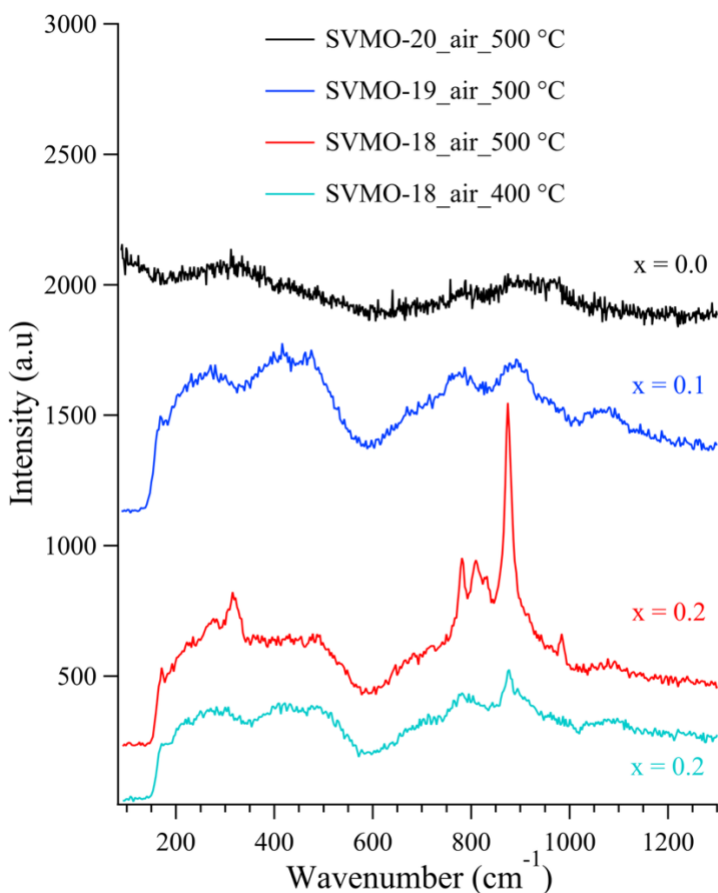


Figure 4.3 *In situ* Raman spectra of SVMO ($x = 0.0, 0.1$, and 0.2) in air at $400\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$.

The spectra in Figure 4.3 show unmistakably that A-site deficiency strongly affects SVMO stability in air at high temperatures. SVMO-18 even shows evidence of Scheelite formation at $400\text{ }^{\circ}\text{C}$. Given this behavior, SVMO-18 is an unsuitable candidate for any high temperature application where oxidizing agents may be present.

3.2.1 Kinetics with isothermal-Raman measurements

To measure how quickly SrMoO_4 forms, we conducted isothermal Raman experiments. In these experiments, SVMO-20 was heated to $700\text{ }^{\circ}\text{C}$ in forming gas. Once the target temperature was reached, the sample was held for 15 minutes, during which no changes in the spectrum were

observed. The gas was then switched from forming gas to air (defined as $t_0 = 0$), and Raman spectra were collected every 5 minutes. (The gas residence time in the manifold is ≤ 20 seconds.) The results are presented in Figure 5.3. Figure 5.3a shows selected spectra at different times after t_0 , while Figure 5.3b displays the growth of intensity of the primary SrMoO_4 over time. Similar results were obtained for SVMO-20 at 600 °C and 500 °C and the non-stoichiometric composition SVMO-18 at 700 °C, 600 °C and 500 °C. (See Appendix B.)

The data in Figure 5.3b can be described using a double exponential kinetic model that includes the sum of two exponential functions with rate constants k_1 and k_2 :

$$Int(t) = A_0 + A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \quad (\text{Eq. 2.3})$$

Other models including single exponential growth and an Avrami model⁶⁰⁻⁶² were tested and were unable to fit the data with sufficient precision. Equation 2.3 expression implies that SrMoO_4 forms through two first-order (or pseudo-first-order) processes, with one occurring faster than the other. Rate constants and activation energies for secondary phase Scheelite formation in SVMO-20, SVMO-19, and SVMO-18 in air are shown in Table 1.3. We note that the first activation energy, $E_{a,1}$, is similar for all three SVMO formulations, suggesting that the first stage of Scheelite formation is the same. The second activation energy, $E_{a,2}$, is smallest for SVMO-18 (outside the limits of experimental uncertainty) and is consistent with SVMO-18 being the least stable formulation of those that were tested with isothermal Raman experiments.

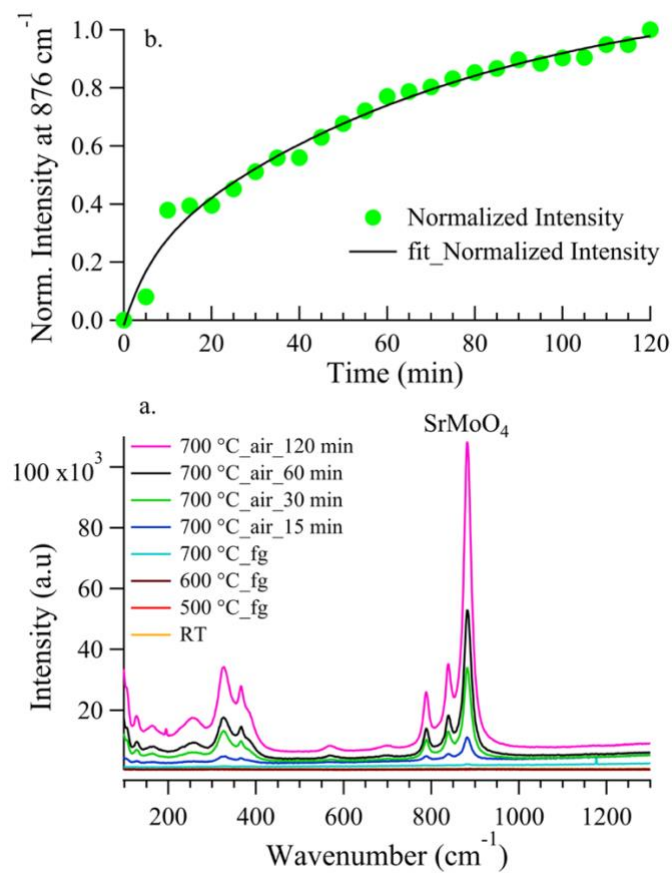


Figure 5.3 *In situ* Raman spectra of SVMO-20 in 5% H_2 /95% N_2 and air from room temperature to 700 °C; (b) Kinetic trace showing the normalized intensity of the SrMoO_4 secondary phase after exposure to air at 700 °C.

Table 1.3 Rate constants determined from fitting data from isothermal Raman data using the SrMoO₄ peak at 876 cm⁻¹ intensity to Equation 2.3.

SVMO	k_1 (/s)	k_2 (/s)	$E_{a,1}$ (eV)	$E_{a,2}$ (eV)	Temp (°C)
SVMO-20	2.3×10^{-4}	1.3×10^{-4}	0.8 ± 0.3	0.4 ± 0.2	500
	5.2×10^{-4}	2.3×10^{-4}			600
					700
	2.7×10^{-3}	5.0×10^{-4}			
SVMO-19*	5.2×10^{-4}	6.6×10^{-5}	0.6 ± 0.4	0.4 ± 0.03	500
	2.8×10^{-3}	1.3×10^{-4}			600
	3.4×10^{-3}				700
		2.1×10^{-4}			
SVMO-18	5.5×10^{-4}	1.2×10^{-4}	0.8 ± 0.4	0.2 ± 0.1	500
	9.6×10^{-4}	1.7×10^{-4}			600
	6.6×10^{-3}				700
		2.6×10^{-4}			

*Findings for SVMO-19 were reported previously in ⁴¹

3.2.2 Kinetics with isothermal-Raman measurements

To determine whether the mass gain observed in the TGA experiment follows the same behavior as in the isothermal Raman results (Figure 5.3b), we performed “pseudo”-isothermal TGA experiments. Again using SVMO-20 as an example, the sample was heated as quickly as possible (50 °C/min) to either 500 °C, 600 °C, or 700 °C in air and then held at that temperature. The results for SVMO-20 at 700 °C are shown in Figure 5.3. The data show that the sample starts gaining mass before it reaches the target temperature. However, the final ~40% of the total mass increase occurs while the temperature is held constant. The isothermal portion of the TGA data was fit using the same double-exponential function given in equation 2.3. The fit appears to be good, suggesting that the observed mass gain is directly linked to the formation of SrMoO₄. (Other fits were also tested but by inspection, none fit the data as well as the double exponential expression.) We repeated these experiments at lower temperatures (600 °C and 500 °C), and these results are also included in Figure 6.3. The data at these temperatures qualitatively follow the same two-exponential behavior, again suggesting that the mechanism responsible for secondary phase formation does not change between 500 °C and 700 °C. Similar results were obtained for all the non-stoichiometric compositions ($x = 0.05, 0.1, 0.15, \text{ and } 0.2$) at all three temperatures, 500 °C, 600 °C, and 700 °C. See Appendix B.

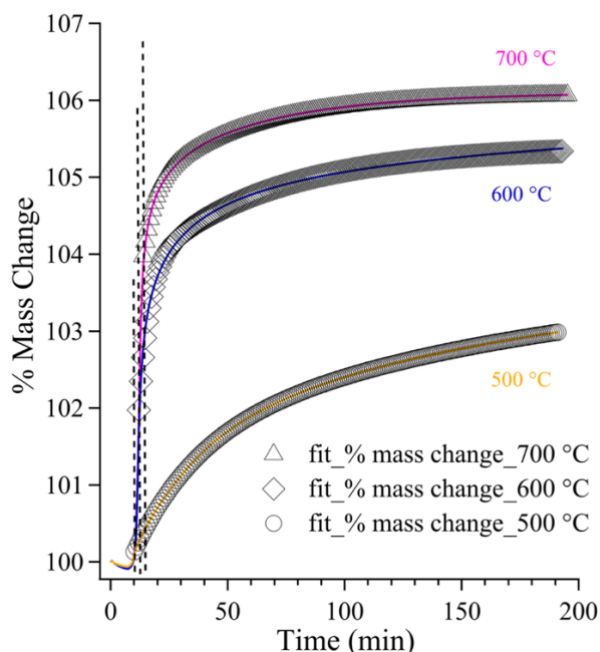


Figure 6.3 Isothermal TGA curves of SVMO-20 in air at 500 °C, 600 °C, and 700 °C with fits to double exponential kinetic model. The dashed vertical lines correspond to the time when the sample has reached its target temperature. The markers superimposed on the data correspond to fits generated by Eq. 2.3.

With isothermal TGA data, we can address how A-site deficiency affects SVMO stability and oxide vacancies in the lattice. Figure 7.3 presents the asymptotic mass gain (%) measured by isothermal TGA in air for $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ at 500 °C, 600 °C, and 700 °C as a function of A-site (Sr) deficiency, x . ($x = 0.0, 0.05, 0.1, 0.15$, and 0.2). Before oxidation, the samples were pre-reduced or equilibrated at low oxygen partial pressure. Under these conditions, the stoichiometric composition ($x = 0.00$) can contain a noticeable amount of reduced B-site cations, such as V^{3+} and Mo^{5+} , together with oxygen vacancies. When the material is exposed to air during the isothermal TGA measurement, these reduced cations are oxidized, and oxygen vacancies are

filled. Since both cation oxidation and vacancy elimination occur at the same time, the total oxygen uptake is relatively high, leading to the relatively large asymptotic mass gains.

The data in Figure 7.3 shows that A-site deficiency has a clear and non-monotonic effect on mass gain. For every composition, the asymptotic mass gain increases as the temperature rises from 500 °C to 700 °C. At a given value of x , the highest mass gain is observed at 700 °C, followed by 600 °C and then 500 °C. This behavior shows that, not surprisingly, oxygen incorporation becomes more favorable at higher temperature.

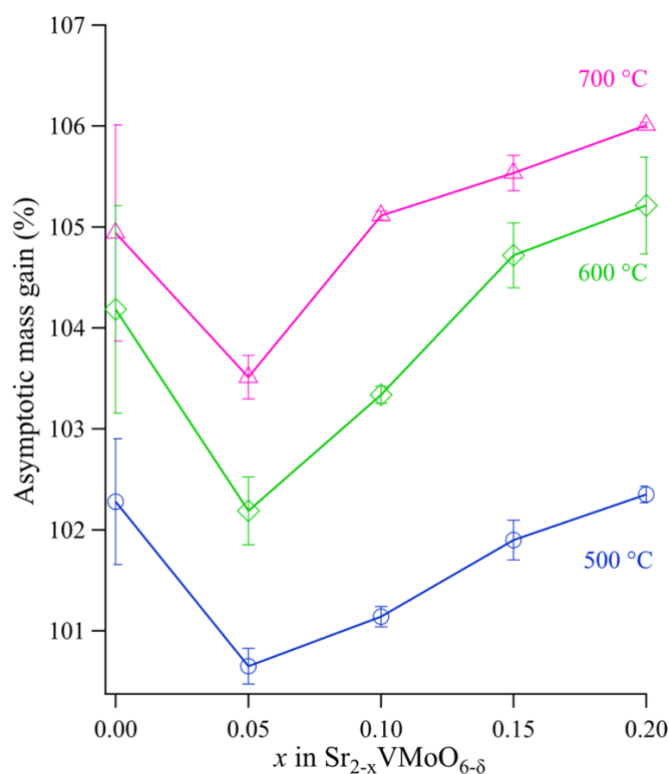


Figure 7.3 Asymptotic mass gain (%) as a function of A-site (Sr) deficiency (x) in $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ double perovskites, determined from isothermal TGA oxidation measurements in air at 500 °C, 600 °C and 700 °C

The effect of Sr deficiency on asymptotic mass-gain in Figure 7.3 is consistent for the different A-site deficient materials at all temperatures and decidedly non-monotonic with A-site deficiency. When a small amount of Sr is removed ($x = 0.05$, SVMO-195), the asymptotic mass gain decreases compared to the stoichiometric sample ($x = 0.00$). This minimum is observed clearly at 500 °C, 600 °C, and 700 °C implying that SVMO-195 is the most resilient to oxidation. Charge balance in the material is likely achieved by adjusting the oxidation states of V and Mo rather than by incorporating additional oxygen. When the Sr deficiency increases further ($x \geq 0.10$), the asymptotic mass gain rises at all temperatures. The largest mass gain is observed at $x = 0.20$ (SVMO-18). This trend suggests that the oxide vacancies introduced by higher A-site deficiencies leaves the material more susceptible to decomposition and secondary phase formation at higher temperatures.

In double perovskites with the general formula $A_2BB'O_6$, the amount of oxygen vacancies (δ) is strongly affected by how deficient the A-site is. When some A-site cations are missing, the crystal adjusts to keep its overall charge balanced, and one common way it does this is by forming oxygen vacancies. In principle, the lowest-temperature mass gain shown in Figure 7.3 (500°C) can be used to assess oxygen vacancy content, δ , using Equation 1. The 500°C data were chosen because at this temperature, the (non-isothermal) TGA data show mass gain starting at 400°C while the (non-isothermal) Raman data do not show Scheelite formation starting until 600°C.

The δ data mirror results from the asymptotic mass gain TGA data shown in Figure 7.3. A-site deficiency affects δ , but in a non-linear way. For the stoichiometric composition ($x = 0.0$,

SVMO-20), oxygen vacancy concentration (δ) is calculated to be 0.6 implying that the B-site cations are not fully oxidized and create oxide vacancies in the BO_6 octahedra. This result is not unexpected, given that the last step in SVMO fabrication is heating the material to 1400°C in forming gas for 12 hours. Under these strongly reducing conditions, the lattice compensates for oxygen vacancies that form by accessing the multiple oxidation states available to the B-site cations (V and Mo). Slightly reducing the amount of Sr in the material ($x = 0.05$, SVMO-195), results in a δ of 0.2, the smallest amount of oxide vacancy for any of A-site deficient materials tested. In this range, charge balance is mainly achieved through changes in the oxidation states of V and Mo, which reduces the need for oxidation vacancies. However, when Sr deficiency increases beyond $x \approx 0.05$, δ rises again. At higher A-site vacancy concentrations, structural distortion and electronic effects make oxygen vacancy formation more favorable. In summary, since the least oxygen vacancy concentration is observed for $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ (where $x = 0.05$), SVMO-195 remains the most stable SVMO composition.

3.2.3 Comparing isothermal Raman and isothermal TGA results.

At first glance, the mass accumulation kinetics observed in isothermal TGA results and the secondary phase formation kinetics (of Scheelite) observed in isothermal Raman measurements appear to agree. Both processes appear to follow behavior described by the sum of two single exponential processes described in Equation 2.3. Other models are unable to describe the data with the precision needed to have confidence in the fit. This agreement is semi-quantitative for SVMO-19 and led this previous report to propose that the two different techniques were measuring different observables associated with the same phenomenon.

Closer, quantitative inspection of these more extensive data suggest that this first interpretation was naïve. The activation energies calculated from the isothermal TGA temperature dependent rate constants fail to show any trend or pattern. For example, SVMO-195 shows the greatest stability in air, but the activation energies for this material include the highest (0.8 eV for E_{a1}) and one of the lowest (E_{a2}) calculated. (See Appendix B for table with isothermal TGA rate constants and Arrhenius plots for different formulations.) Furthermore, the uncertainties associated with the activation energies calculated from isothermal TGA numbers are often as large or larger than the values themselves. This outcome does not inspire confidence that at least the isothermal TGA kinetic data are missing some important process. One possibility is that the isothermal TGA results include at lower temperatures the mass gain associated with filling oxygen vacancies as well as mass gain associated with secondary phase formation. The data may fit the model, but a suitable fit does not mean that the mechanism is accurate. For single perovskite materials, oxygen vacancy filling is known to begin at temperatures as low as 350°C in the single oxide perovskite LSM and 200°C in LSCF.^{63, 64} Above 700 °C, oxygen exchange was controlled by activation energies of 0.9 eV (LSM) and 0.10 eV (LSCF). Of these materials, LSM had an A-site deficiency of 0.02 ((La_{0.8}Sr_{0.2})_{0.98}MnO_{3-δ}), while LSCF was stoichiometric (La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{6-δ}).

4. Conclusions

Experiments described in this work examined the stability of different SVMO formulations in air with a goal of identifying a composition that was distinctively more stable at high temperatures

in air. Given SVMO's high reported conductivities, air stability would imply that this material might be suitable for use as electrodes in next generation solid oxide fuel cells and solid oxide electrolysis cells. The formulations investigated included $\text{Sr}_2\text{VMoO}_{6-\delta}$, (SVMO-20), $\text{Sr}_{1.95}\text{VMoO}_{6-\delta}$, (SVMO-195), $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ (SVMO-19), $\text{Sr}_{1.85}\text{VMoO}_{6-\delta}$ (SVMO-185), and $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$ (SVMO-18).

A combination of independent TGA and vibrational Raman measurements did identify one composition, SVMO-195, that was much more stable than all the others. This material showed the smallest mass accumulation when heated in air and the highest temperature for the onset of mass accumulation. Raman data and isothermal Raman data implied that A-site deficiency *does* play a role in controlling material stability with slightly A-site deficient material, SVMO-19, showing less secondary phase formation than either SVMO-20 or SVMO-18. (Instrument challenges precluded Raman measurements for SVMO-195 and SVMO185.)

Careful kinetic analysis showed that both isothermal TGA and isothermal Raman kinetics describing SVMO degradation in air followed a pair of first-order rate expressions. A temperature dependent study provided the information needed to calculate effective activation energies for these materials using both independent experimental methods. Results agree qualitatively, although a quantitative comparison suggests that the two measurements are not reporting on the same processes.

References

- (1) Geng, H.; Zou, X.; Min, Y.; Bu, Y.; Lu, Q. Advances and Challenges in Perovskite Oxide Design for High-Performance Zinc–Air Batteries: Integrating Experimental Strategies and Machine Learning. *Advanced Functional Materials* **2025**, 2500657.
- (2) Humayun, M.; Li, Z.; Israr, M.; Khan, A.; Luo, W.; Wang, C.; Shao, Z. Perovskite type ABO₃ oxides in photocatalysis, electrocatalysis, and solid oxide fuel cells: State of the art and future prospects. *Chemical Reviews* **2025**, 125 (6), 3165-3241.
- (3) Ingavale, S.; Gopalakrishnan, M.; Enoch, C. M.; Pornrungrroj, C.; Rittirum, M.; Praserttham, S.; Somwangthanaroj, A.; Nootong, K.; Pornprasertsuk, R.; Kheawhom, S. Strategic design and insights into lanthanum and strontium perovskite oxides for oxygen reduction and oxygen evolution reactions. *Small* **2024**, 20 (19), 2308443.
- (4) Irshad, M.; tul Ain, Q.; Zaman, M.; Aslam, M. Z.; Kousar, N.; Asim, M.; Rafique, M.; Siraj, K.; Tabish, A. N.; Usman, M. Photocatalysis and perovskite oxide-based materials: a remedy for a clean and sustainable future. *RSC advances* **2022**, 12 (12), 7009-7039.
- (5) Kumar, S.; Sharma, V.; Kumari, N.; Kaur, G. A.; Saha, A.; Thakur, S.; Shandilya, M. Recent advances in perovskite materials: exploring multifaceted properties for energy harvesting applications. *Ionics* **2024**, 30 (9), 5159-5188.
- (6) Neagu, D.; Irvine, J. T.; Wang, J.; Yildiz, B.; Opitz, A. K.; Fleig, J.; Wang, Y.; Liu, J.; Shen, L.; Ciucci, F. Roadmap on exsolution for energy applications. *Journal of Physics: Energy* **2023**, 5 (3), 031501.
- (7) Sun, H.; Xu, X.; Song, Y.; Shao, Z. Recent Progress in Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ}-Based Multifunctional Materials for Energy Conversion and Storage. *Advanced Functional Materials* **2024**, 34 (51), 2411622.
- (8) Ji, Q.; Bi, L.; Zhang, J.; Cao, H.; Zhao, X. S. The role of oxygen vacancies of ABO₃ perovskite oxides in the oxygen reduction reaction. *Energy & Environmental Science* **2020**, 13 (5), 1408-1428.
- (9) Merkulov, O. V.; Samigullin, R. R.; Markov, A. A.; Patrakeevev, M. V. Impact of A-Site Cation Deficiency on Charge Transport in La_{0.5-*x*}Sr_{0.5}FeO_{3-*δ*}. *Materials* **2021**, 14 (20), 5990.
- (10) Li, M.; Zhao, M.; Li, F.; Zhou, W.; Peterson, V. K.; Xu, X.; Shao, Z.; Gentle, I.; Zhu, Z. A niobium and tantalum co-doped perovskite cathode for solid oxide fuel cells operating below 500° C. *Nature communications* **2017**, 8 (1), 13990.
- (11) Richter, J.; Holtappels, P.; Graule, T.; Nakamura, T.; Gauckler, L. J. Materials design for perovskite SOFC cathodes. *Monatshefte für Chemie-Chemical Monthly* **2009**, 140 (9), 985-999.

- (12) Hegde, G. S.; Ghosh, A.; Badam, R.; Matsumi, N.; Sundara, R. Role of defects in low-cost perovskite catalysts toward ORR and OER in lithium–oxygen batteries. *ACS Applied Energy Materials* **2020**, 3 (2), 1338-1348.
- (13) Ia O, G. J.; Ahn, S. J.; Crumlin, E.; Orikasa, Y.; Biegalski, M. D.; Christen, H. M.; Shao-Horn, Y. Catalytic activity enhancement for oxygen reduction on epitaxial perovskite thin films for solid-oxide fuel cells. *Angewandte Chemie (International ed. in English)* **2010**, 49 (31).
- (14) Pavone, M.; Ritzmann, A. M.; Carter, E. A. Quantum-mechanics-based design principles for solid oxide fuel cell cathode materials. *Energy & Environmental Science* **2011**, 4 (12), 4933-4937.
- (15) Sugiura, S.; Shibuta, Y.; Shimamura, K.; Misawa, M.; Shimojo, F.; Yamaguchi, S. Role of oxygen vacancy in dissociation of oxygen molecule on SOFC cathode: Ab initio molecular dynamics simulation. *Solid State Ionics* **2016**, 285, 209-214.
- (16) Wang, L.; Merkle, R.; Mastrikov, Y. A.; Kotomin, E. A.; Maier, J. Oxygen exchange kinetics on solid oxide fuel cell cathode materials—general trends and their mechanistic interpretation. *Journal of Materials Research* **2012**, 27 (15), 2000-2008.
- (17) Zhang, W.; Meng, J.; Zhang, X.; Zhang, L.; Liu, X.; Meng, J. Co-incorporating enhancement on oxygen vacancy formation energy and electrochemical property of $\text{Sr}_2\text{Co}_{1+x}\text{Mo}_{1-x}\text{O}_{6-\delta}$ cathode for intermediate-temperature solid oxide fuel cell. *Solid State Ionics* **2018**, 316, 20-28.
- (18) Han, J. W.; Yildiz, B. Mechanism for enhanced oxygen reduction kinetics at the (La, Sr) $\text{CoO}_{3-\delta}/(\text{La, Sr})_2\text{CoO}_{4+\delta}$ hetero-interface. *Energy & Environmental Science* **2012**, 5 (9), 8598-8607.
- (19) Sengodan, S.; Choi, S.; Jun, A.; Shin, T. H.; Ju, Y.-W.; Jeong, H. Y.; Shin, J.; Irvine, J. T.; Kim, G. Layered oxygen-deficient double perovskite as an efficient and stable anode for direct hydrocarbon solid oxide fuel cells. *Nature materials* **2015**, 14 (2), 205-209.
- (20) Chen, D.; Chen, C.; Baiyee, Z. M.; Shao, Z.; Ciucci, F. Nonstoichiometric oxides as low-cost and highly-efficient oxygen reduction/evolution catalysts for low-temperature electrochemical devices. *Chemical reviews* **2015**, 115 (18), 9869-9921.
- (21) Guo, J.; Haghshenas, Y.; Jiao, Y.; Kumar, P.; Yakobson, B. I.; Roy, A.; Jiao, Y.; Regenauer-Lieb, K.; Nguyen, D.; Xia, Z. Rational Design of Earth-Abundant Catalysts toward Sustainability. *Advanced Materials* **2024**, 36 (42), 2407102.

- (22) Kumar, N.; Aepuru, R.; Lee, S.-Y.; Park, S.-J. Advances in catalysts for hydrogen production: A comprehensive review of materials and mechanisms. *Nanomaterials* **2025**, 15 (4), 256.
- (23) Du, Z.; Zhao, H.; Li, S.; Zhang, Y.; Chang, X.; Xia, Q.; Chen, N.; Gu, L.; Świerczek, K.; Li, Y. Exceptionally high performance anode material based on lattice structure decorated double perovskite $\text{Sr}_2\text{FeMo}_{2/3}\text{Mg}_{1/3}\text{O}_{6-\delta}$ for solid oxide fuel cells. *Advanced Energy Materials* **2018**, 8 (18), 1800062.
- (24) Huang, Y.-H.; Dass, R. I.; Denyszyn, J. C.; Goodenough, J. B. Synthesis and characterization of $\text{Sr}_2\text{MgMoO}_{6-\delta}$: an anode material for the solid oxide fuel cell. *Journal of the Electrochemical Society* **2006**, 153 (7), A1266.
- (25) Huang, Y.-H.; Dass, R. I.; Xing, Z.-L.; Goodenough, J. B. Double perovskites as anode materials for solid-oxide fuel cells. *Science* **2006**, 312 (5771), 254-257.
- (26) Kim, J.-H.; Manthiram, A. $\text{LnBaCo}_2\text{O}_{5+\delta}$ oxides as cathodes for intermediate-temperature solid oxide fuel cells. *Journal of the Electrochemical Society* **2008**, 155 (4), B385.
- (27) Nikonov, A.; Kuterbekov, K.; Bekmyrza, K. Z.; Pavzderin, N. A brief review of conductivity and thermal expansion of perovskite-related oxides for SOFC cathode. **2018**.
- (28) Tarancón, A.; Skinner, S. J.; Chater, R. J.; Hernandez-Ramirez, F.; Kilner, J. A. Layered perovskites as promising cathodes for intermediate temperature solid oxide fuel cells. *Journal of Materials Chemistry* **2007**, 17 (30), 3175-3181.
- (29) Li, X.; Li, M.; Ma, X.; Miao, J.; Ran, R.; Zhou, W.; Shao, Z. Nonstoichiometric perovskite for enhanced catalytic oxidation through excess A-site cation. *Chemical Engineering Science* **2020**, 219, 115596.
- (30) Liu, H.; Ding, X.; Wang, L.; Ding, D.; Zhang, S.; Yuan, G. Cation deficiency design: A simple and efficient strategy for promoting oxygen evolution reaction activity of perovskite electrocatalyst. *Electrochimica Acta* **2018**, 259, 1004-1010.
- (31) Schoen, A.; Dujardin, C.; Dacquin, J.-P.; Granger, P. Enhancing catalytic activity of perovskite-based catalysts in three-way catalysis by surface composition optimisation. *Catalysis Today* **2015**, 258, 543-548.
- (32) Watanabe, R.; Tsujioka, M.; Fukuhara, C. Performance of Non-stoichiometric Perovskite Catalyst ($\text{A}_x\text{CrO}_{3-\delta}$, A: La, Pr, Nd) for Dehydrogenation of Propane Under Steam Condition. *Catalysis Letters* **2016**, 146 (12), 2458-2467.

- (33) Wu, M.; Chen, S.; Xiang, W. Oxygen vacancy induced performance enhancement of toluene catalytic oxidation using LaFeO₃ perovskite oxides. *Chemical Engineering Journal* **2020**, 387, 124101.
- (34) Wu, Y.; Ni, X.; Beaurain, A.; Dujardin, C.; Granger, P. Stoichiometric and non-stoichiometric perovskite-based catalysts: Consequences on surface properties and on catalytic performances in the decomposition of N₂O from nitric acid plants. *Applied Catalysis B: Environmental* **2012**, 125, 149-157.
- (35) Zhao, A.; Ren, Y.; Wang, H.; Qu, Z. Enhancement of toluene oxidation performance over La_{1-x}CoO_{3-δ} perovskite by lanthanum non-stoichiometry. *Journal of Environmental Sciences* **2023**, 127, 811-823.
- (36) Moradkhani, F.; Kootenaei, A. S.; Maghsoodi, S.; Mirzaei, M.; Azimi, A. A-site deficiency study of La₂CoMnO₆ double perovskite oxide and its catalytic performance in propane total oxidation reaction. *Journal of Sol-Gel Science and Technology* **2023**, 108 (1), 136-148.
- (37) Jiang, L.; Liang, G.; Han, J.; Huang, Y. Effects of Sr-site deficiency on structure and electrochemical performance in Sr₂MgMoO₆ for solid-oxide fuel cell. *Journal of Power Sources* **2014**, 270, 441-448.
- (38) Logvinovich, D.; Aguirre, M.; Hejtmanek, J.; Aguiar, R.; Ebbinghaus, S. G.; Reller, A.; Weidenkaff, A. Phase formation, structural and microstructural characterization of novel oxynitride-perovskites synthesized by thermal ammonolysis of (Ca, Ba) MoO₄ and (Ca, Ba) MoO₃. *Journal of Solid State Chemistry* **2008**, 181 (9), 2243-2249.
- (39) Feng, J.; Qiao, J.; Wang, W.; Wang, Z.; Sun, W.; Sun, K. Development and performance of anode material based on A-site deficient Sr_{2-x}Fe_{1-4x}Ni_{0.1}Mo_{0.5}O_{6-δ} perovskites for solid oxide fuel cells. *Electrochimica Acta* **2016**, 215, 592-599.
- (40) Childs, N. B.; Weisenstein, A.; Smith, R.; Sofie, S.; Key, C. Electrical conductivity of Sr_{2-x}VMoO_{6-y} (x= 0.0, 0.1, 0.2) double perovskites. *Journal of Applied Physics* **2013**, 113 (24).
- (41) Samuel, B. J.; Esakoff, J. A.; Heywood, S. K.; Sofie, S. W.; Walker, R. A. Chemical and Thermal Stability of Sr_{1.9}VMoO_{6-δ}: Implications for High Temperature Energy Conversion Applications. *ACS Omega* **2026**, 11 (6), 9050-9058. DOI: 10.1021/acsomega.5c06796.
- (42) McIntyre, M. D.; Kirtley, J. D.; Singh, A.; Islam, S.; Hill, J. M.; Walker, R. A. Comparing in situ carbon tolerances of Sn-infiltrated and BaO-infiltrated Ni-YSZ cermet anodes in solid oxide fuel cells exposed to methane. *The Journal of Physical Chemistry C* **2015**, 119 (14), 7637-7647.
- (43) Mauger, S. A.; Wang, M.; Cetinbas, F. C.; Dzara, M. J.; Park, J.; Myers, D. J.; Ahluwalia, R. K.; Pylypenko, S.; Hu, L.; Litster, S. Development of high-performance roll-to-roll-coated gas-diffusion-electrode-based fuel cells. *Journal of Power Sources* **2021**, 506, 230039.

- (44) Zaccarine, S. F.; Shviro, M.; Weker, J. N.; Dzara, M. J.; Foster, J.; Carmo, M.; Pylypenko, S. Multi-scale multi-technique characterization approach for analysis of PEM electrolyzer catalyst layer degradation. *Journal of The Electrochemical Society* **2022**, 169 (6), 064502.
- (45) Wagner, C.; Naumkin, A.; Kraut-Vass, A.; Allison, J.; Powell, C.; Rumble Jr, J. NIST X-ray photoelectron spectroscopy database, NIST standard reference database 20, version 3.4 (Web version). *US Department of Commerce* **2003**, 1.
- (46) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. Handbook of X-ray photoelectron spectroscopy; Chastain, J. Perkin-Elmer Corp., Eden Prairie, MN **1992**.
- (47) Biesinger, M. C.; Lau, L. W.; Gerson, A. R.; Smart, R. S. C. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn. *Applied surface science* **2010**, 257 (3), 887-898.
- (48) Gupta, R.; Sen, S. Calculation of multiplet structure of core p-vacancy levels. *Physical Review B* **1974**, 10 (1), 71.
- (49) Silversmit, G.; Depla, D.; Poelman, H.; Marin, G. B.; De Gryse, R. Determination of the V2p XPS binding energies for different vanadium oxidation states (V5+ to V0+). *Journal of Electron Spectroscopy and Related Phenomena* **2004**, 135 (2-3), 167-175.
- (50) Silversmit, G.; Depla, D.; Poelman, H.; Marin, G. B.; De Gryse, R. An XPS study on the surface reduction of V2O5 (0 0 1) induced by Ar+ ion bombardment. *Surface Science* **2006**, 600 (17), 3512-3517.
- (51) Baltrusaitis, J.; Mendoza-Sanchez, B.; Fernandez, V.; Veenstra, R.; Dukstiene, N.; Roberts, A.; Fairley, N. Generalized molybdenum oxide surface chemical state XPS determination via informed amorphous sample model. *Applied Surface Science* **2015**, 326, 151-161.
- (52) Clayton, C.; Lu, Y. Electrochemical and XPS evidence of the aqueous formation of Mo2O5. *Surface and Interface Analysis* **1989**, 14 (1-2), 66-70.
- (53) Scanlon, D. O.; Watson, G. W.; Payne, D.; Atkinson, G.; Egdell, R.; Law, D. Theoretical and experimental study of the electronic structures of MoO3 and MoO2. *The Journal of Physical Chemistry C* **2010**, 114 (10), 4636-4645.
- (54) Spevack, P.; McIntyre, N. Thermal reduction of molybdenum trioxide. *The Journal of Physical Chemistry* **1992**, 96 (22), 9029-9035.
- (55) Son, L. H.; Phuc, N. X.; Phuc, P. V.; Hong, N. M.; Hong, L. V. Observation of phase decomposition of Sr2FeMoO6 by Raman spectroscopy. *J. Raman Spectrosc.* **2001**, 32 (10), 817.

- (56) Porto, S. P. S.; Scott, J. Raman Spectra of CaWO_4 , SrWO_4 , CaMoO_4 , and SrMoO_4 . *Phys. Rev.* **1967**, 157 (3), 716.
- (57) Botto, I. L.; Baran, E. J.; Pedregosa, J. C.; Aymonino, P. J. The vibrational spectrum of barium divanadate. *Monatsh. Chem.-Chem. Mont.* **1979**, 110, 895.
- (58) Brett, D. J.; Atkinson, A.; Brandon, N. P.; Skinner, S. J. Intermediate temperature solid oxide fuel cells. *Chemical Society Reviews* **2008**, 37 (8), 1568-1578.
- (59) Zhu, B.; Yang, X.; Xu, J.; Zhu, Z.; Ji, S.; Sun, M.; Sun, J. Innovative low temperature SOFCs and advanced materials. *Journal of Power Sources* **2003**, 118 (1-2), 47-53.
- (60) Avrami, M. Kinetics of phase change. I General theory. *J. Chem. Phys.* **1939**, 7 (12), 1103.
- (61) Avrami, M. Kinetics of phase change. II transformation-time relations for random distribution of nuclei. *J. Chem. Phys.* **1940**, 8 (2), 212.
- (62) Avrami, M. Granulation, phase change, and microstructure kinetics of phase change. III. *J. Chem. Phys.* **1941**, 9 (2), 177.
- (63) Armstrong, E. N.; Duncan, K. L.; Wachsman, E. D. Effect of A and B-site cations on surface exchange coefficient for ABO₃ perovskite materials. *Physical Chemistry Chemical Physics* **2013**, 15 (7), 2298-2308.
- (64) Kan, C.; Kan, H.; Van Assche IV, F.; Armstrong, E.; Wachsman, E. Investigating oxygen surface exchange kinetics of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ using an isotopic tracer. *Journal of The Electrochemical Society* **2008**, 155 (10), B985-B993.

CHAPTER FOUR

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions

Experiments described in this thesis were designed to study, understand, and improve how $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ (SVMO) behaves under conditions commonly encountered in high temperature, solid-state energy conversion devices. Compositions with equal amounts of vanadium and molybdenum were studied over a range of A-site deficient SVMO formulations ($x = 0.0\text{-}0.2$). A variety of characterization techniques were used to evaluate material stability at temperatures up to 1000 °C under inert, reducing, and oxidizing conditions. The results clarify how SVMO stability is influenced by temperature, oxygen partial pressure, and A-site deficiency, and they provide insight into the mechanisms responsible for secondary phase formation at high temperatures in oxidizing atmospheres.

Chapter 2 presents work examining how the double perovskite $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ (SVMO-19) behaves under conditions typically encountered in solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs). In this study, we used several independent methods to evaluate SVMO-19 stability at different temperatures and under a wide variety of atmospheric conditions, identifying both the conditions where SVMO-19 remains stable and those that cause degradation. *In situ* Raman measurements show that SVMO-19 is stable up to 1000 °C in reducing environments and in mildly oxidizing atmospheres containing CO_2 and H_2O . These observations suggest that SVMO-19 may be suitable for CO_2 electrolysis and combined $\text{CO}_2/\text{H}_2\text{O}$ electrolysis, and that it may remain stable as a fuel electrode in reversible SOFC/SOEC devices even during fuel flow disruptions. However, in strong oxidizing environments, SVMO-19 rapidly

decomposes to form secondary phases such as SrMoO_4 , SrVO_3 , and $\text{Sr}_2\text{V}_2\text{O}_7$ at temperatures $\geq 600^\circ\text{C}$. Thermogravimetric analysis (TGA) shows that SVMO-19 begins accumulating mass at approximately 400°C . These data also show that SVMO remains stable in nitrogen (N_2) at temperatures up to 900°C , consistent with the temperature – dependent Raman data. Analysis of SVMO oxidation kinetics shows that SVMO decomposition follows two separate first order (or pseudo-first order) processes with activation energies of 0.53 ± 0.01 eV and 0.70 ± 0.19 eV; the similarity of these values suggests they represent similar processes, assigned tentatively to secondary phase formation occurring at the surface and within the bulk of the material, respectively.

A similar analysis of SVMO oxidation kinetics was performed using Avrami kinetic model. However, the Avrami rate constants produced a single linear fit, yielding an activation energy of $E_a = 0.62 \pm 0.12$ eV. We note that the activation energies calculated from all three sets of rate constants (double exponential fast, double exponential slow, Avrami) are quite similar. This observation shows that the energetics of SVMO-19 decomposition are largely insensitive to the model used to describe the process. Based on the goodness of fits, we propose that the double exponential model is more appropriate to describe the processes. Overall, these results show that while SVMO-19 is suitable as a fuel electrode in solid oxide cells (even under weakly oxidizing conditions), its use as an oxygen electrode is limited because it tends to form secondary phases at high temperatures in air.

Chapter 3 examines SVMO stability in air at elevated temperatures as a function of SVMO A-site deficiency. In addition to the SVMO-19 characterized in Chapter 2, SVMO formulations in this chapter included $\text{Sr}_2\text{VMoO}_{6-\delta}$, (SVMO-20), $\text{Sr}_{1.95}\text{VMoO}_{6-\delta}$. (SVMO-195),

$\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ (SVMO-19), $\text{Sr}_{1.85}\text{VMoO}_{6-\delta}$ (SVMO-185), and $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$ (SVMO-18). A combination of independent TGA and Raman measurements showed that the material with the smallest (but nonzero) A-site deficiency, SVMO-195, was significantly more stable than all other formulations. The origin of this stability is not immediately apparent, but XPS measurements suggest that SVMO-195 stands apart from the other materials with an equimolar mixture of V and Mo on the surface B-sites. Most other formulations present surfaces that are Mo rich. Distributions of V and Mo oxidation states also change with varying A-site deficiency with SVMO-195 also having a V:Mo average charge ratio approaching 1.0. In most other formulations, the V has a higher averaged oxidation state than Mo. These correlations deserve further investigation.

Future Directions

Further investigations into SVMO's use as an electrode material in SOFCs and SOECs should follow two important directions: 1) a focus on material stability as a function of B-site composition, and 2) a focus on performance in SOFCs and SOECs. Each will be discussed.

Synthesis and Characterization of SVMO with Tunable B-site V:Mo ratios

A key future direction of this PhD research is to design and study SVMO materials where the ratio of vanadium (V) to molybdenum (Mo) at the B-site can be carefully adjusted (V:Mo of 80:20; 60:40; 50:50; 40:60; 20:80). The main goal of this work would be to control how much of each element is present and then understand how this changes the material's properties. Results presented in Chapter 3 show clearly that SVMO-195 is more stable than all other formulations

tested, and the XPS data show unique correlations between the surface activity and average oxidation states with V and Mo, the two, equimolar B-site cations. To achieve SVMO double perovskite materials having different B-site compositions, reliable synthesis methods must be developed to produce pure, uniform materials over a wide range of compositions. Detailed structural analysis is needed to confirm that the correct crystal structure forms and that V and Mo are evenly distributed. Studying defects, especially oxygen vacancies, will be important, because changing the V:Mo ratio will affect charge balance and possibly, B-site cation distribution.

Important question to answer is how these new SVMO materials behave under SOFC/SOEC relevant conditions, including temperature and oxygen partial pressure (PO_2). One important series of studies should vary PO_2 over a wider range than was tested in this work. Changing the atmosphere above SVMO samples to a CO_2/CO mixture should allow PO_2 variation over many orders of magnitude. Correlating SVMO stability with temperature and PO_2 for all formulations will help identify conditions best suited for SVMO use in applications. Longer-term experiments are also needed to understand material durability.

Two important characterization tools were not available during our studies of SVMO: X-ray photoelectron spectroscopy (XPS) and conductivity. Both should be leveraged to better understand how SVMO composition changes elemental surface composition and charge carrying capabilities. X-ray photoelectron spectroscopy (XPS) should be used to study how the oxidation states of V and Mo change with changing B-site ratios. By examining samples in both oxidizing and reducing conditions, it will become possible to see how V and Mo change their oxidation states and whether they change together or separately. Because XPS mainly probes the surface, it

should be combined with techniques that study the bulk to get a complete picture. This work provides important insight into the electronic structure and chemical behavior of the materials.

The second technique that was unavailable for these studies was conductivity. Together with long-term stability, conductivity is the second property that will determine whether SVMO will be suitable for use in SOFCs and SOECs. All work in this dissertation was motivated by earlier studies reporting that SVMO had exceptionally high conductivity after being heated in reducing atmospheres. These results from more than a decade ago were never validated with the new batches of different SVMO formulations. Of particular importance will be conductivity or impedance studies that separate contributions to conductivity from electronic and ionic conductivities. The earlier reports by Childs, *et al.* worked solely with A-site deficient materials, so determining how electronic and ionic conductivity change with changing B-site ratios will also be critical in assessing a SVMO formulation's suitability for use in SOFCs and SOECs. Overall, understanding these links will allow SVMO materials to be designed in a more targeted way for specific applications and conditions.

Electrochemical Performance and Durability

The final and most significant future step is to carry out *operando* spectroscopic and electrochemical studies of SVMO based electrodes in functioning SOFCs and SOECs. To take this next step, membrane electrode assemblies (MEAs) will need to be fabricated consistently. These MEAs with SVMO anodes and/or cathodes will then be tested at operational temperatures and under relevant gas phase conditions. Initial versions of such a cell were fabricated by the Sofie research group, and the general structure of this assembly is shown in Figure 1.4. The fuel electrode (or anode in SOFC applications) consisted of a SVMO-CeO₂ composite with the CeO₂

added to increase oxide conductivity. The other electrode was a traditional LSM cathode and this cell had a traditional YSZ electrolyte.

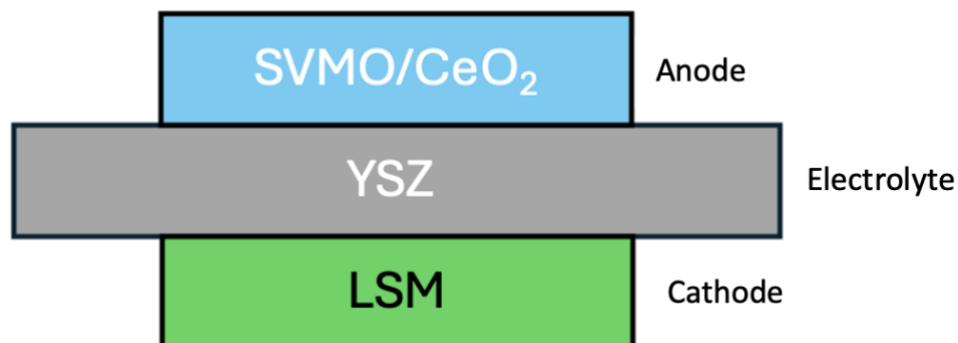


Figure 1.4 Schematics showing membrane electrode assemblies with SVMO/CeO₂ fuel electrodes

Preliminary results from the first cells we tested were instructive but not very promising as described in Figure 2.4 below. Figure 2.4 shows an image of the anode after it had been heated to 800 °C under N₂. The image shows discoloration of the electrode and the *operando* Raman spectra show a strong feature from Scheelite providing clear evidence that the anode was not stable as it heated to operational temperatures.

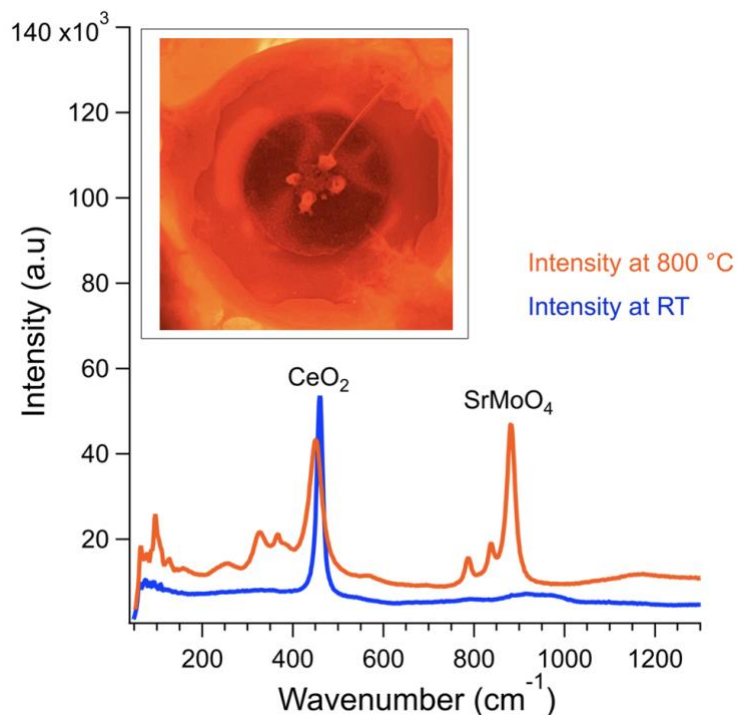


Figure 2.4 *In situ* temperature dependent Raman spectra of SVMO/CeO₂ cell at room temperature and in nitrogen at 800 °C

The Scheelite feature that is evident in the conditioned electrode at 800 °C does not appear in the room temperature spectrum (blue trace) acquired before the sample was heated. The room temperature spectrum is marked by a single feature at 460 cm⁻¹ assigned to CeO₂. When heated to 800 °C in nitrogen (orange trace), the spectrum changes notably: the ceria peak decreases in intensity and broadens slightly. CeO₂ is known to lose oxygen at temperatures above 400 °C (to form Ce₂O₃ + ½ O₂), so we propose that CeO₂ reduction generated O₂ that then drove secondary phase formation in the SVMO.

Figure 3.4. presents the Raman spectra from the same SVMO/CeO₂ cell at 800 °C under two conditions: N₂ (pink trace) and 40 sccm H₂ (black trace). The spectrum acquired under N₂ is the

same as the one shown in Figure 2.4. The high intensity and multiple peaks indicate clear structural changes for this mixture when heated to 800 °C under an inert atmosphere.

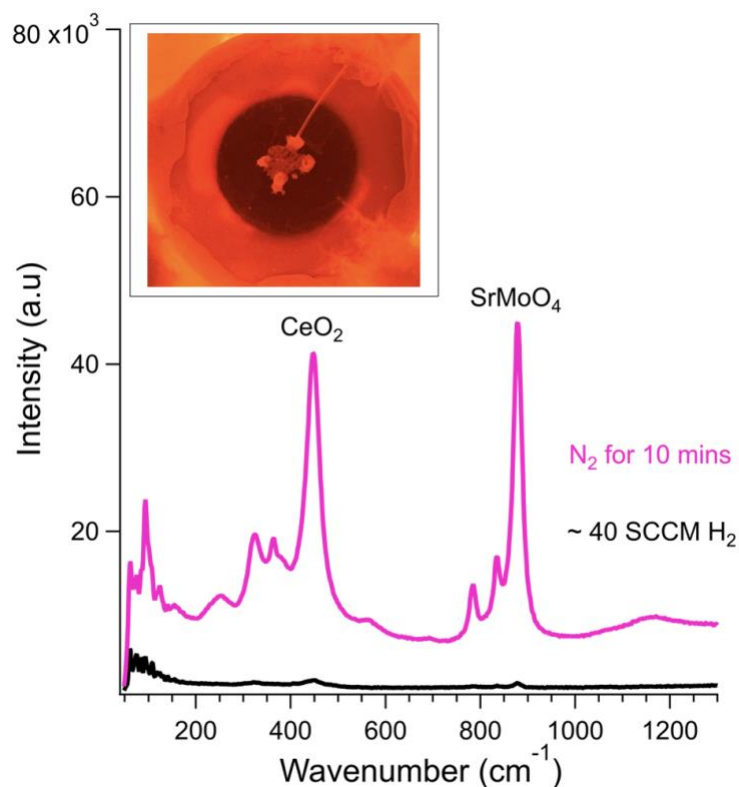


Figure 3.4 *In situ* temperature dependent Raman spectra of SVMO/CeO₂ cell in nitrogen and 40 sccm H₂ at 800 °C (sccm: standard cubic centimeters per minute)

To test the reversibility of these changes, the gas flow was changed from 60 sccm N₂ to 40 sccm H₂ (in a balance of 60 sccm N₂). Notably, under these conditions, both the Scheelite and the CeO₂ features almost completely disappeared, showing that the secondary phase formation in this anode was in fact reversible. This result suggests that these material composites might still be viable electrodes in functioning SOFCs and SOECs.

APPENDICES

APPENDIX A

Supporting Information for Chapter 2

Chemical and Thermal Stability of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$: Implications for High Temperature Energy Conversion Applications

Bamidele J. Samuel¹, Julia A. Esakoff^{2,3}, Stephen K. Heywood^{2,3}, Stephen W. Sofie^{2,3}, Robert A. Walker^{1,3*}

¹Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717

²Department of Mechanical and Industrial Engineering, Montana State University, Bozeman, MT 59717

³Montana Materials Science Program, Montana State University, Bozeman, MT 59717

Supporting Information

Summary: 8 pages, 6 figures.

SI Figure 1: *In Situ* Raman spectra of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ in N_2 from room temperature to 1000 °C

SI Figure 2: *In Situ* Raman spectra of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ in 20% CO_2 from room temperature to 1000 °C

SI Figure 3: *In Situ* Raman spectra of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ in N_2 with 3% steam from room temperature to 1000 °C

SI Figure 4: Room-temperature powder XRD patterns of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$: (a) as-fabricated, (b) after heating at 1000 °C in forming gas (5% H_2 , 95% N_2), and (c) after heating at 1000 °C in air

SI Figure 5: Kinetic trace of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ degradation at 700 °C under REDOX gas conditions, with fits to double exponential and Avrami kinetic models

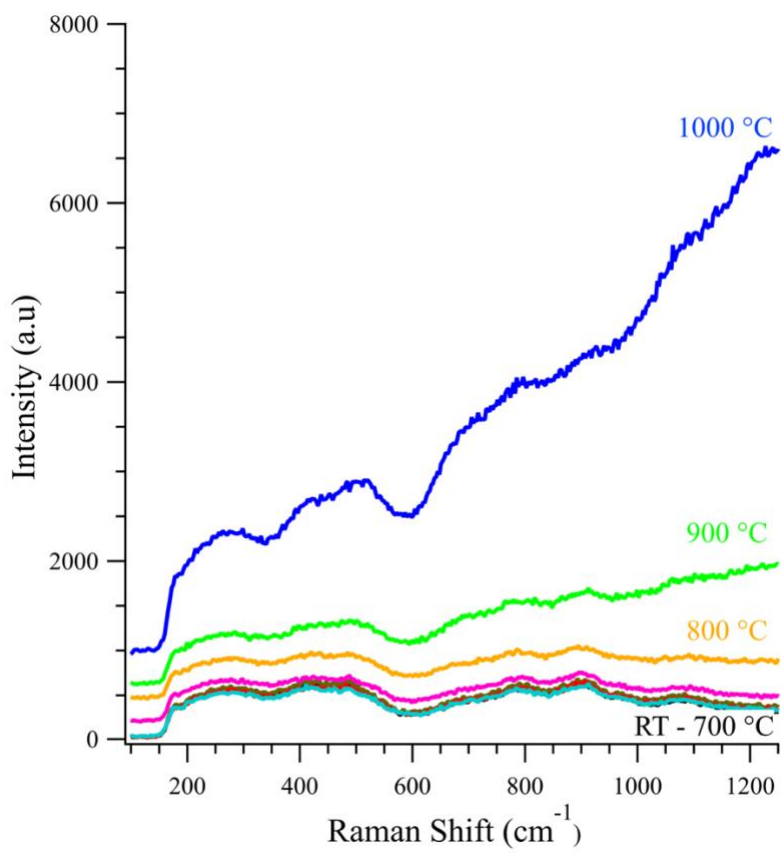


Figure S1: *In Situ* Raman spectra of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ from room temperature to 1000 °C under N_2 .

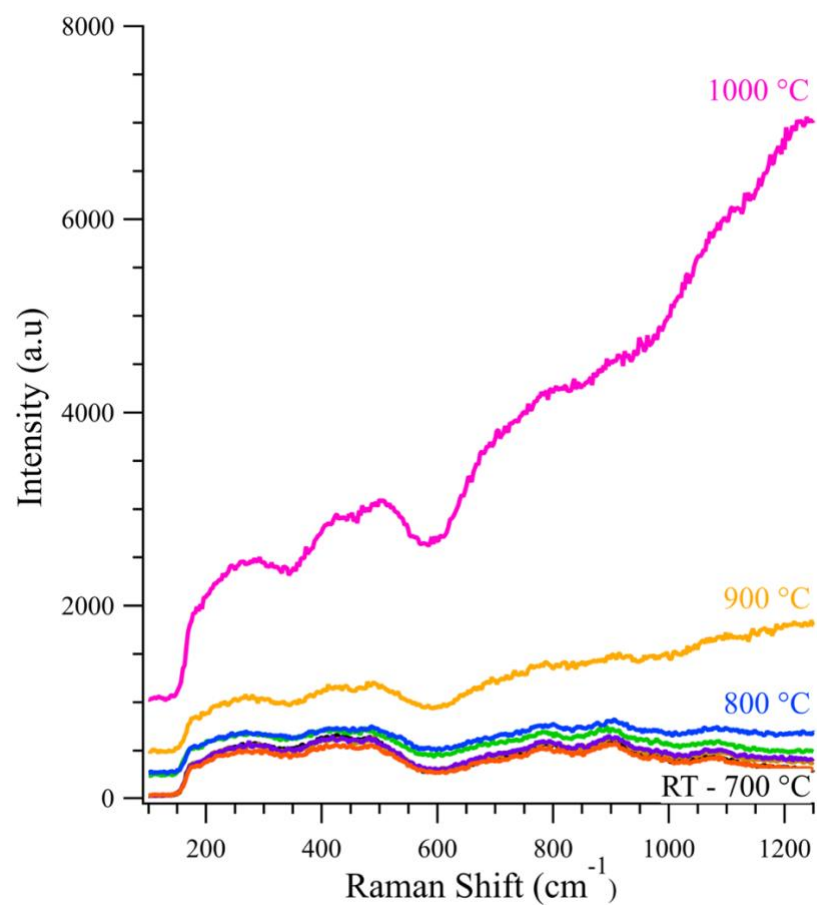


Figure S2: *In Situ* Raman spectra of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ from room temperature to 1000 °C under 20% CO_2 /80% N_2 .

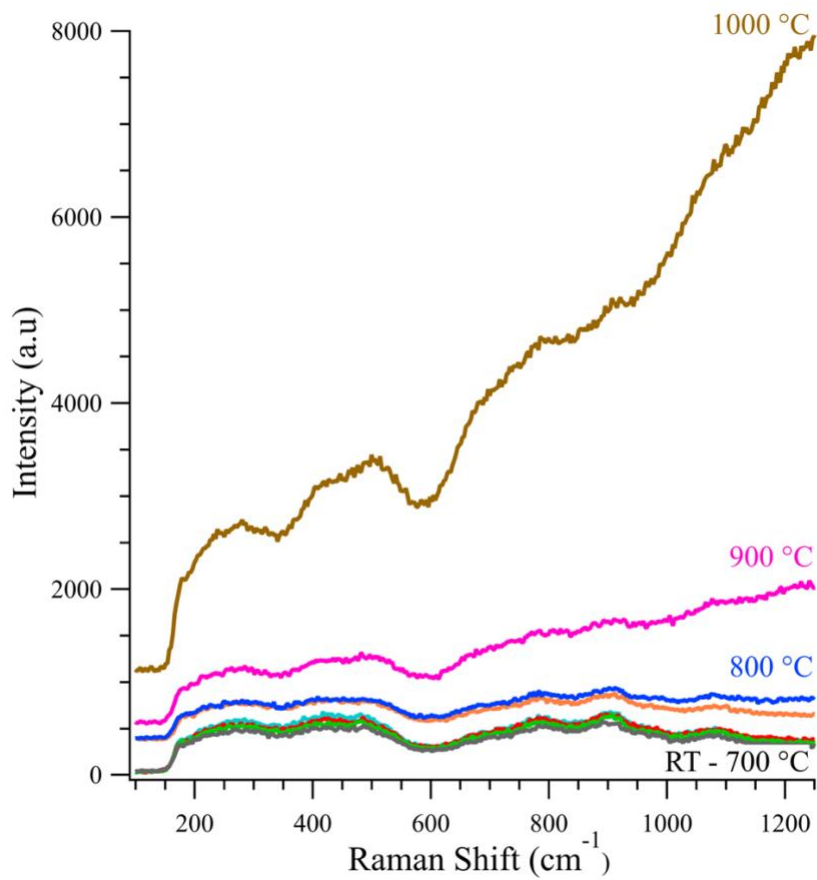


Figure S3: *In Situ* Raman spectra of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ from room temperature to 1000 °C in humidified N_2 containing ~ 3% steam.

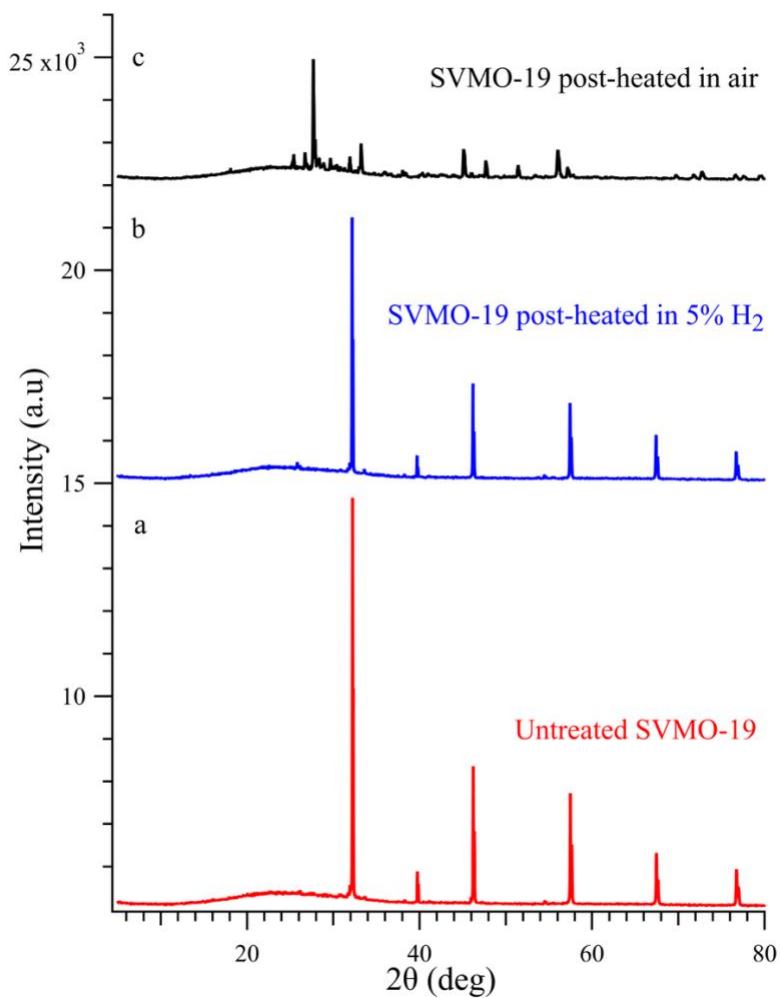


Figure S4: Room-temperature powder XRD patterns of $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$: (a) as-fabricated, (b) after heating at 1000 °C in forming gas (5% H_2 , 95% N_2), and (c) after heating at 1000 °C in air. Space group for SVMO (Pm-3m)

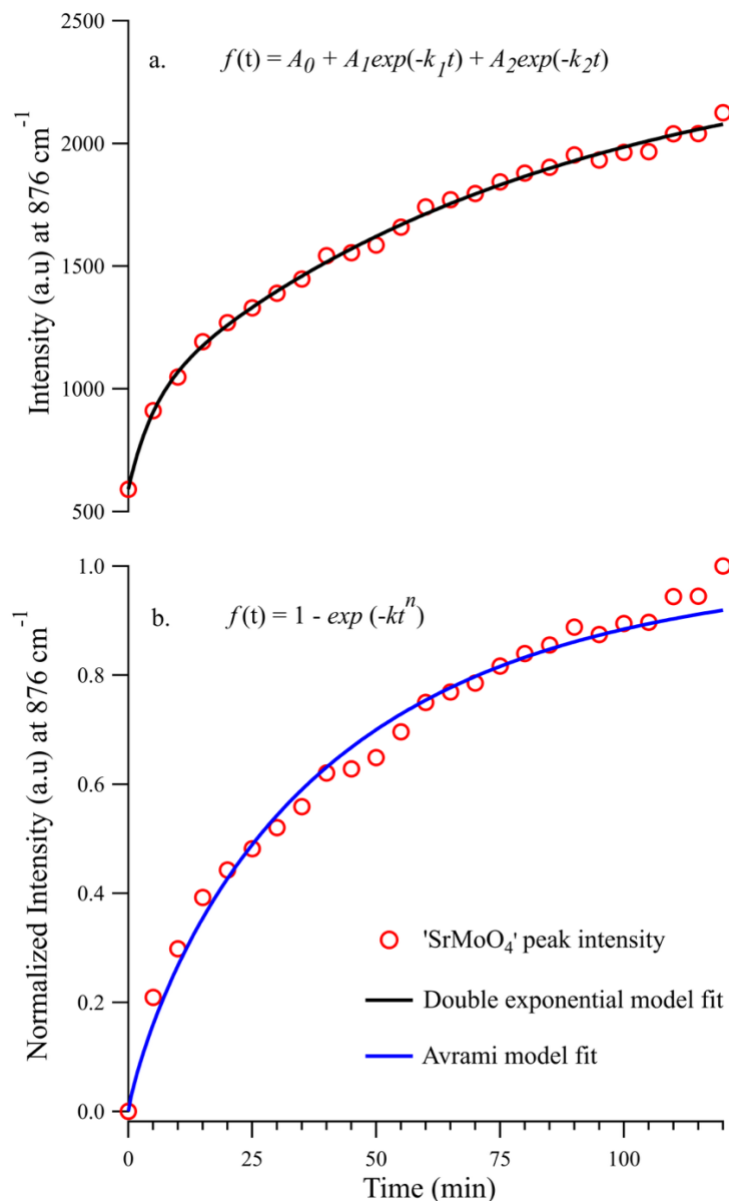


Figure S5: Kinetic trace of Sr_{1.9}VMoO_{6-δ} degradation at 700 °C taken under isothermal conditions. The sample is heated to 700 °C under forming gas, and then the atmosphere is switched to air. In air, SVMO-19 begins to decompose to form secondary phases including SrMoO₄. SrMoO₄ has a strong, sharp Raman feature at 876 cm⁻¹. The plots above show the growth of this feature (relative to baseline) after the atmosphere has been changed from reducing to oxidizing. The data are fit by both a double exponential function (top) and the Avrami model (bottom). See manuscript for more details.

APPENDIX B

Supporting Information for Chapter 3

The Role of A-site Deficiency in $\text{Sr}_{2.0-x}\text{VMoO}_{6-\delta}$ Stability

Bamidele J. Samuel¹, Stephen K. Heywood^{2,3}, Julia A. Esakoff^{2,3}, Stephen W. Sofie^{2,3}, Robert A. Walker^{1,3*}

¹Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717

²Department of Mechanical and Industrial Engineering, Montana State University, Bozeman, MT 59717

³Montana Materials Science Program, Montana State University, Bozeman, MT 59717

Supporting Information

Summary: 15 pages, 12 figures and 1 Table.

SI Figure 1: Dependence of lattice parameters on Sr deficiency (x) in as-fabricated $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ double perovskites

SI Figure 2: TGA curves of SVMO-195, SVMO-19, SVMO-185, and SVMO-18 in N_2 and air from 25 to 900 °C

SI Figure 3: *In situ* Raman spectra of SVMO-19 in air from room temperature to 1000 °C.

SI Figure 4: *In situ* Raman spectra of SVMO-18 in air from room temperature to 1000 °C.

SI Figure 5: (a) *In situ* Raman spectra of SVMO-18 in 5% H_2 and air from room temperature to 700 °C; (b) kinetic trace showing the normalized intensity of the SrMoO_4 secondary phase after exposure to air at 700 °C.

SI Figure 6: (a) *In situ* Raman spectra of SVMO-18 in 5% H_2 and air from room temperature to 600 °C; (b) kinetic trace showing the normalized intensity of the SrMoO_4 secondary phase after exposure to air at 600 °C.

SI Figure 7: (a) *In situ* Raman spectra of SVMO-18 in 5% H₂ and air from room temperature to 500 °C; (b) kinetic trace showing the normalized intensity of the SrMoO₄ secondary phase after exposure to air at 500 °C

SI Figure 8: (a) *In situ* Raman spectra of SVMO-20 in 5% H₂ and air from room temperature to 600 °C; (b) kinetic trace showing the normalized intensity of the SrMoO₄ secondary phase after exposure to air at 600 °C.

SI Figure 9: (a) *In situ* Raman spectra of SVMO-20 in 5% H₂ and air from room temperature to 500 °C; (b) kinetic trace showing the normalized intensity of the SrMoO₄ secondary phase after exposure to air at 500 °C.

SI Figure 10: Isothermal TGA curves of SVMO-195, SVMO-19, SVMO-185, and SVMO-18 in air at 500 °C, 600 °C, and 700 °C with fits to the double exponential kinetic model. The dashed vertical lines correspond to the time when the sample has reached its target temperature. The markers (o, ◇, and Δ) superimposed on the data correspond to fits generated by eq. 2.

SI Figure 11: Arrhenius plots for SVMO-20, SVMO-195, SVMO-19 kinetic data from isothermal TGA measurements

SI Figure 12: Arrhenius plots for SVMO-185, and SVMO-18 kinetic data from isothermal TGA measurements.

SI Table 1: Rate constants determined from fitting isothermal TGA data to Equation 2

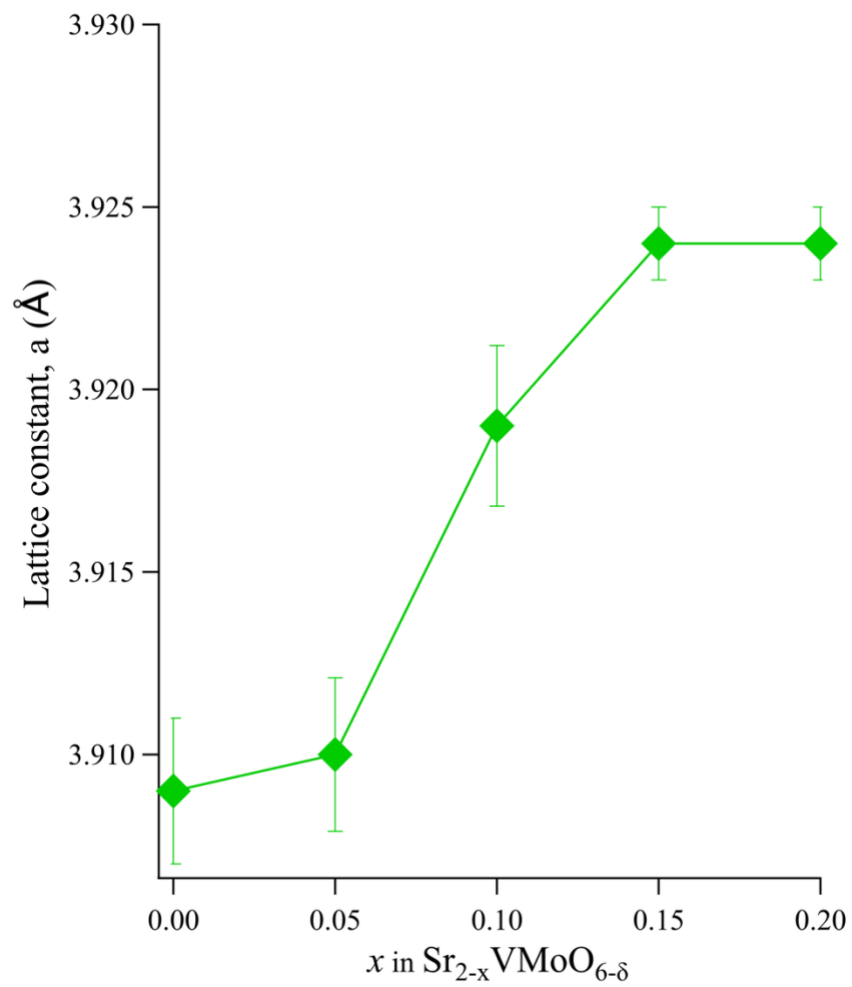


Figure S1: Dependence of lattice parameters on Sr deficiency (x) in as-fabricated $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ double perovskites

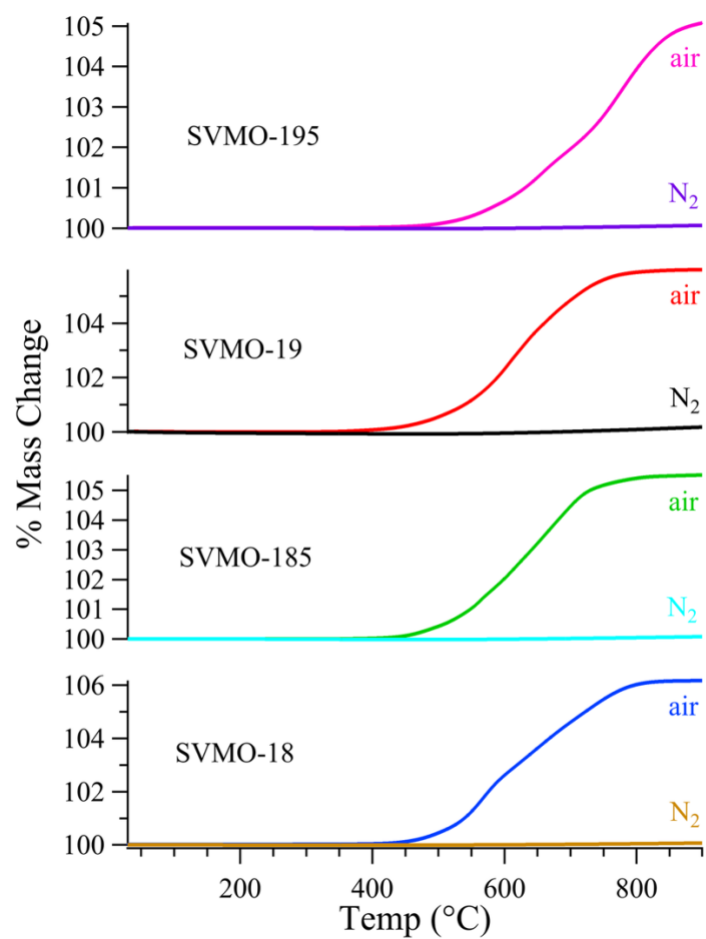


Figure S2: TGA curves of SVMO-195, SVMO-19, SVMO-185, and SVMO-18 in N₂ and air from 25 to 900 °C

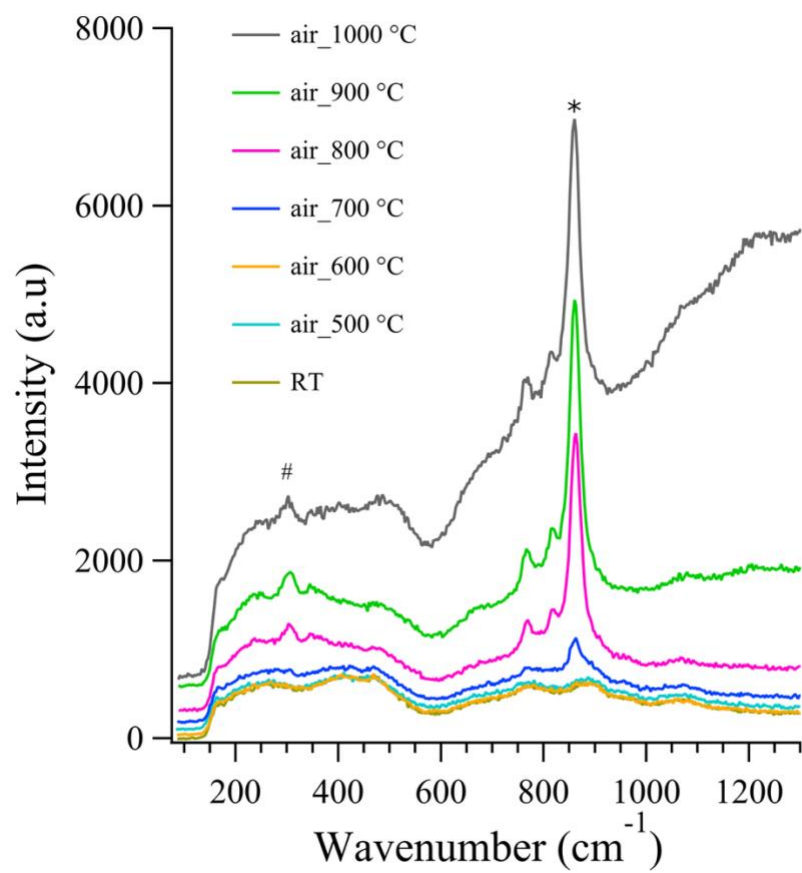


Figure S3: *In situ* Raman spectra of SVMO-19 in air from room temperature to 1000 °C.

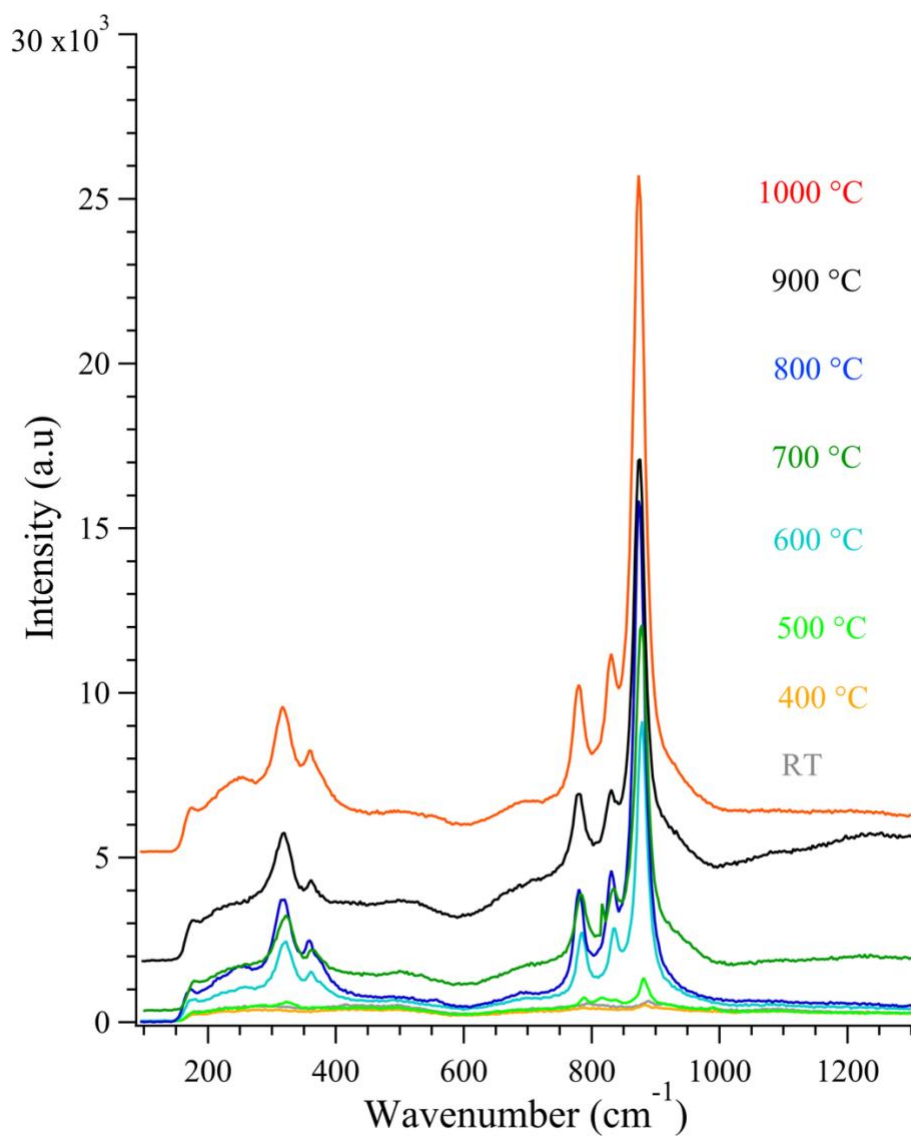


Figure S4: *In situ* Raman spectra of SVMO-18 in air from room temperature to 1000 °C.

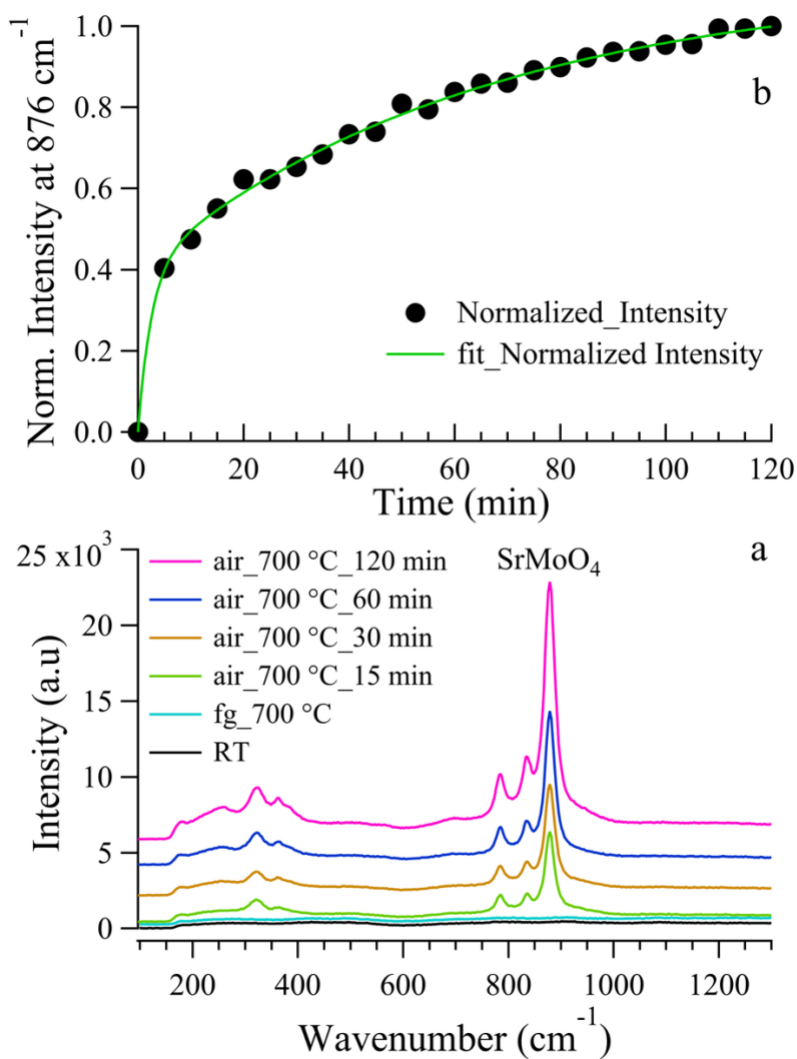


Figure S5: (a) *In situ* Raman spectra of SVMO-18 in 5% H₂ and air from room temperature to 700 °C; (b) kinetic trace showing the normalized intensity of the SrMoO₄ secondary phase after exposure to air at 700 °C.

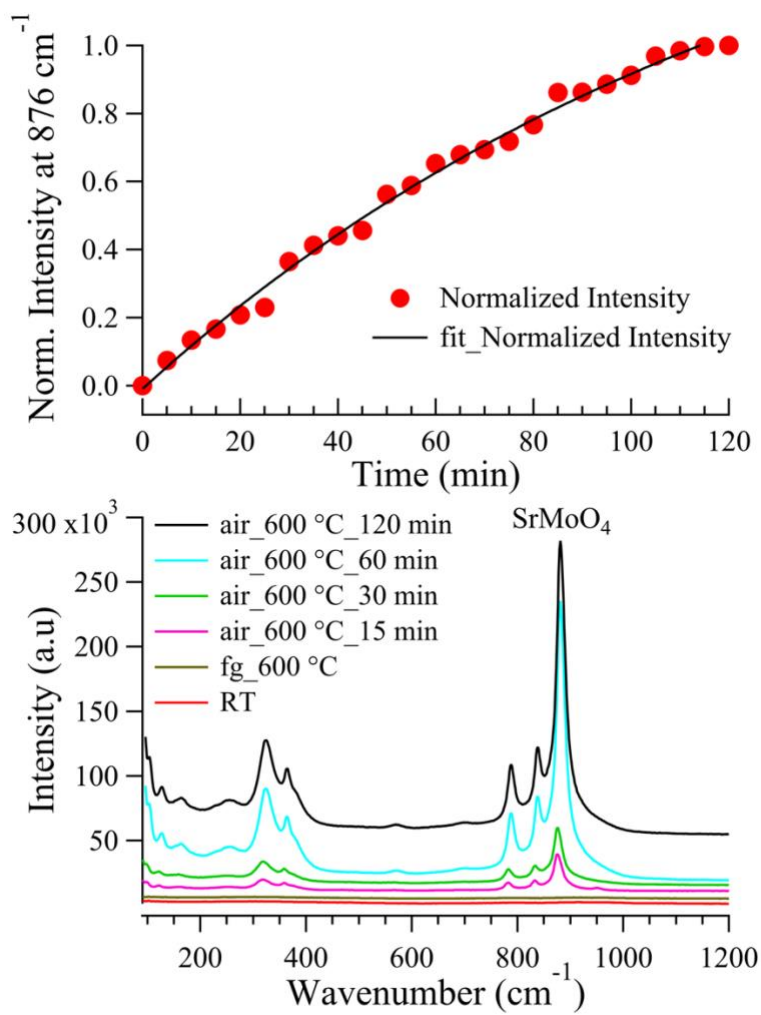


Figure S6: (a) *In situ* Raman spectra of SVMO-18 in 5% H₂ and air from room temperature to 600 °C; (b) kinetic trace showing the normalized intensity of the SrMoO₄ secondary phase after exposure to air at 600 °C.

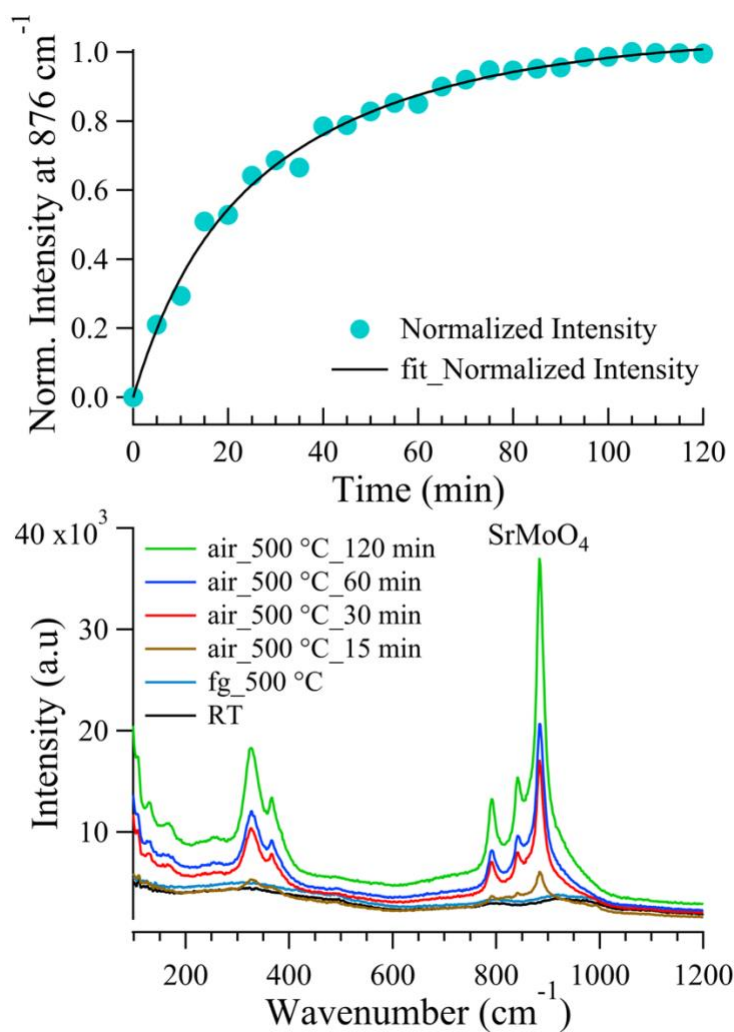


Figure S7: (a) *In situ* Raman spectra of SVMO-18 in 5% H₂ and air from room temperature to 500 °C; (b) kinetic trace showing the normalized intensity of the SrMoO₄ secondary phase after exposure to air at 500 °C.

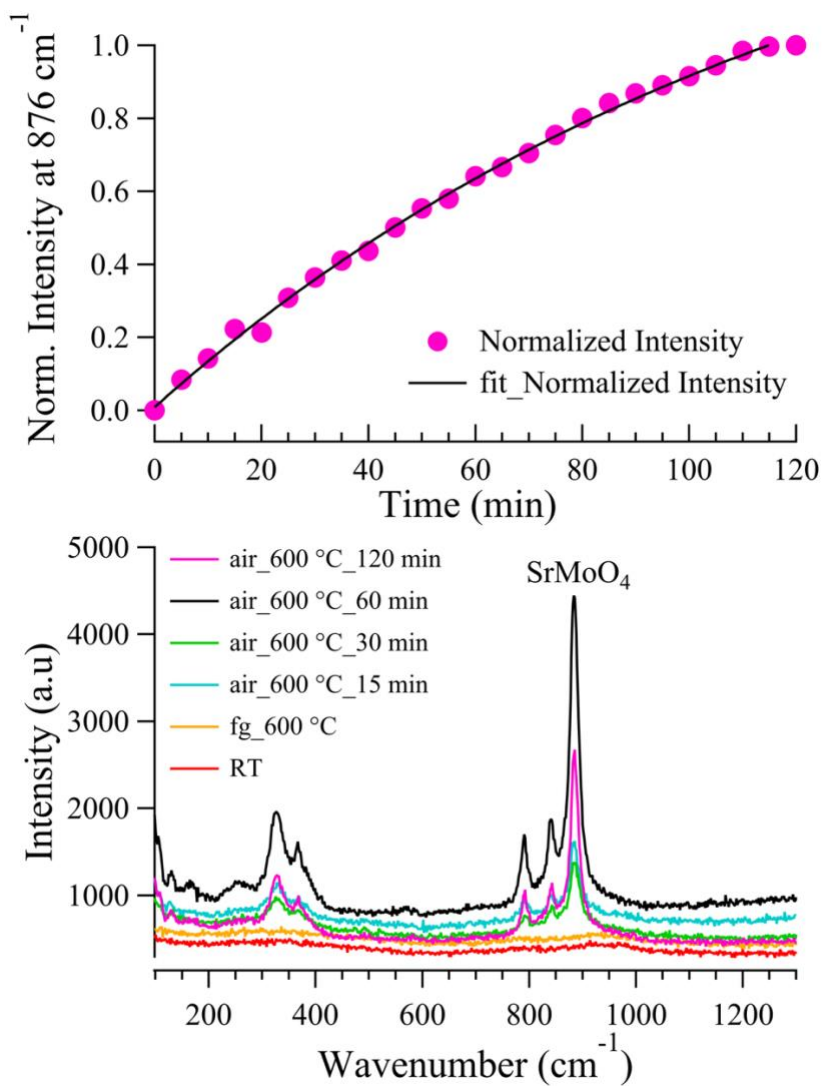


Figure S8: (a) *In situ* Raman spectra of SVMO-20 in 5% H_2 and air from room temperature to 600 °C; (b) kinetic trace showing the normalized intensity of the SrMoO_4 secondary phase after exposure to air at 600 °C.

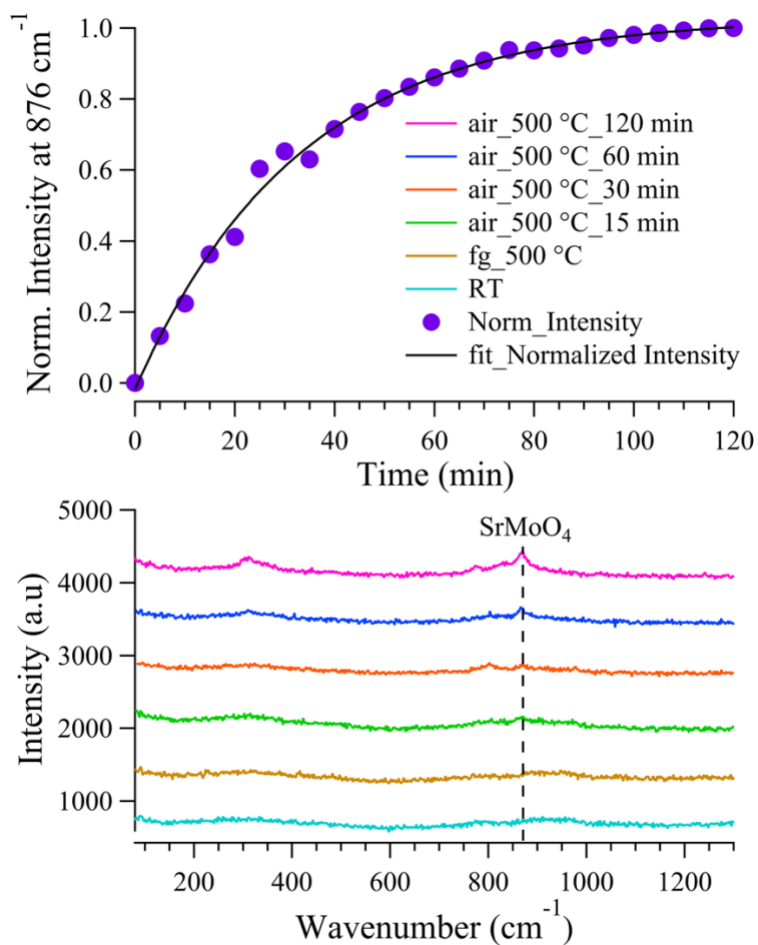


Figure S9: (a) *In situ* Raman spectra of SVMO-20 in 5% H₂ and air from room temperature to 500 °C; (b) kinetic trace showing the normalized intensity of the SrMoO₄ secondary phase after exposure to air at 500 °C.

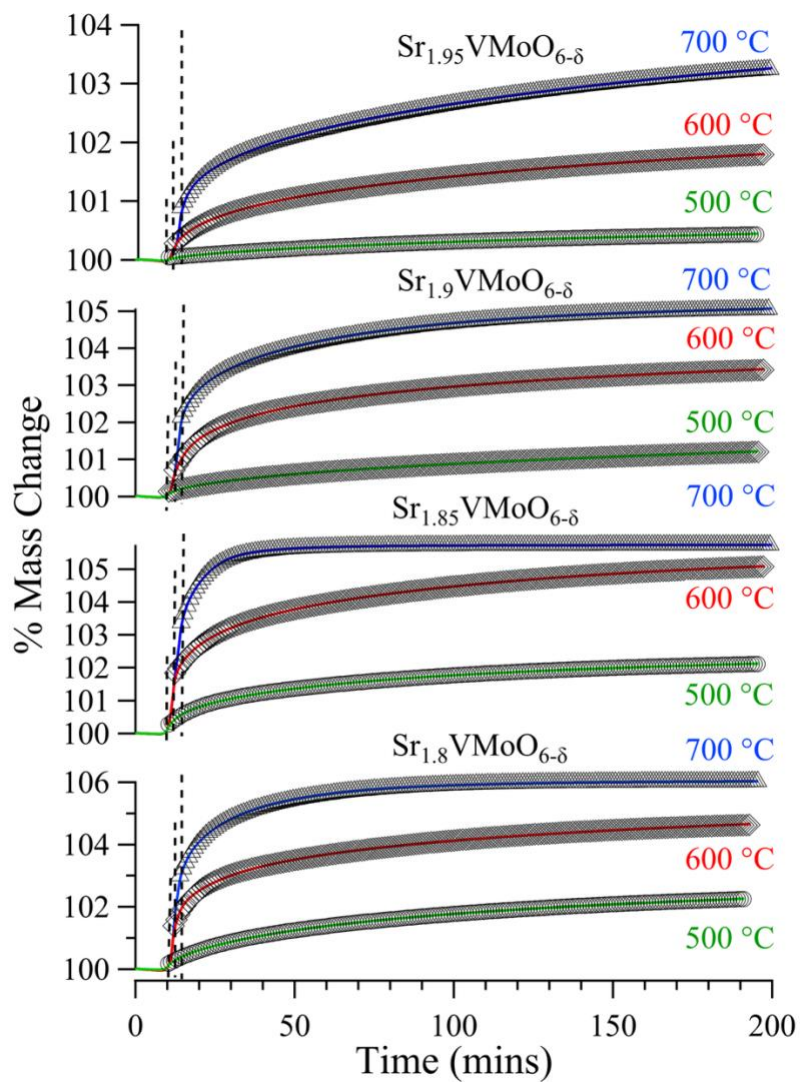


Figure S10: Isothermal TGA curves of SVMO-195, SVMO-19, SVMO-185, and SVMO-18 in air at 500 °C, 600 °C, and 700 °C with fits to the double exponential kinetic model. The dashed vertical lines correspond to the time when the sample has reached its target temperature. The markers (o, ◇, and Δ) superimposed on the data correspond to fits generated by eq. 2.

Table 1. Rate constants determined from fitting isothermal TGA data to Equation 2

SVMO	k_1 (/s)	k_2 (/s)	$E_{a,1}$ (eV) $\pm$ <i>unc</i>	$E_{a,2}$ (eV) $\pm$ <i>unc</i>	Temp. (°C)
	7.5×10^{-4}	1.2×10^{-4}			500
SVMO-20	3.2×10^{-3}	2.7×10^{-4}	0.6 ± 0.5	0.5 ± 0.3	600
	2.9×10^{-3}	2.9×10^{-4}			700
	5.8×10^{-4}	1.2×10^{-4}			500
SVMO-195	1.8×10^{-3}	1.7×10^{-4}	0.8 ± 0.3	0.2 ± 0.5	600
	2.4×10^{-3}	1.6×10^{-4}			700
	3.2×10^{-4}	7.8×10^{-5}			500
SVMO-19	1.6×10^{-3}	1.8×10^{-4}	0.7 ± 0.3	0.5 ± 0.01	600
	2.3×10^{-3}	3.4×10^{-4}			700
	1.9×10^{-3}	1.8×10^{-4}			500
SVMO-185	1.8×10^{-3}	1.8×10^{-4}	0.1 ± 0.9	0.4 ± 0.7	600
	2.1×10^{-3}	4.4×10^{-4}			700
	1.6×10^{-3}	1.6×10^{-4}			500
SVMO-18	2.9×10^{-3}	2.9×10^{-4}	0.3 ± 0.3	0.4 ± 0.4	600
	3.6×10^{-3}	7.8×10^{-4}			700

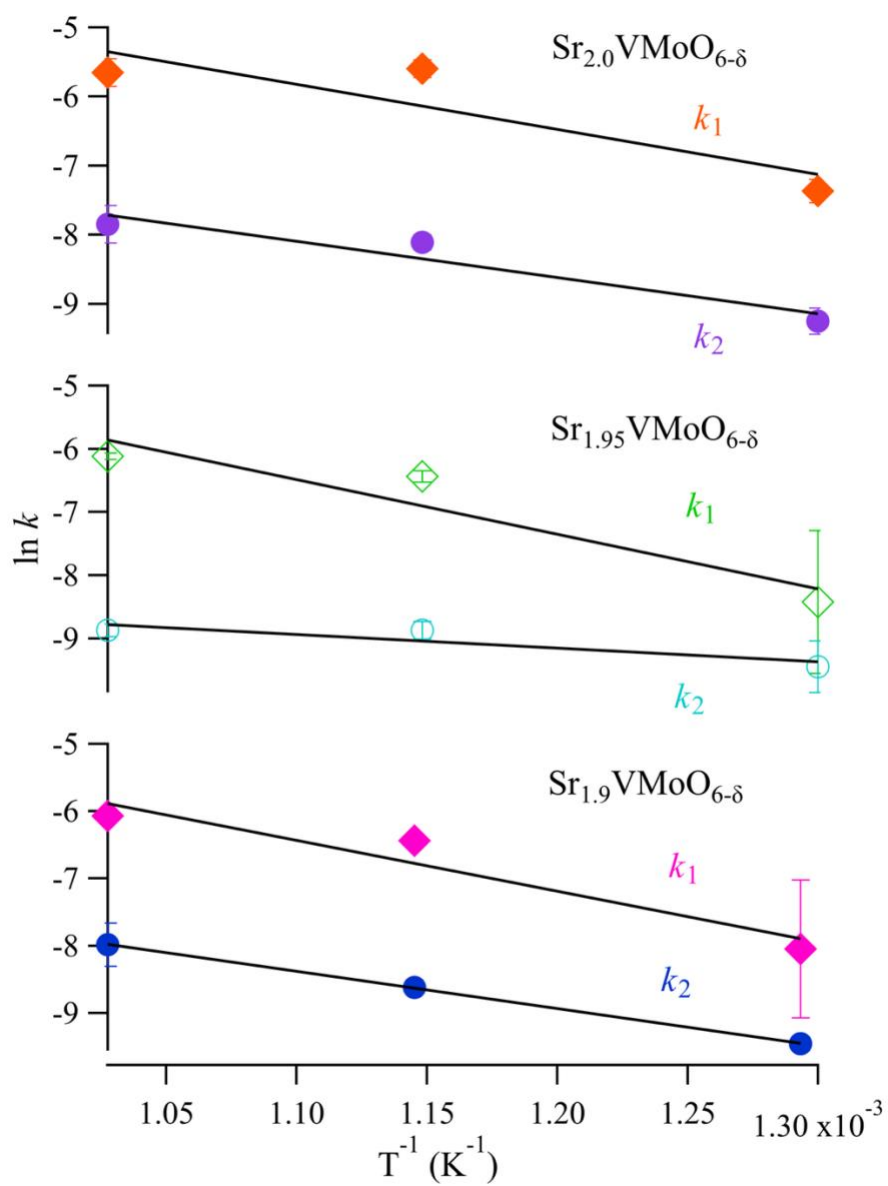


Figure S11: Arrhenius plots for SVMO-20, SVMO-195, SVMO-19 kinetic data from isothermal TGA measurements

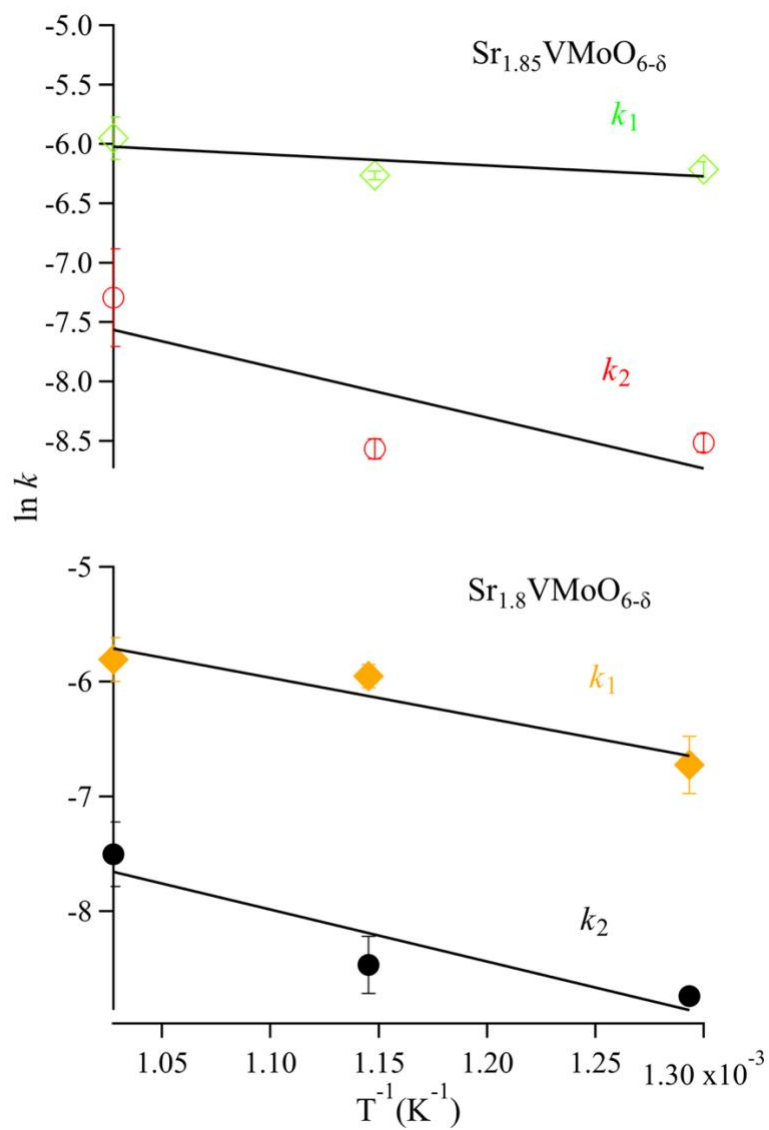


Figure S12: Arrhenius plots for SVMO-185, and SVMO-18 kinetic data from isothermal TGA measurements.

APPENDIX C

Kinetic Modeling Considerations

Assessing the Goodness of Fit using Kinetic Models

The isothermal Raman and TGA data presented in Chapters 2 and 3 were analyzed using kinetic modeling. In this approach, mathematical expressions are used to describe how a system changes with time and temperature. To describe the rate of secondary phase formation (isothermal Raman) and mass uptake (isothermal TGA), several models were considered. The models considered include a single first-order reaction with an offset, a double first-order model representing two independent processes, and an Avrami-type model with an offset.

The quality of each model was evaluated using the chi-square (χ^2) statistic, which measures the difference between the experimental data and the model prediction. A smaller χ^2 value indicates a better agreement between the model and the data, while a larger value indicates a poorer fit. By comparing χ^2 values for different models, the most suitable model was selected in a consistent and objective manner. An important consideration is that χ^2 will necessarily decrease with more independent parameters in the model used to fit the data, so comparing absolute χ^2 values between fits having different numbers of variables is not a mathematically rigorous criterion. Nevertheless, the models themselves were chosen based on their physical interpretation with the intent of being as simple as possible while still capturing the precision of the data. The fitted curves closely followed the experimental data, showing that the model captured the key physical behavior.

Fitting parameters are adjustable quantities within a model that are optimized to match the experimental data. These parameters determine important features such as the reaction rate (k_i) and relative amplitudes (A_i) of the contributing reactions. A single first-order model with an offset typically includes three parameters, while a double first-order model may require five or

six parameters, and an Avrami model typically has four parameters. Increasing the number of parameters generally improves the numerical fit and reduces χ^2 . However, using too many parameters can lead to overfitting, where the model begins to capture random noise instead of the true physical trend, making the parameters less physically meaningful. Therefore, the selected model should balance accuracy and simplicity. The best model is one that uses the smallest number of parameters while still providing an accurate and physically meaningful description of the data.

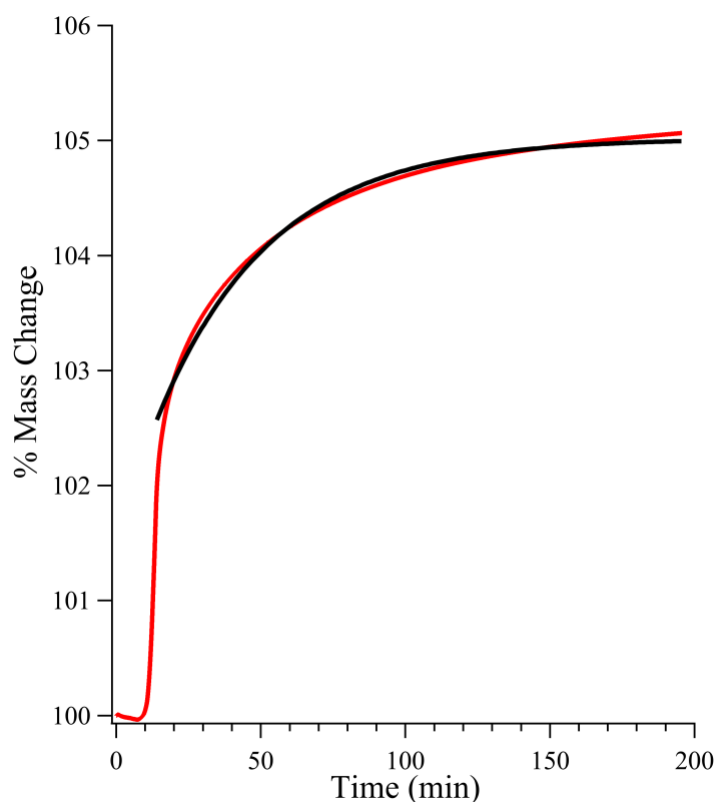


Figure 1. Isothermal TGA curve of SVMO-19 in air at 700 °C. The solid black curve superimposed on the data correspond to fit generated by Eq. 1 below

Eq. 1 describes a single first-order reaction model with offset and 3 fitting parameters:

$$A = A_0 + A_1 \exp(-k_1 t)$$

Eq. 1

$$\chi^2 = 420$$

$$A_0 = 105; A_1 = -3.49; k_1 = 4.22 \text{ E-4 s}^{-1}$$

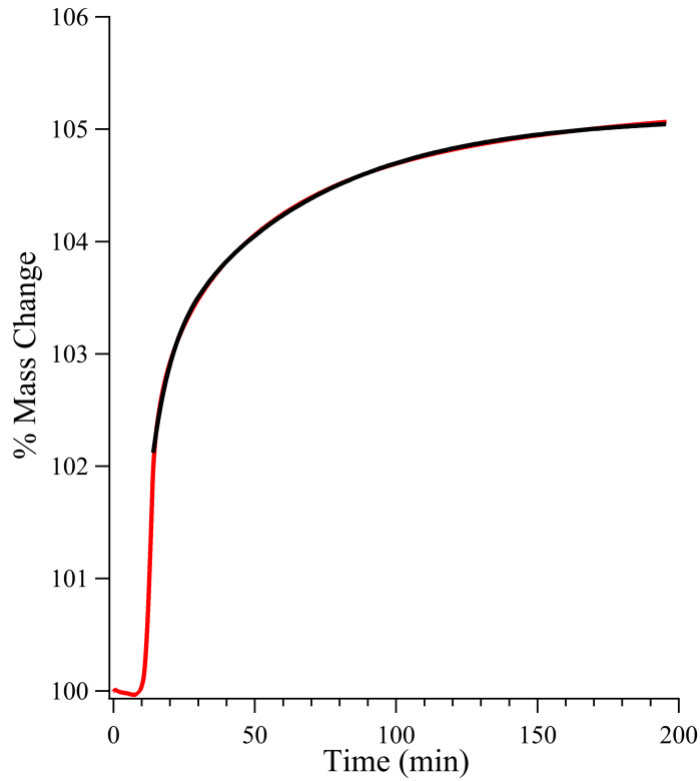


Figure 2. Isothermal TGA curve of SVMO-19 in air at 700 °C. The solid black curve superimposed on the data correspond to fit generated by Eq. 2 below

Eq. 2 describes a double first-order reaction model with offset and 5 fitting parameters:

$$A = A_0 + A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t)$$

Eq. 2

$$\chi^2 = 15.7$$

$$A_0 = 105; A_1 = -2.70; A_2 = -8.89; k_1 = 2.69 \text{ E-3 s}^{-1}; k_2 = 3.11 \text{ E-4 s}^{-1}$$

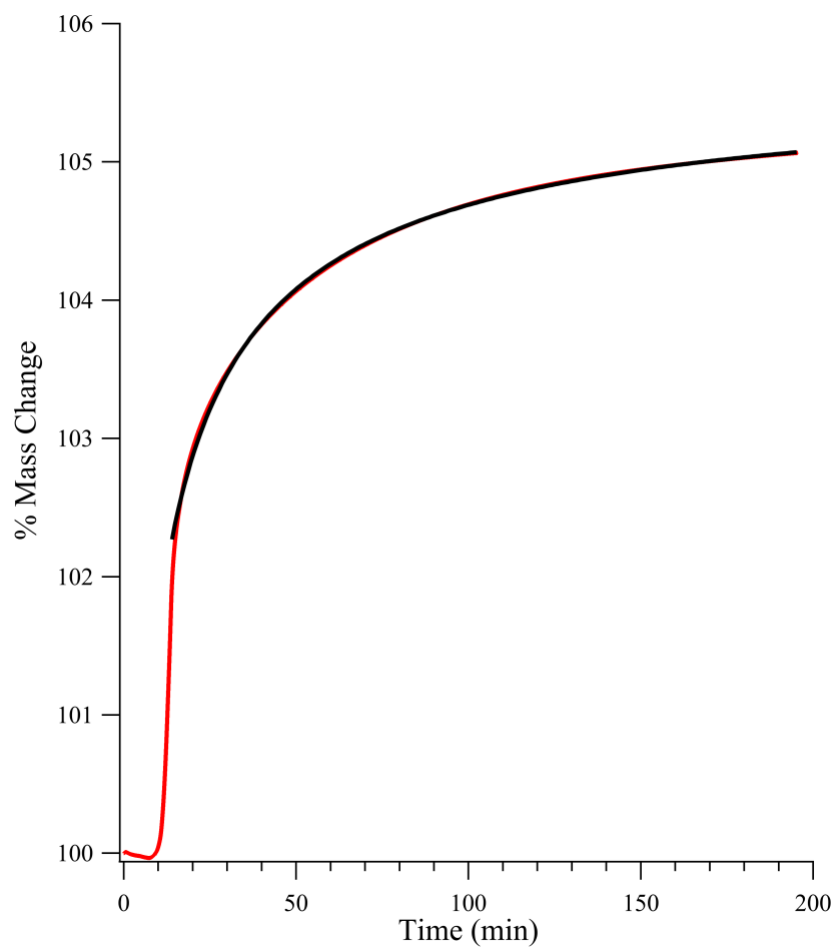


Figure 3. Isothermal TGA curve of SVMO-19 in air at 700 °C. The solid black curve superimposed on the data correspond to fit generated by Eq. 3 below.

Eq. 3 describes a single reaction, quasi-Avrami, with offset and 4 fitting parameters:

$$A = A_0 - A_1 \exp(-k_1 t^n) \quad \text{Eq. 3}$$

$$\chi^2 = 48$$

$$A_0 = 106; A_1 = 35.7; k_1 = 1.31; n = 0.231$$

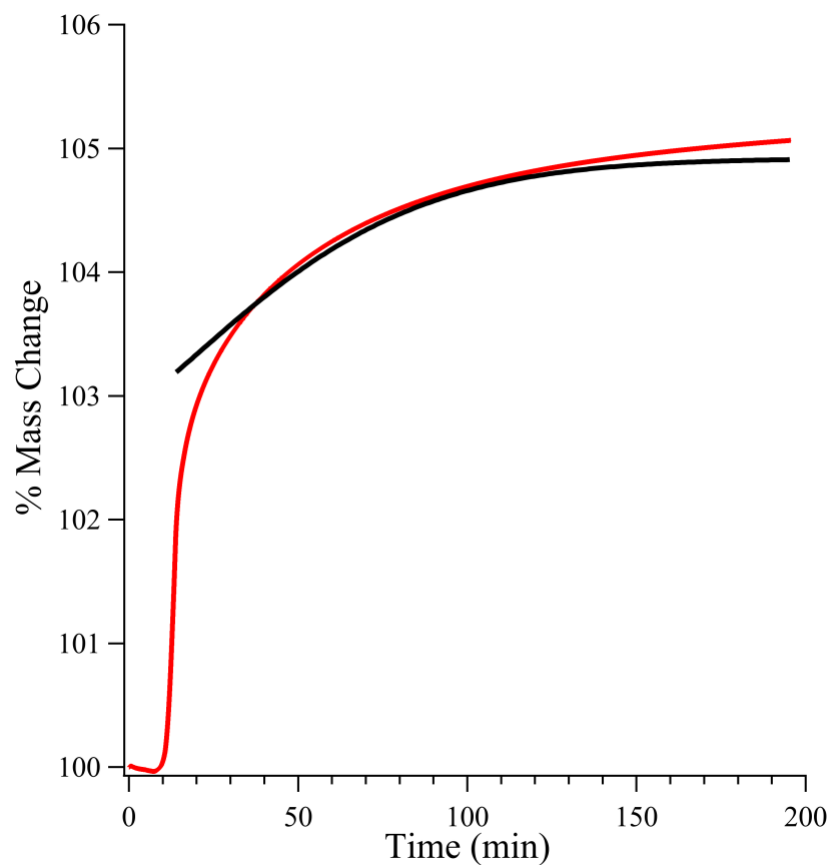


Figure 4. Isothermal TGA curve of SVMO-19 in air at 700 °C. The solid black curve superimposed on the data correspond to fit generated by Eq. 4 below.

Eq. 4 describes a double reaction, “Avrami” each, with offset and 5 fitting parameters:

$$A = A_0 - \exp(-k_1 t^{n_1}) - \exp(-k_2 t^{n_2}) \quad \text{Eq. 4}$$

$$\chi^2 = 2793$$

$$A_0 = 105; k_1 = 9.55 \text{ E-3}; k_2 = 1.06 \text{ E-3}; n_1 = 1.62; n_2 = 1.19$$

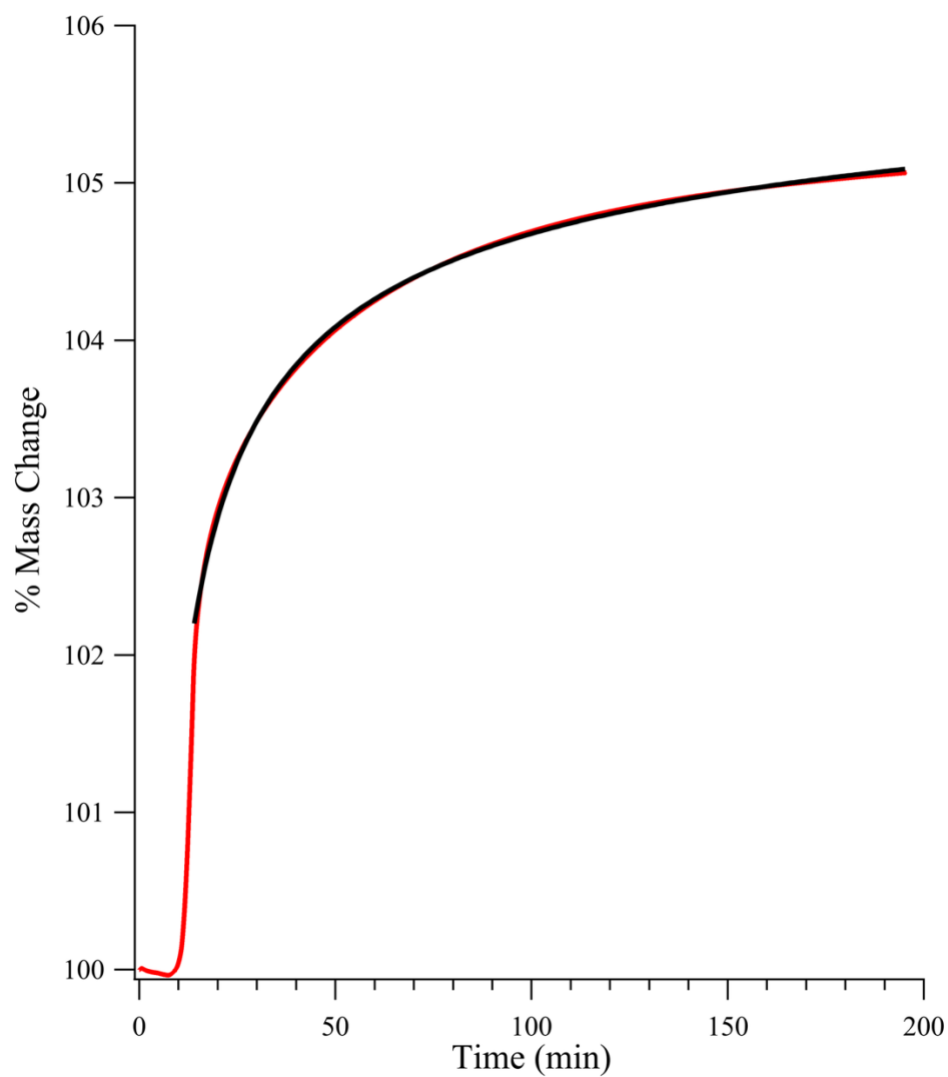


Figure 5. Isothermal TGA curve of SVMO-19 in air at 700 °C. The solid black curve superimposed on the data correspond to fit generated by Eq. 5 below.

Eq. 5 describes a single reaction, “Avrami” with offset and 3 fitting parameters:

$$A = A_0 - \exp(-kt^n) \quad \text{Eq. 5}$$

$$\chi^2 = 42.4$$

$$A_0 = 108; k = -3.126; n = -0.236$$