PHASE TRANSFORMATIONS IN CALCIUM SUBSTITUTED LANTHANUM
FERRITE

by
Patrick M. Price

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DEFENSE COMMITTEE AND FINAL READING APPROVALS

of the dissertation submitted by

Patrick M. Price

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The following individuals read and discussed the dissertation submitted by student Patrick M. Price, and they evaluated his presentation and response to questions during the final oral examination. They found that the student passed the final oral examination.

Darryl Butt, Ph.D. Chair, Supervisory Committee

William B. Knowlton, Ph.D. Member, Supervisory Committee

Dmitri Tenne, Ph.D. Member, Supervisory Committee

Charles Lewinsohn, Ph.D. Member, Supervisory Committee

The final reading approval of the dissertation was granted by Darryl Butt, Ph.D., Chair of the Supervisory Committee. The dissertation was approved for the Graduate College by John R. Pelton, Ph.D., Dean of the Graduate College.

DEDICATION

This dissertation is dedicated to my wife for her constant encouragement, support, and patience.

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ABSTRACT

Increasing world energy demands are still heavily dependent on fossil fuels. To meet these demands, crude oil is increasingly being extracted from remote locations where natural gas pipelines do not exist. It is not profitable for oil and gas companies to transport natural gas by ship or truck from these remote locations so it is combusted on site in the form of gas flares. Critics oppose this practice due to the environmental impact from pollution and carbon emissions created during the flaring process. Oil and gas companies are eager to find profitable ways to eliminate natural gas lines in order to reduce environmental impacts and avoid costly lawsuits and political opposition. Building new pipeline infrastructures have been pursued, however construction is slow and costly. A cost effective alternative to gas transportation is the onsite conversion of natural gas to transportable liquid products such as ammonia or methanol. The first intermediate step in this process is the conversion of natural gas to synthesis gas, or “syngas” for short. In this process, natural gas (CH_4) is oxidized at high temperature to form a gas mixture composed principally of hydrogen, carbon monoxide, and carbon dioxide.

Syngas reactors may use oxygen ion conducting membranes that transport oxygen from one side to the other when a chemical potential gradient is applied at high temperatures, typically in the range 750-900°C. The chemical potential is created when one side of the syngas membrane is exposed to air and the other side is exposed to a

reducing, methane atmosphere. Materials selected for syngas membranes need to be chemically stable in reducing environments at high temperatures, have good chemical selectivity with high flux, and have mechanical properties that allow for the fabrication of thin membranes operated under pressure.

Perovskite materials are a class of complex oxides with a common ABO_3 crystal structure. Of these, lanthanum ferrites ($LaFeO_3$) have been shown to display superior chemical stability at high temperatures under reducing atmospheres making them a good choice for syngas membranes. In perovskites, oxygen conduction occurs via the hopping of oxygen to available oxygen vacancy sites. Lanthanum ferrite does not intrinsically have a high concentration of oxygen vacancies and therefore is not a good ion conductor. Oxygen flux can be increased by doping $LaFeO_3$ with a divalent alkaline metal cation (M^{2+}) on the trivalent lanthanum site (La^{3+}) site creating a charge imbalance resulting in the formation of additional oxygen vacancies. Of the available alkaline cations, calcium and strontium are the most promising substituents for syngas membrane applications.

This study focuses primarily on calcium substituted lanthanum ferrites. Despite the great interest in these materials, the phase stability of the lanthanum calcium ferrite (LCF) materials system is not very well understood in the scientific literature. In this study, we have synthesized LCF materials using solid state reactions and characterized the phase stability under oxidizing and reducing atmospheres.

This investigation began by accessing the phase stability of LCF materials in air and argon atmospheres. The calcium solubility in the lanthanum ferrite perovskite structure was identified for samples sintered at 1250°C using room temperature x-ray diffraction (XRD), scanning electron microscopy, and energy dispersive spectroscopy.

We identified structural transitions using thermal analysis techniques and characterized the resulting crystal structure and changes in thermal expansion with high temperature XRD. We used thermal analysis techniques to identify the phase transition temperature of the previously reported order-disorder transformation. The behavior of two phase materials composed of the perovskite and Grenier structures treated above the order-disorder transition temperature was studied and show that they form single grains with a nominal composition between the two initial phases.

Thermal expansion and magnetic behaviors of divalent, alkaline-doped lanthanum ferrites ($\text{La}_{0.9}\text{M}_{0.1}\text{FeO}_3$, $\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) were assessed using a combination of dilatometry, magnetometry, time of flight neutron diffraction, and high temperature XRD. Néel temperatures were determined through vibrating sample magnetometry and correlated well with changes in thermal expansion behavior observed during both dilatometry and x-ray diffraction. Differences in changes of the observed Néel temperatures due to divalent substitution were shown to be related to a combination of charge compensating mechanisms and differences in the Fe-O-Fe bond angle associated with the superexchange interaction.

The stability of lanthanum calcium ferrites in reducing atmospheres were investigated through measured mass changes associated with decomposition of the material. The partial pressure of oxygen (P_{O_2}) was controlled by varying $\text{H}_2/\text{H}_2\text{O}$ ratios via pre-mixed gases and by bubbling hydrogen through water baths at controlled temperatures. Three regions of mass loss were identified, two of which were discovered to be associated discrete decompositions. Calcium substituted samples are shown to decrease the thermal stability of the compound; but rather than incrementally increasing

the required P_{O_2} for decomposition, substituted samples partially decompose at a single P_{O_2} , the extent of which was dependent on the amount of Ca substitution and the isothermal temperature. All samples were found to fully decompose at the same oxygen partial pressure (P_{O_2}) as pure lanthanum ferrite.

The oxidation and resulting atomic structure of the $LaCa_2Fe_3O_8$ compound, also known as the Grenier phase, was investigated before and after the order-disorder transformation (ODT). The Grenier compound was synthesized in air using traditional solid state reactions. Thermal analysis characterization shows that the material undergoes the order-disorder transformation in both oxygen and argon atmospheres with dynamic, temperature dependent, oxidation upon cooling. Results from scanning transmission electron microscope (STEM) images suggest that the Grenier phase has preferential segregation of Ca and La on the two crystallographic A-sites before the ODT, but a random distribution afterwards. Furthermore, STEM images suggest the possibility that oxygen excess may exist in La rich regions in microdomains rather than at microdomain boundaries as previously suggested.

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LIST OF ABBREVIATIONS

AFM	Antiferromagnetic
at%	Atomic Percent
CTE	Coefficient of Thermal Expansion
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive Spectroscopy
EELS	Electron Energy Loss Spectroscopy
HAADF	High Angle Annular Dark Field
LCF	Lanthanum Calcium Ferrite
LR1	Loss Region One
LR2	Loss Region Two
LR3	Loss Region Three
MFC	Mass Flow Controller
ND	Neutron Diffraction
ODT	Order-Disorder Transformation
O→R	Orthorhombic to Rhombohedral
P _{O₂}	Oxygen Partial Pressure

psi	Pounds per Square Inch
SEM	Scanning Electron Microscopy
SS	Stainless Steel
STEM	Scanning Transmission Electron Microscopy
SOFC	Solid Oxide Fuel Cell
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analyzer
T _N	Néel Temperature
VSM	Vibrating Sample Magnetometry
XRD	X-Ray Diffraction

CHAPTER ONE: INTRODUCTION

This dissertation is composed of four papers. The first two papers in Chapters Two and Three are published in the Journal of the American Ceramic Society. The papers in Chapters Four and Five have been submitted for publication in the Journal of the American Ceramic Society. The papers contained in this dissertation focus on the investigation of structure, phase transformations, expansion behavior, and the chemical stability in reducing atmospheres of materials in the lanthanum calcium ferrite (LCF) system.

In Chapter Two, the effect of calcium substitution in the lanthanum ferrite system has been investigated using thermal analysis, electron microscopy, and diffraction techniques. High temperature structural transformations have been identified and changes in thermal expansion behavior have been evaluated. Chapter Three compares the nonlinear thermal expansion behavior of divalent substituted lanthanum ferrite around the Néel temperature using magnetometry, diffraction, and dilatometry. Chapter Four investigates the decomposition behavior of calcium substituted lanthanum ferrites in reducing atmospheres using thermal analysis and diffraction techniques. In Chapter Five, high resolution scanning transmission electron microscopy (STEM) and thermal analysis techniques have been implemented to investigate high temperature phase transformations of the $\text{LaCa}_2\text{Fe}_3\text{O}_{8+y}$ Grenier compound.

A broad overview of the calcium substituted lanthanum ferrites is given in the following sections of this chapter.

1.1 Applications of Lanthanum Calcium Ferrite Materials

Lanthanum Calcium Ferrites (LCF) belongs to a class of materials known as mixed ionic and electronic conductors. Dense, non-porous, membranes synthesized out of LCF materials will spontaneously transport oxygen through the material with high flux and chemical selectivity when a chemical potential gradient is applied at temperatures in excess of 700°C.^{1,2} High temperature oxygen conducting membranes have a wide range of potential applications in commercial devices such as fuel cell cathodes, oxygen separation, and syngas production. Lanthanum calcium ferrite membranes have been specifically identified as a promising material for oxygen conducting membranes in syngas reactors, due to the combination of high oxygen flux rates and necessary chemical and mechanical stability in reducing atmospheres as discussed in the patent held by Air Products Inc (US 6,942,290).² The ability to reliably produce syngas in a cost effective manner benefits both the environment and economy. Much of the natural gas at remote oil extraction facilities around the world is combusted rather than collected due to the difficulties and costs associated with transportation of the fuel. The combustion of natural gas wastes resources and contributes to the accumulation of the carbon dioxide and pollution in the atmosphere. The utilization of syngas reactors, in conjunction with other chemical processing techniques to produce liquid products, will enable oil companies to monetize remote natural gas, while simultaneously reducing the carbon footprint of the industry. Liquid products produced from syngas can be easily transported by combining

them directly with the crude oil and using the existing transportation networks to deliver them to refineries where they can then be separated.

In addition to uses as oxygen conducting membranes, LCF materials have also been identified as a potential catalyst for the oxidation of volatile organic compounds and use as membranes for the oxidation of ammonia to nitric oxide.^{3–10}

1.2 Crystal Structures in the $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ System

A thorough understanding of the crystal structures found in the lanthanum calcium ferrite system is helpful to understand the structural phase transformations, oxygen vacancy ordering, and the formation of secondary phases discussed in this study. The variable composition of LCF materials is represented by the chemical formula $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$, where x indicates the fraction of calcium substitution and the parameter δ describes the degree of oxygen nonstoichiometry in the compound. The following gives a brief overview of the phases and crystal structures known to exist in $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ compounds.

1.2.1 The Perovskite Structure

Lanthanum ferrite (LaFeO_3) has the ABO_3 perovskite crystal structure with orthorhombic Pnma (Spacegroup #62) symmetry. The perovskite structure shown in Figure 1.1 has two cation sites, which will be referred to as A and B, and one anion site, which is nearly always occupied by oxygen, though some fluoride perovskites are known to exist. The A-site cations, typically occupied by rare earth and alkaline earth elements, are larger than the B-site cations, which are typically occupied by transition metals. In the ideal perovskite structure, the B-site cation is octahedrally coordinated to six oxygen

atoms and the A-site cation is coordinated to 12 oxygen anions, though this A-site coordination to oxygen may be reduced to 10 or even 8 in distorted perovskites.

Figure 1.1 Structural representation of the ideal cubic perovskite unit cell. The A-site cation is located in the center of the unit cell. The B-site cation is located at the center of the octahedra. The oxygen anions are located at the vertices of the octahedra and are shown in black.

1.2.1.1 Octahedral Tilting in Perovskites

Perovskites are able to accommodate a wide range of chemical substitution because the oxygen formed octahedra can cooperatively tilt to reduce changes in lattice energies due to cation size variances. The ability to vary composition allows for the control and tailoring of perovskite properties giving rise to numerous technological applications. The ideal perovskite structure is has a cubic unit cell with no cooperative

tilting of the octahedra producing tetrahedral bond angles of 180° in all directions. The cooperative tilting of the octahedra reduces the symmetry of the structure and (B-site)-O-(B-site) bond angles deviate from 180° . In 1972, Glazer demonstrated that only 23 possible space groups resulting from octahedral tilting are allowed by symmetry.¹¹ This number was later reduced to only 15 possible space groups based on group-theoretical analysis.¹² Glazer identified that the cooperative tilting resulted in two states of relative octahedral rotations along a stack of octahedra. First, an entire stack of octahedra can be rotated together in the same direction. This situation is referred to as in-phase tilting. The second situation, known as anti-phase tilting, occurs when octahedra are rotated in an alternating clockwise and counter clockwise fashion. Each of the 15 possible space groups in the perovskite system are described by the tilting behavior in three mutually orthogonal directions aligned along the pseudo-cubic [100] type directions where, by convention, in-phase tilting is designated by the + symbol and anti-phase tilting is designated by the - symbol. Figures 1.2 and 1.3 give schematic representations of in-phase and anti-phase tilting.

Figure 1.2 In-phase tilting rotations of octahedra. The spheres represent the locations of the A-site cations.

Figure 1.3 Anti-phase tilting rotations of octahedra. The spheres represent the locations of the A-site cations.

1.2.1.2 The Orthorhombic Unit Cell

The reduction to the Pnma orthorhombic symmetry with the $\mathbf{a}^+ \mathbf{b}^- \mathbf{b}^-$ tilt system requires that the unit cell be expanded. A diagram of the orthorhombic unit cell relative to

the ideal cubic perovskite unit cell is shown in Figure 1.4. It is often useful for ease of visualization and comparison to reduce measured perovskite lattice parameters in proportion to what is referred to as the pseudo-cubic unit cell with the single lattice parameter of $\mathbf{a}_{pc}$ containing only one formula unit of LaFeO_3 in the lanthanum ferrite system. The diagram in Fig. 1.1 shows that the Pnma orthorhombic unit cell is doubled axis ($\mathbf{b}=2\mathbf{a}_{pc}$) along the $\mathbf{b}$ -axis and the orthorhombic $\mathbf{a}$ and $\mathbf{c}$ lattice parameters run diagonally through the ideal cubic unit cell giving $\mathbf{a} \approx \mathbf{c} \approx \sqrt{2}\mathbf{a}_{pc}$. This results in an orthorhombic unit cell volume that is 4 times greater than the pseudo-cubic unit cell with 4 LaFeO_3 equivalents. The Pbnm setting commonly found in literature is equivalent to the Pnma setting where:

$$\mathbf{a}_{Pnma} = \mathbf{b}_{Pbnm} \qquad \mathbf{b}_{Pnma} = \mathbf{c}_{Pbnm} \qquad \mathbf{c}_{Pnma} = \mathbf{a}_{Pbnm}$$

The Pnma $\mathbf{a}$ and $\mathbf{c}$ lattice parameters are dimensionally very close but structurally unique and cannot be freely exchanged from refined diffraction data. If a material with the cubic structure was extended to the orthorhombic unit cell, then the $\mathbf{a}$ and $\mathbf{c}$ Pnma lattice parameters would indeed be equivalent. However, the octahedral tilting reduces the symmetry of the structure, resulting in different symmetry elements along each axis. The long form Herman-Mauguin notation for the orthorhombic structure is composed of 4 elements. The first element is the lattice descriptor that gives the centering element of the lattice. The next three symbols following the lattice descriptor are mirror planes, glide planes, and 2-fold rotation or screw axes. The first of the 3 symmetry elements following the lattice descriptor acts on the $[100]$, the second on the $[010]$, and the third on the $[001]$ axis of the unit cell. We can see from the short Herman-Mauguin notation for space group #62 Pnma (the long form is $P 2_1/n 2_1/m 2_1/a$) that the structure has a primitive

lattice (P) with a diagonal n-glide plane (n) perpendicular to the **a** axis, a mirror plane (m) perpendicular to the **b** axis (the doubled long axis of the perovskite), and an a-glide plane (a) perpendicular to the **c** axis with a glide component half of the lattice parameter **a**. Therefore, even though the **a** and **c** lattice parameters are similar in the LaFeO_3 Pnma structure (or **a** and **b** for Pbnm), the atom positions and distortion of the octahedral are not equivalent in the two directions. In Rietveld refinement, it is the atom positions that define the **a** and **c** lattice parameters.

Coordinate Transformation Cubic $\rightarrow$ Orthorhombic

Figure 1.4 Inset of the orthorhombic Pnma unit cell shown in black into 8 cubic unit cells shown in white.

1.2.1.3 The Rhombohedral Unit Cell

The $R\bar{3}C$ rhombohedral unit cell is described by one length lattice parameter and one angular lattice parameter. There is one LaFeO_3 equivalent in the rhombohedral unit cell in the lanthanum ferrite system with a unit cell volume one fourth that of the

orthorhombic structure. The $R\bar{3}C$ perovskite has the $a^- a^- a^-$ tilt system containing three anti-phase tilts.

1.2.2 The Grenier and Brownmillerite Structures

The Grenier ($\text{LaCa}_2\text{Fe}_3\text{O}_8$, $P2_1ma$) and brownmillerite ($\text{Ca}_2\text{Fe}_2\text{O}_5$, $Pbnm$) compounds are structurally similar to that of the perovskite structure.^{13, 14} The similarity between these structures will be covered only briefly here and the reader is directed to Chapter Two for a more detailed discussion. A schematic comparing the crystal structures is shown in Figure 2.1. The Grenier and brownmillerite phases may be considered derivatives of the perovskite structure with ordered oxygen vacancies in the pseudo-cubic [101] direction. The formation of ordered oxygen vacancies in these two phases results in what may be described as the effective collapse of octahedra (FeO_6) into tetrahedra (FeO_4). The difference between the three structures is therefore reflected in the stacking sequence, or corner sharing of the octahedra and tetrahedra (T) given as follows: OO (perovskite), OOT (Grenier), and OTOT' (brownmillerite). The similarity of these crystal structures allow for the seamless stacking of layers of octahedra on top of tetrahedra, resulting in intergrowth structures first identified by other investigations and seen in scanning transmission electron microscopy images in this study as shown in Figures 1.5 and 1.6.¹⁵⁻¹⁷

Figure 1.5 STEM image of the intergrowth of the perovskite (P) and Grenier (G) phases in a sample prepared with 60% Ca substitution.

Figure 1.5 High resolution STEM image of the intergrowth of the perovskite (P) and Grenier (G) phases in a sample prepared with 60% Ca substitution.

1.3 A-site Calcium Substitution

Oxygen is conducted through dense ceramic membranes by hopping to vacant oxygen lattice positions. Pure lanthanum ferrite is not considered to be a good oxygen conductor because it contains a relatively low numbers of oxygen vacancies. One strategy to increase oxygen flux is to increase the number oxygen vacancies via the substitution of divalent cations on the trivalent lanthanum site. This creates a charge imbalance, which is compensated by the formation of additional oxygen vacancies. The alkaline earth elements Ca, Sr, and Ba are commonly used as dopants for this purpose. In addition to charge compensation via the formation of oxygen vacancies, the valence state of iron

may also be converted from Fe^{3+} to Fe^{4+} in iron containing perovskites. Both of these charge compensating mechanisms are observed in the LCF system, the extent of which is dependent on the thermal and environmental conditions. The Shannon ionic radii of the Ca^{2+} cation is 1.34 Å, which is < 3% smaller than the La^{3+} cation (1.36 Å). However, the conversion of Fe^{3+} (0.645 Å) to Fe^{4+} (0.585 Å) results in a volume change of roughly 18%.

Calcium forms a solid solution in the perovskite structure with variable composition. In contrast, the Grenier and brownmillerite structures have not been shown to display any appreciable compositional variation and therefore exist as line compounds on the phase diagram. Increasing the calcium concentration in the perovskite phase will increase the population of oxygen vacancies and tetravalent iron resulting in an increase in oxygen flux through the material. A threshold exists after which further calcium substitution will no longer increase flux rates due to the formation of ordered oxygen vacancies, which is essentially the localized formation of tetrahedra found in the Grenier and brownmillerite structures. The composition at which the ordering of oxygen vacancies occurs is not fixed and is dependent on the temperature and oxygen partial pressure the material is exposed to. When enough calcium is added to the system, macroscopic secondary phases will be visible in scanning electron microscope imaging.

1.5 Order-Disorder Transformation and Microdomains

Previous investigations have demonstrated that the $\text{LaCa}_2\text{Fe}_3\text{O}_{8+y}$ Grenier compound undergoes a phase transformation at high temperatures, which appears to be cubic by x-ray diffraction. Originally, this was thought to be attributed to the disordering of oxygen vacancies forming a perovskite at high temperatures. However, transmission

electron microscopy of quenched samples revealed a complicated morphology of ordered oxygen vacancies on the nanoscale, which were referred to as microdomains.¹⁸ The discussion in Chapter Five has revisited this topic using modern electron imaging techniques.

1.6 Ordered Oxygen Vacancies and the Limits of Diffraction

The overall goal of this research was to characterize the phase stability and transformations in the $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ system with a particular focus on compositions with potential applications as oxygen conducting membranes. The formation of small domains of ordered oxygen vacancies decrease the oxygen flux in these membranes and can lead to the spontaneous formation of the Grenier and brownmillerite compounds in oxygen deficient atmospheres. Under reducing conditions, these localized formations of secondary phase will decompose at substantially higher oxygen partial pressures than LCF compounds where the oxygen vacancies remain largely disordered. The decomposition behavior of LCF materials is the primary focus of the investigation presented in Chapter Four.

Diffraction is routinely used to characterize the structure and phase purity of materials. However, diffraction techniques have two major limitations when characterizing the LCF system. First, small concentrations of secondary phases are not detectable using XRD due to the similarity of phases. This results in the overlapping of many of the diffracted intensities. In addition, LCF perovskites have higher intensity peaks than ordered oxygen vacancy structures due to differences in structure factors. Second, microdomain texture and small domains of ordered oxygen vacancies cannot be detected using diffraction because the coherent scattering domain of these features is

outside the resolving power of x-ray or neutron diffraction, regardless of the concentration present in the sample. The use of diffraction to characterize compounds in the LCF system needs to be approached with great care. Investigators need to understand the limitations of the technique, and the results need to be verified by other means. Lanthanum calcium ferrites heated above 1300°C may have a microdomain texture that is not detectable with diffraction techniques, possibly leading to incorrect conclusions about the solubility of calcium and phase purity.

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CHAPTER TWO: PHASE TRANSFORMATIONS IN CALCIUM SUBSTITUTED LANTHANUM FERRITE*

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Phase Transformations in Calcium Substituted Lanthanum Ferrite

Patrick M. Price¹

Ellen Rabenberg¹

David Thomsen¹

Scott T. Misture³

Darryl P. Butt^{1, 2, *}

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¹*Department of Materials Science & Engineering, Boise State University
1910 University Dr., Boise, ID 83725*

²*Center for Advanced Energy Studies,
995 University Boulevard, Idaho Falls, ID 83401*

³*Kazuo Inamori School of Engineering,
1 Saxon Drive, Alfred University, Alfred, NY 14802*

Abstract

Phase equilibria in the $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ (LCF) system were assessed at temperatures below 1350°C in both simulated air and argon atmospheres using a combination of differential scanning calorimetry, thermogravimetric analysis, scanning electron microscopy, and high temperature x-ray diffraction. The solubility limit of Ca in the perovskite structure was determined to be 38% A-site substitution. A high temperature orthorhombic to rhombohedral transition was identified and the dependence on oxygen partial pressure and effect on thermal expansion was characterized. A partial, pseudo-binary LaFeO_3 - $\text{CaFeO}_{2.5}$ phase diagram is presented that is based on these analyses combined with data available in the open literature.

2.1 Introduction

Increases in world energy demands cannot be met by traditional fossil fuel consumption alone. Therefore, there is a strong motivation to develop new technologies that can sustainably supplement world energy requirements. One such technology is the utilization of ion conducting ceramic oxide membranes for use in high temperature electrochemical devices for energy conversion such as the solid oxide fuel cell (SOFC), the conversion of natural gas into synthesis gas (syngas), oxidation of other hydrocarbons, hydrogen and oxygen production, and hybrid energy systems.¹⁻⁵ Materials belonging to the perovskite family have been shown to be suitable candidates as oxygen transport membranes because of the combination of excellent high temperature thermal and chemical stability, high oxygen flux rates, and the ability to conduct electrons. One such example of these materials is calcium doped lanthanum ferrites ($\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$), which will be referred to as LCF.⁶

LCF materials are mixed ion conductors (MIC) with excellent thermal, chemical, and mechanical stability under reducing conditions, making them suitable candidates for the applications listed above.⁷⁻¹⁰ However, a better understanding of the phase stability and structure of these materials is needed in order to optimize the performance and reliability of LCF-based devices in commercial applications.

Three distinct crystal stacking sequences exist in the LCF system: ABO_3 (perovskite), $\text{A}'\text{A}_2\text{B}_3\text{O}_8$ (Grenier), and $\text{A}'_2\text{B}_2\text{O}_5$ (brownmillerite). However, these three crystal structures are subtle variations of one another. The Grenier and brownmillerite phases may be considered derivatives of the perovskite structure with ordered oxygen vacancies in the pseudo-cubic [110] direction. The formation of ordered oxygen vacancies in these two phases results in what may be described as the effective collapse of octahedra (BO_6) into tetrahedra (BO_4). The difference between the three structures (Figure 2.1) is therefore reflected in the stacking sequence or corner sharing of the octahedra and tetrahedra (T) given as follows: OOOO (perovskite), OOTOOT (Grenier), and OTOT'OTOT' (brownmillerite). Nearly identical planes of corner sharing octahedra are common to all three crystal structures. This similarity allows the seamless stacking of multiple crystal structures, known as intergrowths, by sharing of planes of octahedra. Such intergrowth structures were first observed nearly 30 years ago by several research groups using high resolution transmission electron microscopy.¹¹⁻¹³

Pure lanthanum ferrite (LaFeO_3) has the orthorhombic, Pbnm , ABO_3 perovskite structure.¹⁴ When calcium is substituted into lanthanum ferrite, a solid solution is formed with Ca^{2+} (1.34 Å) on the La^{3+} (1.36 Å) A-site. In addition to the small difference in ionic radii, the difference in valence results in a charge imbalance on the A-site. As a result,

Figure 2.1 Relationship between the orthorhombic perovskite, Grenier, and brownmillerite crystal structures. The red squares represent a line of ordered oxygen vacancies.

there are two probable charge compensating mechanisms.¹⁵ First, one oxygen vacancy may form for every two calcium ions added. Second, the valence state of iron may change from Fe^{3+} to Fe^{4+} . The extent to which each of these compensation mechanisms occurs has been shown to be affected by the thermal history and partial pressure of oxygen during synthesis of the material. When synthesized under extremely high partial pressures of oxygen, it is possible to synthesize a CaFeO_3 perovskite where charge is compensated almost entirely by the formation of tetravalent iron.^{16, 17} Conversely, synthesizing samples under reducing conditions ($P_{\text{O}_2} \leq 10^{-6}$ atm) will result in charge compensation primarily by the formation of oxygen vacancies as determined by Mossbauer spectroscopy.¹⁸ Previous studies have reported the simultaneous existence of both oxygen vacancies and tetravalent iron in LCF samples treated in air.^{19, 20} It has also been observed that Fe^{4+} will disproportionate into a mixture of Fe^{3+} and Fe^{5+} at sufficiently low cryogenic temperatures.²¹ This research is focused on temperatures well

above those where charge disproportionation has been observed, therefore, we do not consider this potential mechanism in this study. The solid solubility limit of Ca is reached when oxygen vacancies order in a common plane, forming intergrowths of the perovskite and the Grenier phases.

The Grenier phase ($\text{LaCa}_2\text{Fe}_3\text{O}_8$) has the orthorhombic, $P2_1ma$ structure and the brownmillerite phase ($\text{Ca}_2\text{Fe}_2\text{O}_5$) has the orthorhombic $Pbnm$ structure.^{22, 23} The Grenier phase has not been shown to accept any significant non-stoichiometry. Multiple phases and intergrowths are found in samples having compositions between the solid solubility limit of Ca and that of the Grenier phase, and compositions intermediate between the Grenier and brownmillerite phases.

Multiple research groups have characterized the properties and performance of LCF materials, but there has been limited focus on these subtle structural transformations, which are difficult to observe experimentally. In addition, there is a wide range of processing routes used to synthesize LCF, which have led to different interpretations in the structure and composition of the resulting material. A preliminary pseudo-ternary diagram of the LCF system has been published, but only for compositions quenched from 1100°C.²⁴ Consequently, the diagram does not address the possibility of equilibrium high temperature structures such as those found in strontium substituted lanthanum ferrite.²⁵ There is a need to develop a comprehensive phase diagram of the LCF system using in-situ high temperature measurements under controlled atmospheric conditions. The focus of this research is to begin this process.

In this study, we synthesized LCF materials using solid-state synthesis techniques followed by characterization with differential scanning calorimetry (DSC),

thermogravimetric analysis (TGA), high temperature x-ray diffraction (HTXRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). We have determined the solubility limit of Ca in the lanthanum ferrite structure in samples synthesized in air using Rietveld refinement of XRD patterns. We have identified a reversible orthorhombic to rhombohedral (O→R) phase transition at elevated temperatures and shown the dependency on calcium composition and oxygen partial pressure. A volume reduction and change in the thermal expansion coefficient is associated with the O→R transition.

2.2 Experimental Procedures

Lanthanum calcium ferrite samples were synthesized using solid-state chemical decomposition reactions. Stoichiometric portions of calcium carbonate (Puritronic® CaCO₃, 99.99% pure metals basis), iron (III) oxide (Fe₂O₃, 99.995% pure), and lanthanum (III) oxide (Reacton® La₂O₃ 99.999%) were combined to achieve desired compositions from pure LaFeO₃ to La_{0.5}Ca_{0.5}FeO₃. Batch sizes were at least 30 g to ensure a molar variance no greater than ±0.00005 moles during the weighing process based on scale accuracy and precision accessed with a standard. Lanthanum oxide is hygroscopic and reacts with moisture in the air to form La(OH)₃.²⁶ The moisture content of each precursor powders was determined and corrected for by loss on ignition (LOI) measurements via thermogravimetric analysis (Netsch STA-449, Burlington, MA 01803) prior to mixing each batch. Precursor powders were mixed with yttria-stabilized zirconia ball mill media and isopropyl alcohol (IPA) in nylon jars for 12 hours on a table top mixer, and subsequently calcined at 1000°C for 8 hours in a box furnace. The calcined powders formed a cake-like compact, which was crushed and then mixed as described above for

an additional 10 hours. The calcined mixture was dried and isostatically pressed into green pellets. The pellets were sintered in air at 1100°C for 6 hours to complete the solid-state reaction process and then increased to either 1250°C or 1300°C for 24 hours.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to investigate the sintering and reaction behavior of the sintered precursor powders. Sintered pellets were ground and polished with silicon carbide paper with final polishing performed using 1200 grit paper. The polished pellets were thermally etched for 45 minutes in air using a tube furnace, which was preheated to 1100°C. Images of the etched surfaces were obtained by SEM (Hitachi model S4500 FESEM, Schaumburg, Illinois and a Leo model 1430VP SEM, Thornwood, NY). The latter was equipped with an energy dispersive x-ray (EDS) detector (Oxford Instruments) using the Link ISIS software package for EDS data analysis.

The orthorhombic (Pbnm) structure of synthesized samples was verified using x-ray diffractometer (Bruker AXS D8, Madison, WI) with parallel beam geometry at room temperature. Phase transitions and expansion behavior were characterized with high-temperature XRD (HT-XRD) on a Siemens D5000 (Siemens, Karlsruhe, Germany) with Bragg Brentano geometry.²⁷ Diffraction data were analyzed with the Rietveld method using the General Structure Analysis System (GSAS), EXPGUI graphical user interface, and an automated scripting language developed by Vogel and co-workers.²⁸⁻³⁰

Simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis were used to investigate the thermal stability of lanthanum calcium ferrites in oxygen and oxygen deficient atmospheres. All experiments were performed in a Netzsch STA-449 equipped with a simultaneous DSC-TG carrier, graphite furnace, alumina

protective tube, and 85 μ l platinum rhodium (Pt/Rh) crucibles with lids. Temperature calibrations were performed via the melting of 5 pure metals. Correction files with empty crucibles were obtained prior to all DSC-TGA experiments in order to remove background and noise from the sample signal. The Pt/Rh crucible and lid containing the powders sample was placed on the DSC-TGA carrier along with an empty Pt/Rh crucible and lid used as a reference. All samples were ramped at 10° C/min with flow rate of 50 ml/min. Premixed 20% O₂–Ar gas to simulate air or high purity argon (99.999%) were used for all experiments.

2.3 Results and Discussion

Initial x-ray diffraction patterns of the synthesized samples collected using parallel beam geometry and an area detector are shown in Figure 2.2. From these data, the perovskite structure appears to persist up to 50% calcium substitution on the A-site (La_{0.5}Ca_{0.5}FeO₃). Specimens with calcium substitutions of 60-90% have diffraction patterns consistent with mixtures of perovskite and Grenier phases (60%) or mixtures of Grenier and brownmillerite phases (70-90%). The 100% Ca-substituted sample has a diffraction pattern consistent with the Ca₂Fe₂O₅ brownmillerite structure. The orthorhombic superlattice reflections are strongest in the LaFeO₃ diffraction pattern, reduce in intensity with calcium substitution, and disappear in the La_{0.5}Ca_{0.5}FeO₃ specimen. X-ray reflections are shifted to a higher angle with increasing calcium substitution suggesting a contraction of the unit cell, which is consistent with the findings in previous investigations of the LCF system.^{10, 20, 31-36} The diffraction pattern of the

Figure 2.2 XRD patterns collected using an area detector with parallel beam geometry. The area detector does not have the sensitivity to detect a secondary phase in compositions with 0-50% Ca on the A-site. Perovskite and Grenier peaks are observed in samples containing 60% Ca. Grenier and brownmillerite peaks are present in samples containing 70-90% Ca.

Figure 2.3 X-ray reflections from $\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_{3-\delta}$ using parallel beam geometry and a scintillation detector. The diffraction pattern is consistent with the orthorhombic (Pbnm) perovskite structure and agrees well with the indexed peaks from Taguchi *et al.*²⁰

$\text{La}_{0.8}\text{Ca}_{0.2}\text{FeO}_3$ specimen, shown in Figure 2.3, was collected with parallel beam geometry and a scintillation detector and is consistent with the indexed structure reported by Taguchi *et al.*,²⁰ also shown in Figure 2.3 for comparison. In addition, the diffraction patterns of LaFeO_3 and $\text{La}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$ match well with the indexed patterns reported for these compositions.²⁰ The diffraction patterns for compositions for $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ ($x = 0.3, 0.4, 0.5$) appear to have the perovskite structure similar to that reported by other authors.^{19, 31, 36}

The SEM micrographs in Figure 2.4 show the microstructure of synthesized, polished, and thermally etched LCF samples. The final composition, analyzed by EDS, was within 10% of expected stoichiometry with a maximum standard deviation of less than 0.5 at% for calcium doping up to 30% Ca on the A-site. The mean composition of the 40% Ca doped sample was 35% Ca with a maximum standard deviation of 4 at%. Grain growth is significantly reduced in the 10, 20, and 30% Ca-substituted specimens. The observed grain size in the 10-30% Ca samples increases slightly with increasing Ca substitution as shown in the inset of Figure 2.5. A significant increase in grain growth was observed in the 40% Ca-substituted sample. The etched surface appears to have pitted morphology, and an elongated columnar secondary phase is distributed sparsely throughout the surface. Additionally, EDS analysis revealed a standard deviation of less than 1 atomic percent (at%) in specimens with Ca substitution up to 30%, indicating homogenous mixing. The standard deviation increased to nearly 2 at% the 40% specimen, indicating a decrease in homogeneity. By 50% Ca substitution, the secondary phase is ubiquitous throughout the surface. Similar results were observed by Hung *et al.*³¹ in that

Figure 2.4 Secondary electron images of samples sintered at 1250°C, polished, and thermally annealed at 1100°C in air. Smaller grain sizes were observed in the samples containing Ca versus pure LaFeO₃. Secondary phases are visible in the La_{0.6}Ca_{0.4}FeO_{3-δ} and La_{0.5}Ca_{0.5}FeO_{3-δ} samples.

Figure 2.5 Grain area distribution for LCF specimens sintered at 1250°C obtained from image analysis of thermally etched specimens. The box plots show the mean (solid square), median (line), the 25th and 75th percentiles bounded by the box, and minimum and maximum outliers.

the observed diffraction patterns were consistent with the perovskite structure but SEM images revealed the formation of secondary phases that were not immediately evident in the XRD data.

The apparent contradiction between diffraction patterns indicating a phase pure perovskite and SEM images indicating multiple phases requires further explanation. Previous investigations have revealed that the $\text{LaCa}_2\text{Fe}_3\text{O}_8$ Grenier structure is a line compound and therefore exhibits negligible solid solubility, and will tend to phase separate or form intergrowth structures.³⁷ In contrast, calcium substitution in the perovskite phase results in a solid solution where Ca substitutes for La on the A-site. Consequently, as indicated by the SEM observations, there is a composition somewhere between that of the single phase Ca-substituted perovskite and $\text{LaCa}_2\text{Fe}_3\text{O}_8$, where a two phase region must exist. Calculated GSAS x-ray diffraction patterns for $\text{La}_{0.6}\text{Ca}_{0.4}\text{FeO}_3$, $\text{LaCa}_2\text{Fe}_3\text{O}_8$, and $\text{Ca}_2\text{Fe}_2\text{O}_5$ shown in Figure 2.6 may be used to elucidate the absence of obvious impurity peaks in the experimental diffraction patterns. The simulation was configured with equal amounts of each phase. Due to the structural similarity discussed above, the strongest reflections of the perovskite phase are convoluted with the strongest reflections of the Grenier phase. Furthermore, the intensities of perovskite reflections are approximately 2.5 times greater than those of the Grenier phase. From these simulations, it becomes clear the Grenier phase will not be observable in diffraction patterns unless there is both enough material present to provide sufficient intensity and the diffractometer or refinement technique has sufficient resolution to deconvolute the patterns.

Figure 2.6 Simulated diffraction patterns (GSAS) with equal phase fractions for the perovskite, Grenier, and brownmillerite phases. The perovskite phase has a nearly 250% stronger peak intensity compared to the Grenier and brownmillerite patterns.

Figure 2.7 X-ray diffraction pattern of $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$. Rietveld refinement was used to quantify the fraction of the Grenier and perovskite phases. Based on the phase fractions, the solubility limit of Ca in the perovskite structure is approximately 38% or $\text{La}_{0.62}\text{Ca}_{0.38}\text{FeO}_{3-\delta}$.

Figure 2.8 Comparison between orthorhombic lattice parameters fit by Rietveld refinement or single peak analyses. Diffraction patterns fit with multiphase Rietveld refinement correctly display the expected discontinuity in the lattice parameters near the solid solubility limit.³¹

The Grenier phase observed in the SEM images of the 40% Ca substituted sample was not present in the diffraction pattern due a combination of low concentrations and low reflection intensity from the vacancy ordered phase as shown in the simulated XRD patterns shown in Figure 2.6. The SEM images in Figure 2.4 show large amounts of secondary phases in the $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$ sample, but no extra peaks are present in the diffraction pattern shown in Figure 2.2 due to the convolution of the peaks as shown in simulated data (Figure 2.6). The intensity differences and convolution of perovskite reflections with that of secondary phases make it difficult to access phase purity purely from XRD data and may lead to the misidentification of solid solubility of Ca in the perovskite structure. Increased resolution is needed for quantitative analysis such as that provided by a monochromatic parallel beam instrument.

The diffraction pattern of $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$ is shown in Figure 2.7, which was collected on a monochromatic parallel beam Bruker D8 with a scintillation detector for maximum resolution. The perovskite and Grenier peaks are clearly evident in this XRD scan. The solid solubility of Ca in the perovskite structure is 38% based on the calculated phase fractions from multiphase Rietveld refinement using the GSAS program. As discussed above, single peak fits from our diffraction data and the data reported by Hung *et al.*³¹ suggest that the lattice parameters decrease linearly for all compositions shown in Figure 2.8, including $\text{La}_{0.5}\text{Ca}_{0.5}\text{FeO}_3$. Because the unit cell contraction is due to Ca substitution, these results would suggest that the Ca solubility persisted up to 50%. However, this conclusion is incorrect as highlighted by the SEM observations. The apparent decrease in the lattice parameter is due to the shifting of the centroid of the reflection (shown in Figure 2.7) due to the convolution of reflections from the perovskite and Grenier phases. This convoluted peak is actually formed from the superposition of eight unique reflections (three perovskite, five Grenier) each with a unique d-spacing. This demonstrates that single peak fits do not accurately reflect the true LCF orthorhombic lattice parameters, especially when secondary phases are present. In Figure 2.8, the lattice parameters determined by Rietveld refinement are compared to those obtained by single peak fits. Lattice parameters derived from the Rietveld method correctly show that the contraction of the unit cell does not persist past the solubility limit Ca. X-ray diffraction has been the most common method of accessing the phase purity and structure of LCF in literature. The data reported here show that additional characterization and refinement techniques are needed to properly access the LCF system

Figure 2.9 DSC data from $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ ($x = 0.1, 0.2, 0.3$, and 0.4) in 20% O_2 -80%Ar (solid lines) and pure, UHP Ar (line + triangle) atmospheres. Peaks in the DSC curves indicate O→R phase transitions in the temperature range 543 to 1004°C. The DSC data suggests that increases in Ca concentration and decreases in oxygen partial pressure reduce the O→R phase transition temperature. Additionally larger Ca concentrations resulted in larger differences between the phase transition temperatures observed in air and argon atmospheres.

Figure 2.10 HTXRD reflections of the 100% peak in (a) LaFeO_3 and (b) $\text{La}_{0.7}\text{Ca}_{0.3}\text{FeO}_{3-\delta}$. The reflections are shifted horizontally to increase visibility. The peak splitting and reduction in intensity after the orthorhombic to rhombohedral phase transition is evident in the LaFeO_3 specimen. The peak splitting is less evident in the 30% Ca substituted sample, but the reduction in intensity is still observed.

due to the structural similarity and relative scattering strength of the perovskite, Grenier, and brownmillerite phases.

The differential scanning calorimetry data for synthesized LCF samples are shown in Figure 2.9. Previous authors have shown the orthorhombic (Pbnm) to rhombohedral (R-3c) (O→R) structural phase transition occurs at 1004°C in pure LaFeO₃.²⁵ The onset temperature of the O→R transition in LaFeO₃ was found to be 1000°C in this study, which is in good agreement with the previously published value. The structural transition was confirmed by high temperature XRD data as shown in Figure 2.10. This figure shows that the orthorhombic peaks persist to the transition temperature measured by DSC. An obvious broadening and sharp drop in intensity of the 100% orthorhombic (200), (121), and (002) peak is noticeable after this structural transition. Diffraction patterns collected above the transition temperature were consistent with the rhombohedral (R-3c) structure by Rietveld refinement as indicated by the formation of the 100% rhombohedral (110) and (104) reflections shown in Figure 2.10.

The endothermic peaks of the calcium substituted samples in Figure 2.9 also suggest a first order structural orthorhombic to rhombohedral phase transition. The O→R phase transition temperature is reduced with increasing Ca content. Lowering the partial pressure of oxygen (P_{O_2}) was also shown to reduce the temperature of this phase transformation. The O→R phase transition temperature was only decreased by a few degrees for LaFeO₃ in 100% Ar. However, in Ca-substituted samples, a larger difference was observed in the O→R phase transition temperature in oxidizing and argon atmospheres, reaching approximately a 60°C reduction in the transition temperature of the 40% substituted sample. The thermal energy associated with the O→R phase

transition appears to be lowered in Ca-substituted samples as indicated by the smaller endothermic peaks in Figure 2.9. The structure of the rhombohedral phase above the O→R transition was confirmed by HTXRD. The splitting of reflections after the O→R transition in Ca-substituted samples is not as obvious as in the LaFeO_3 diffraction pattern. However, the sharp reduction in intensity and peak broadening is still visible as shown in Figure 2.10(b) for the 30% Ca sample.

As the temperature is increased above the O→R transition temperature, the symmetry increases as indicated by a reduction peak splitting caused by the rhombohedral distortions until a second order rhombohedral to cubic transition is observed. The cubic structure was confirmed by HTXRD in the $\text{La}_{0.6}\text{Ca}_{0.4}\text{FeO}_3$ at 1100°C.

Refined lattice parameters from the HTXRD data are shown in Figures 2.11 and 2.12. Figure 2.11 shows a typical example of the anisotropic thermal expansion for each lattice parameter. Figure 12 shows the volume expansion for each composition above and below the O→R transition temperature. The thermal expansion coefficient increases above the O→R transition temperature. The mismatch in thermal expansion coefficients above the O→R transition increases with increasing calcium substitution resulting in a 78% increase in the $\text{La}_{0.6}\text{Ca}_{0.4}\text{FeO}_3$ specimen.

In addition to solubility limits, intergrowth formation, and secondary phases in the LCF system, we also need to consider the possibility of an order-disorder (O-D) transition of the Grenier phase and associated microdomain formation. Grenier *et al.*³⁸ reported an order-disorder transition of oxygen vacancies in $\text{LaCa}_2\text{Fe}_3\text{O}_8$. which they

Figure 2.11 Expansion behavior of individual lattice parameters in the 30% Ca.

Figure 2.12 Unit cell volumes for LCF samples calculated from HTXRD data. The percent Ca concentration on the A-site is indicated on the top left corners. A rough estimate of the linear thermal expansion coefficient ($\alpha \times 10^6 \text{ K}^{-1}$) derived from linear regression is given in each plot for comparison. The rate of thermal expansion increases after the O→R phase transition. Increasing the Ca concentration exaggerates differences in thermal expansion between the orthorhombic and rhombohedral phases. A first order phase transition to the cubic structure is also shown for the 40% Ca sample at approximately 1100°C.

observed after quenching samples heat treated in air from 1400°C. However, the O-D phase transition temperature was not reported. The DSC data in Figure 2.13 suggest that this O-D transition occurs at approximately 1320°C. Furthermore, the thermogravimetric data show a weight gain at the O-D transition temperature for samples heated in air. The gain in oxygen is rapid and the material continues to gain oxygen as it is cooled, resulting in a final mass that is greater than the initial mass. This observed mass change is consistent with weight gains found in quenched samples by Grenier. The order disorder transition also occurs in the oxygen deficient, pure Ar atmosphere as indicated by the endothermic peak in Figure 2.13. On cooling, samples exposed to argon exhibited a greater exothermic energy associated with the reversal back to the original structure compared to samples run in air. This is not surprising since samples cooled in oxidizing conditions do not completely revert back to the low temperature structure but rather form microdomains as found by Alario-Franco and Grenier.^{12, 37, 38}

Based on the above discussion one would expect the synthesis temperature to play a role in determining the low temperature crystal structure(s) of LCF materials. The P_{O_2} will affect the relative fractions of tetravalent iron and oxygen vacancies, and will therefore influence the solubility limit of Ca in the perovskite structure. If the synthesis temperature used during conventional solid-state reactions is relatively low, for example <1100°C, the precursor powders will not fully react and grain growth will be slow. However, if LCF materials are processed at high temperatures in air to ensure full reactions above the order-disorder transition, microdomain formation is possible. Furthermore, microdomains appear to be perovskite by diffraction due to their small

Figure 2.13 (a) DSC data of the Grenier phase in both air and argon atmospheres. The energy associated with the endothermic order-disorder reaction can be seen at 1320°C. (b) Simultaneous thermogravimetric data showing a small weight gain in air due to the absorption of oxygen at the phase transition. The sample continues to gain weight or absorb oxygen as the sample is cooled.

Figure 2.14 A proposed pseudo-binary phase diagram of the LCF system. The solid lines represent phase boundaries measured in air and the horizontal dashed lines represent boundaries measured in argon atmosphere.^{22, 38-40}

domain size making them only detectable by HRTEM. Therefore, samples synthesized in air should be processed at temperatures below 1300°C to avoid microdomain formation.

A summary of the work reported here, as well as data collected from literature, is shown in a pseudo-binary phase diagram in Figure 2.14. The O→R structural transition and an antiferromagnetic to paramagnetic transition are shown for oxidizing (solid lines) and oxygen deficient (dashed lines) atmospheres.^{18, 21} The solubility limit of Ca in the perovskite structure was only measured for samples synthesized in air, but it is expected that the limit would be reduced in oxygen deficient atmospheres due to the increasing concentration of oxygen vacancies resulting in vacancy ordering. The order-disorder transition temperature was only slightly dependent on the concentration of oxygen in the environment.

2.4 Conclusions

Calcium doped lanthanum ferrites were synthesized by solid state reactions. The Grenier phase ($\text{LaCa}_2\text{Fe}_3\text{O}_8$) was found to undergo an order-disorder transition at 1320°C. As previously reported by Grenier *et al.*, LCF materials cooled in air after exceeding the order disorder transition temperature have a complicated microdomain structure, which falsely appear to be cubic perovskite by diffraction methods. For this reason, the LCF specimens in this study were synthesized well below 1320°C.

Rietveld refinement of XRD data indicates the solubility limit of calcium in the perovskite structure is 38% in samples synthesized by solid state reactions in air at 1250°C. Grain sizes were substantially decreased in 10, 20, and 30% Ca substituted samples. A large increase in grain size was observed in the 40% sample, possibly indicating small amounts of secondary phases or intergrowths may enhance grain growth.

Calcium doped lanthanum ferrites undergo an orthorhombic to rhombohedral transition at elevated temperatures which is first order in nature. The O→R transition temperature decreases with increasing calcium concentration and decreasing partial pressure of oxygen. Increasing the temperature further will result in a second order transition to the cubic structure which was observed in the $\text{La}_{0.6}\text{Ca}_{0.4}\text{FeO}_{3-\delta}$ specimen. The coefficient of thermal expansion is increased after the phase transition for all compositions. The increase in expansion coefficients after the O→R transition is increased with larger calcium concentrations.

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2.6 Author Justification

The research presented in this publication was carried out and authored by Patrick Price as a partial fulfillment of the requirements for a Doctoral degree in Materials Science and Engineering at Boise State University, under the advisement and supervision of Dr. Darryl P. Butt. Ellen Rabenberg assisted with sample synthesis and Dr. Scott Misture and David Thomsen assisted with the collection of high temperature x-ray diffraction data. Dr. Darryl P. Butt contributed greatly with financial support and

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CHAPTER THREE: THERMAL EXPANSION OF ALKALINE-DOPED
LANTHANUM FERRITE NEAR THE NÉEL TEMPERATURE*

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Thermal Expansion of Alkaline-Doped Lanthanum Ferrite Near the Néel Temperature^{*}G.L. Beausoleil II¹Patrick M. Price¹David Thomsen¹Alex Punnoose²Rick Ubic^{1,3}Scott T. Misture⁴Darryl P. Butt^{1,3}

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¹*Department of Materials Science & Engineering and* ²*Department of Physics, Boise State University, 1910 University Dr., Boise, ID 83725*

³*Center for Advanced Energy Studies,
995 University Boulevard, Idaho Falls, ID 83401*

⁴*Kazuo Inamori School of Engineering,
1 Saxon Drive, Alfred University, Alfred, NY 14802*

Abstract

The thermal expansion and magnetic behaviors of divalent, alkaline-doped lanthanum ferrites ($\text{La}_{0.9}\text{M}_{0.1}\text{FeO}_3$, $\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) were assessed using a combination of dilatometry, magnetometry, time of flight neutron diffraction, and high temperature x-ray diffraction. These materials are candidate materials for syngas membranes and the thermal expansion properties need to be well understood. Néel temperatures were determined through vibrating sample magnetometry and correlated well with changes in thermal expansion behavior observed during both dilatometry and x-ray diffraction. The Néel temperatures observed for pure, Ca-doped, Sr-doped, and Ba-doped lanthanum ferrites were 471, 351, 465, and 466°C, respectively. The effects of divalent substitutions on the magnetic behavior were attributed to charge compensation mechanisms and structural changes in the material.

3.1 Introduction

Divalent cation-doped lanthanum ferrite materials ($\text{La}^{3+}_{1-x}\text{M}^{2+}_x\text{FeO}_{3-\delta}$) exhibit a variety of useful properties including multi-ionic conductivity and multi-ferroic behavior.¹ These materials have been suggested as candidates for high temperature electrochemical devices such as oxygen conducting membranes for use in synthesis gas (syngas) or oxygen production, solid oxide fuel cell cathodes, and as catalysts for the oxidation of hydrocarbons.^{2,3} Consequently, it is important to understand structural and magnetic phase transformations that may occur at elevated temperatures in order to optimize the performance and reliability of commercial devices.

Lanthanum ferrite (LaFeO_3 , LF) is an orthorhombic (Pbnm) perovskite with a canted, G-type anti-ferromagnetic (AFM) structure. It undergoes a transition to a

paramagnetic state above the Néel temperature ($T_N \approx 477^\circ\text{C}$).⁴ The AFM behavior in LF is caused by magnetostatic coupling resulting in a super-exchange interaction between iron ions through adjoining oxygen atoms (Fe-O-Fe). Previous studies have shown a correlation between anti-ferromagnetic behavior, the Néel temperature, and thermal expansion in various perovskite systems.⁵⁻⁸ Selbach *et al.*⁹ demonstrated the existence of magnetic contributions to thermal expansion behavior in LF. Their results show that the Néel temperature can be observed indirectly through thermal expansion measurements due to non-linear thermal expansion caused by magnetoelastic coupling and thermally induced spin excitations that increase the Pauli repulsion.⁹⁻¹¹

Despite their technological relevance, magnetic contributions to thermal expansion behavior of divalent substituted lanthanum ferrites have not yet been reported in the open literature. Substitution of divalent cations on the trivalent lanthanum A-site creates a charge imbalance, which requires compensation through either the formation of oxygen vacancies or an increase in the iron valence from Fe^{3+} to Fe^{4+} .^{12, 13} (Although it is possible for Fe^{4+} to disproportionate into a mixture of Fe^{3+} and Fe^{5+} in orthoferrite systems, this has only been observed below 200 K.^{14, 15}) In addition to electronic and chemical changes, the different ionic radii of cation substitutions will affect the local structure of the material. Previous studies have reported that divalent, cation substitutions in LSF and LCF, cause a reduction in the Néel temperatures, to approximately 390°C for 10% Sr doped^{4, 16} and $350\text{-}400^\circ\text{C}$ for 20% Ca doped.^{15, 17}

In this study, the alkaline metals Ca^{2+} , Sr^{2+} , and Ba^{2+} were substituted for La^{3+} on the A-site in order to produce samples with the composition $\text{La}_{0.9}\text{M}_{0.1}\text{FeO}_3$ (M=Ca, Sr, Ba). Here, we show the impact of divalent cation substitutions on the Néel temperature,

and thermal expansion and magnetic behavior using a combination of high temperature x-ray diffraction, time of flight neutron diffraction, dilatometry, and magnetometry.

3.2 Experimental Procedures

Divalent cation-doped lanthanum ferrite materials were synthesized through multi-step solid state reactions under oxidizing conditions in air using the precursor powders, La_2O_3 (99.99% purity; Alfa Aesar, MA, United States), Fe_2O_3 (99.995%; Alfa), CaCO_3 (99.995%; Alfa), SrCO_3 (99.995%; Alfa), and BaCO_3 (99.997%; Alfa). The adsorbed gas contents of the powders were measured and compensated for using thermogravimetric analysis immediately prior to batching due to their hydrophilic nature. Batch sizes were at least 30 g in order to ensure a molar variance of no greater than ± 0.00005 moles during the weighing process. Precursor powders were mixed with yttria stabilized zirconia media and isopropyl alcohol (IPA) in polymer jars for 12 hours on a table top mixer, and were subsequently calcined at 1000°C for 6 hours in a box furnace. The calcined powders formed a cake-like compact that was subsequently crushed and mixed as described above for an additional 10 hours. The calcined mixture was dried and isostatically pressed into green pellets. The pellets were sintered at 1350°C for 24 hours for densification. Once the sintering was complete, a few of the pellets were crushed using a mortar and pestle and ball milling to an approximately 1-2 μm particle size for powder diffraction and magnetic characterization.

The Pbnm orthorhombic structure of synthesized samples was verified using a Bruker (5465 East Cheryl Parkway, Madison WI 53711, USA) AXS D8 x-ray diffractometer (XRD) with parallel beam geometry at room temperature. The expansion behavior was characterized by high-temperature XRD (HT-XRD) using a Siemens (601

Pennsylvania Ave, Washington DC, USA) D5000 XRD with Bragg Brentano geometry between room temperature and 600°C. Atomic Bond angles and magnetic moments were characterized with neutron diffraction on the SMARTS beam line at Los Alamos National Laboratory. Diffraction data from XRD and neutrons were analyzed using the Rietveld method and the General Structure Analysis System (GSAS) code with the EXPGUI graphical user interface.^{18, 19}

Thermal expansion behavior was further measured by dilatometry using a Netzsch (129 Middlesex Turnpike, Burlington MA 01803) model 402E with an alumina standard supplied by Netzsch. Dilatometry samples were cut into 25 mm long rods from sintered pellets and were heated during dilatometry at 10°C/min from room temperature to 1000°C in certified dry air (80% N₂-20% O₂).

The Néel temperature was measured by vibrating sample magnetometry (VSM) with a Lake Shore 7404 VSM (575 McCorkle Blvd, Westerville OH 43082). Samples were loaded into a pre-tested, non-magnetic boron-nitride sample holder and magnetization was measured as a function of temperature in 5°C increments in a resistive heated tube furnace under a field of 0.5 T.

3.3 Results and Discussion

Alkaline substituted lanthanum ferrite samples were fabricated with nominal stoichiometry of La_{0.9}M_{0.1}FeO_{3-δ} (M=Ca, Sr, Ba; sample code LMF). The powder XRD patterns for sintered samples are shown in Figure 3.1 and exhibit the expected orthorhombic structure (Pbnm, #62). Neither the LF, LCF, nor LSF showed any secondary peaks. However, there was a minor peak for the LBF sample at about 31° 2θ,

Figure 3.1 XRD patterns at room temperature for all samples. Patterns are normalized and offset for comparison. Rietveld refinement for LF sample is shown in lower box with cumulative χ^2 and peak indexing.

Table 3.1 Lattice parameters and volume of each sample determined from XRD.

	a (Å)	b (Å)	c (Å)	V (Å ³)
LF	5.5679±0.0002	5.5602±0.0002	7.8550±0.0003	243.1758±0.0140
LCF	5.5497±0.0005	5.5350±0.0006	7.8195±0.0008	240.1951±0.0435
LSF	5.5555±0.0003	5.5337±0.0003	7.8584±0.0004	241.5890±0.0224
LBF	5.5557±0.0004	5.556±90.0003	7.8540±0.0005	242.4716±0.0262

Figure 3.1 Lattice parameters a , b , c , and volume of each sample at room temperature. The c parameter has been adjusted by $c_{\text{shown}} = c_{\text{fit}}/\sqrt{2}$. Error bars intentionally left out, for error value see Table 3.1.

which can be attributed to a minor impurity of $\text{BaLa}_2\text{Fe}_2\text{O}_7$ but is not expected to contribute significantly to any of the magnetic or expansion results described in this paper. The refined lattice parameters and unit cell volumes determined from Rietveld analysis of the XRD data are listed in Table 3.1 and are compared to each other in Figure 3.2. These values are consistent with those found in the open literature for LaFeO_3 .^{1, 4, 15} The estimated Shannon ionic radii are dependent on the coordination, valence, and spin of each cation. In LaFeO_3 , the A-site of the perovskite structure is coordinated with 12 oxygen sites, giving the ionic radii: $\text{La}^{3+}=1.36$, $\text{Ca}^{2+}=1.34$, $\text{Sr}^{2+}=1.44$, and $\text{Ba}^{2+}=1.61$ Å. Intuitively, the larger ionic radii of Sr and Ba would be expected to result in an increase in lattice parameters. However, the introduction of divalent cations caused a decrease in

the calculated lattice parameters for all samples. This behavior can be explained if charge compensation is dominated by the conversion of Fe^{3+} to Fe^{4+} . The formation of tetravalent iron would cause a reduction in lattice parameters due to the smaller ionic radius of Fe^{4+} (0.585 Å) as compared to Fe^{3+} (0.645 Å).

The high temperature XRD data showed that the volume expansion about the Néel temperature, shown in Figure 3.3, is continuous, implying that the transition is of second order. For temperatures lower than $T/T_N < 0.5$, the volume expansion was observed to be linear and is projected within Figure 3.3 to higher temperatures using a dashed line. After $T/T_N > 0.5$, the volume expansion begins increasing faster than the low temperature projection until $T/T_N = 1$, where it then begins to decrease back to the projected expansion rate. This same behavior has been seen in other studies of lanthanum ferrite to show the magnetoelastic effect on thermal expansion.^{4,9} The changes in lattice parameters as a function of temperature can also be seen in Figure 3.4 where shifts in the linearity about or near T_N can be seen. In the case of LF, there was a very subtle shift in all three parameters occurring just prior to T_N . The LCF samples showed a significant shift in the change in b and a subtle shift in the change in a and c . The LSF did not show a significant change but the expansion of all three parameters began to diverge from each other. No noticeable change in the expansion of LBF could be seen. However, despite the lack of any significant trend in how the lattice expansion changes for any single parameter, it is worth noting that in all three doped samples, the b parameter showed the smallest changes. In addition, for the LCF and LSF samples, the most significant shift in lattice expansion also occurred for the b parameter and the shift was toward a smaller expansion.

Figure 2.3 Volume expansion measured by XRD about T_N and a 'linear' expansion line (dashed) to illustrate non-linear volume expansion. Initial values for volume can be seen in Figure 3.2 and Table 3.1.

Figure 3.3 Changes in lattice parameters found during HT-XRD. Initial values of lattice used are the values refined from the room temperature patterns and are shown in Fig. 2 and Table 1. Néel temperatures are annotated with a drop line for each sample. a) The LF sample showed a gradual change in the lattice expansion. b) The LCF sample shows a very dramatic change in the b parameter at T_N and a slight variation in the a and c parameters just before T_N . c) The LSF sample doesn't show a dramatic change in expansion but does show a slight divergence in the parameters relative to each other prior to T_N . d) Like LF, the LBF sample shows a gradual change in lattice expansion about T_N .

Figure 3.5 Coefficients of thermal expansion found through dilatometry. The change in the linearity of the CTE indicates the Néel temperature and is annotated by the drop lines.

Table 3.2 Bond angles and moment/ion found through neutron diffraction. There are two angles available for the O1-Fe-O2. The moments are refined along the a-axis and the super exchange of Fe^{3+} -O- Fe^{3+} occurs along the c-axis and corresponds to the Fe-O1-Fe bond angle.

Formula	Bond Angles (°)		(μ_B/Fe)
	Fe-O1-Fe	Fe-O2-Fe	Moment
LaFeO₃	156.8	156.8	3.77
La_{0.9}Ca_{0.1}FeO₃	156	157.9	3.15
La_{0.9}Sr_{0.1}FeO₃	161.3	157.7	2.8
La_{0.9}Ba_{0.1}FeO₃	161.4	159.7	3.08

Dilatometry was used to find the instantaneous coefficients of thermal expansion (CTE) as shown in Figure 3.5. The T_N values measured by dilatometry for LF, LCF, LSF, and LBF are 457°C, 341°C, 440°C, and 442°C, respectively, and are consistent those found in literature for LF, LCF, and LSF. The T_N for LBF has not been previously reported in the literature. The Néel temperatures determined are listed with other temperatures found in literature in Table 3.3 and are indicated in Figure 3.5 by drop lines.^{4, 17} In all four samples, the CTE increases linearly as the temperature approaches the sample's respective T_N for and then decreases or plateaus afterwards. The CTE behavior from dilatometry is consistent with the data from high temperature XRD, where the volume expansion behaved non-linearly about the T_N . The dilatometry data in Figure 3.4 demonstrates that the CTE of lanthum ferrite increases linearly at a rate of 0.0102(T) for $T < T_N$, reaches a local maximum near T_N , and decreases linearly at a rate of 0.0055(T) for $T > T_N$. The data in Figure 3.5 also clearly shows that all the divalent-doped samples behave similarly, reaching a local maximum CTE near T_N . The non-linear volume expansion behavior and variations in the instantaneous CTE around T_N shown in Figure 3.5 are consistent with expansion behavior around T_N found in undoped LaFeO_3 by Selbach *et al.*⁹ These results illustrate that the same magnetoelastic contribution or coupling to the thermal expansion found in LaFeO_3 is also found in divalent substituted lanthanum ferrites.

Magnetization measurements were measured by VSM as function of temperature in order to directly determine the Néel temperature as shown in Figure 3.6. The T_N values are indicated by relatively sharp peaks shown in Figure 3.6. The T_N of LaFeO_3 was 471°C. The LSF and LBF samples had slightly lower values of T_N , 465°C and 466°C

respectively, and the T_N of LCF was the most suppressed at 351°C. Above T_N , the magnetization of LF remained relatively constant until approximately 520°C was reached and then decreased more rapidly with increasing temperature as the material became more paramagnetic. In the cases of the doped samples, the magnetization decreases relatively rapidly at temperatures above T_N . The T_N values measured by magnetometry are consistent with the transition temperatures determined by dilatometry and further validate the conclusion that magnetostatic coupling is the mechanism of magnetic contribution to thermal expansion.

Figure 3.6 Magnetometry showing the Néel temperature of each sample at the peak prior to the change from anti-ferromagnetic to paramagnetic. The magnetizations are offset and normalized to better illustrate the relative changes in T_N .

Table 3.3 Comparisons of the Néel temperatures found for all samples observed in this study and T_N listed in literature.

Composition	T_N (°C) from Dilatometry	T_N (°C) from VSM	Komornicki ¹⁵	Fossdal ⁴	Wattiaux ¹⁶
LaFeO ₃	457	471	477°C	450°C	452°C
La _{0.9} Ca _{0.1} FeO ₃	341	351	-	-	-
La _{0.9} Sr _{0.1} FeO ₃	440	465	-	380°C	≈400°C
La _{0.9} Ba _{0.1} FeO ₃	442	466	-	-	-
La _{0.9} Ca _{0.2} FeO ₃	-	-	277°C	-	-

The suite of characterization methods used in this study demonstrated that Ca substitutions result in a larger decrease in the Néel temperature compared to Sr or Ba substitutions where only very small changes in T_N were observed. If the reduction in Néel temperature was solely due to charge compensation by the formation of tetravalent iron then all three of the divalent-doped lanthanum ferrite materials studied here would be expected to have approximately the same Néel temperature. Therefore, the differences in the observed values of T_N must be associated at least in part by another competing mechanism. As stated earlier, divalent substitutions on the trivalent A-site requires charge compensation by either the creation of oxygen vacancies or the oxidation of Fe^{3+} ($3d^5$) to Fe^{4+} ($3d^4$). In the event of that the valence Fe^{3+} changes to Fe^{4+} , the number of unpaired electrons available for magnetic coupling across the Fe-O-Fe bond (i.e., super-exchange) is reduced. Additionally, the coupling of Fe^{3+} -O- Fe^{4+} is weakly ferromagnetic and will reduce the Néel temperature as it breaks up the long range AFM ordering and cause an increase in the paramagnetic behavior of the material. The reduction in the Néel temperature of LCF observed in our materials was consistent with the experimental results of Komornicki *et al.*¹⁵ in which oxidized LCF samples, which were charge

compensated almost entirely by the formation of Fe^{4+} , showed a significant reduction in T_N (see Table 3.3). Alternatively, Grenier *et al.*²⁰ found that the Néel temperature remained nearly constant regardless of the amount of divalent calcium substitution in LCF materials annealed in a low oxygen partial pressure environment. Grenier *et al.* showed that there was no evidence of Fe^{4+} using Mössbauer spectroscopy, indicating that the charge compensation was exclusively associated with the formation of oxygen vacancies. Therefore, the AFM Fe^{3+} -O- Fe^{3+} coupling remained unaffected in samples populated by only Fe^{3+} because magnetic nearest neighbors remain unchanged throughout all of his compositions. The contrasting work of Komorniki *et al.*¹⁵ and Grenier *et al.*²⁰ clearly show that the extent of the suppression of the Néel temperature is dependent on the charge compensating mechanisms (Fe^{4+}/V_O ratio), which is dependent on both the concentration of divalent substitution and the partial pressure of oxygen to which the materials are exposed.

In addition to charge compensation mechanisms, structural distortions can also affect the Néel temperature. A correlation between AFM, T_N , and the Fe-O-Fe bond angle has been investigated by several authors for RFeO_3 compounds.^{21, 22} These authors have suggested that as the Fe-O-Fe bond angle is increased along the direction of the super-exchange interaction, there is more overlap between the iron e_g (high energy d-orbital) and the oxygen 2p orbitals, resulting in an increase AFM strength and T_N . Zhou and Goodenough²³ showed a linear correlation between T_N and $\cos^4(\omega/2)/d^7$, where $\omega = (180-\theta)$, θ is the distortion angle, and d is the Fe-O bond length. Using this relationship, we can estimate the difference between the expected T_N for calcium, strontium, or barium substituted samples through linear extrapolation of data from Zhou and Goodenough. The

neutron diffraction data in Table 3.2 indicate that the Fe-O1-Fe bond angle is increased from 156.8° in LaFeO_3 to 161.3° in LSF and 161.4° in LBF, and is reduced to 156.0° in LCF (the bond angle of interest lies along the Pbnm c-axis and only incorporates the O1 position). A simple calculation based on the difference of observed bond angles gives an estimated increase in T_N of about 50°C for LSF and LBF as compared to LCF.

The Néel temperature of oxidized, Ca-substituted samples is greatly reduced because of the nearly complete charge compensation through the formation of tetravalent iron, rather than oxygen vacancies, and a slight decrease in the Fe-O1-Fe bond angle. The Sr- and Ba-doped samples also have a suppressed T_N due to the formation of Fe^{4+} , but also have increased Fe-O1-Fe bond angles, which increases the magnetic coupling, and thus increases the strength of the super-exchange interactions between the remaining Fe^{3+} pairs. The estimated increase in T_N (50°C) due to the increase in bond angle is not sufficient to explain the large difference in T_N ($\Delta \approx 100^\circ\text{C}$) between LCF and the LSF and LBF samples. Consequently, it is likely that partial charge compensation by vacancies is more prevalent in the LSF and LBF systems than in the LCF system.

It is interesting that only the Fe-O1-Fe bond angle increased with divalent cation substitutions, while the Fe-O2-Fe bond angle remained nearly constant. The ideal cubic perovskite unit cell contains three equivalent oxygen lattice sites. In non-cubic perovskites, octahedral tilting reduces the symmetry and the unit cell needs to be expanded. In the case of the Pbnm orthorhombic structure, the reduction of symmetry creates two unique oxygen lattice sites (O1 and O2). There are twice as many O2 lattice sites (8) as there are O1 lattice sites (4). The O1 oxygen atoms are located at the vertices of the FeO_6 octahedra and align along the long c-axis of the Pbnm unit cell, as shown in

Figure 3.7. Hudspeth *et al.*²⁴ correctly deduced that the direction of the AFM moment was ambiguous in neutron diffraction data due to the nearly equivalent pseudo-cubic lattice parameters, as was the case in our neutron diffraction data. However, the correlation between the Néel temperature and the calculated Fe-O1-Fe bond angle suggests that the super-exchange interaction occurs along the Pbnm c-axis (Pnma b-axis). This assumption is further strengthened by fact that super-exchange is maintained along the symmetrically similar elongated axes of the lanthanum ferrite perovskite derivatives, known as the Grenier and brownmillerite structures. These results are consistent with neutron diffraction data of LaFeO_3 shown by Peterlinneumaier and Steichele,²⁵ which indicate that the direction of AFM is slightly canted along the a-axis of the Pbnm unit cell. It is suspected that direction of the canted AFM behavior is preserved along the a-axis in the divalent cation-substituted lanthanum ferrite materials studied here.

Figure 3.7 Pbnm structure of LaFeO_3 . The O1 site oxygen atoms shown in white are located at the vertices of the FeO_6 octahedra and are aligned along the Pbnm c-axis. The large A-site cations are shown in green. The iron cations are shown in the center of the octahedra.

3.4 Conclusions

The thermal expansion behavior of pure LaFeO_3 and $\text{La}_{0.9}\text{R}_{0.1}\text{FeO}_3$ ($\text{R}=\text{Ca}, \text{Sr}, \text{Ba}$) was correlated with AFM to paramagnetic phase transformations using a combination of dilatometry, vibrating sample magnetometry, and high temperature x-ray diffraction. Néel temperatures were determined through dilatometry, XRD, and VSM were in agreement and were consistent with values available in literature. This is the first such study that has used a combination of these three techniques to measure both the Néel temperature and expansion behavior for alkaline-doped perovskites. The results confirm the results of Selbach *et al.*⁹ that the thermal expansion behavior has contributions from magneto-static coupling.

Differences between observed Néel temperatures in LF, LCF, LSF, and LBF specimens were attributed to both the nature of the charge compensation mechanism and the effect of the substituent on the super-exchange bond angle. For divalent calcium-substituted LaFeO_3 , the coupling is significantly disrupted by the presence of tetravalent iron from charge compensation and a smaller Fe-O1-Fe bond angle. For strontium and barium-substituted LaFeO_3 , it is suspected that charge compensation was accomplished by both the reduction of iron and the formation of oxygen vacancies, the latter of which would offset the disruption to the long range magnetic ordering caused by the reduction of iron ions compared to the calcium doped samples. In addition, this disruption is mitigated by an increase in both the bond angle and the strengthening of the Fe-O1-Fe super-exchange interaction. The correlation between calculated bond angles from neutron diffraction data and Néel temperatures suggest that the super-exchange still occurs along the c-axis of the Pbnm unit cell for divalent doped samples. The directions of the

antiferromagnetic moment in LCF, LSF, and LBF were ambiguous in our neutron diffraction data, but likely remained slightly canted along the a-axis, as is suggested in literature for the case of pure LF.

3.5 Author Justification

The research presented in this publication was carried out and authored by Patrick Price as a partial fulfillment of the requirements for a Doctoral degree in Materials Science and Engineering at Boise State University and Geoffrey Beausoleil as a partial fulfillment of the requirements for a Master's degree in Materials Science and Engineering, under the advisement and supervision of Dr. Darryl P. Butt. Patrick Price and David Thomsen synthesized the materials used in the study, collected high temperature x-ray and neutron diffraction data, and analyzed diffraction data using Rietveld refinement. David Thomsen and Geoffrey Beausoleil collected and analyzed dilatometry and vibrating sample magnetometry data. Scott Misture kindly donated time on his high temperature diffractometer. Dr. Darryl P. Butt contributed greatly with financial support and technical guidance throughout the research and provided in-depth critical reviews of the article during the writing process.

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CHAPTER FOUR: STABILITY AND DECOMPOSITION OF CA SUBSTITUTED LANTHANUM FERRITE IN REDUCING ATMOSPHERES

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Stability and Decomposition of Ca Substituted Lanthanum Ferrite
in Reducing Atmospheres

Patrick M. Price¹

Darryl P. Butt^{1,2}

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¹*Department of Materials Science & Engineering and* ²*Department of Physics, Boise State University, 1910 University Dr., Boise, ID 83725*

²*Center for Advanced Energy Studies,
995 University Boulevard, Idaho Falls, ID 83401*

Abstract

Lanthanum calcium ferrite perovskites ($\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ $x = 0, 0.1, 0.2, 0.3, 0.4$) were synthesized in air and subsequently decomposed in reducing atmospheres. The partial pressure of oxygen (P_{O_2}) was controlled by varying $\text{H}_2/\text{H}_2\text{O}$ ratios via pre-mixed gases and by bubbling hydrogen through water baths at controlled temperatures. Three regions of mass loss were identified, two of which were discovered to be associated with discrete decompositions. Calcium was shown to decrease the thermal stability of the perovskite compound, but rather than incrementally increasing the required P_{O_2} for decomposition, substituted samples partially decompose at a single P_{O_2} . The extent of the decomposition was dependent on the amount of calcium substitution and the isothermal temperature. All samples were found to fully decompose at the same oxygen partial pressure as pure lanthanum ferrite for all experimental temperatures.

4.1 Introduction

There is a strong motivation to develop new technologies that can sustainably supplement world energy requirements and reduce carbon emissions. One such technology is the utilization of ion conducting ceramic oxide membranes for use in high temperature electrochemical devices for energy conversion such as the solid oxide fuel cell (SOFC), the conversion of natural gas into synthesis gas (syngas), oxidation of other hydrocarbons, hydrogen and oxygen production, and hybrid energy systems.¹⁻⁵ Syngas reactors can be used in conjunction with other technologies for onsite production of easily transportable liquid products from natural gas that would otherwise be flared at remote oil extraction facilities. Calcium substituted lanthanum ferrite materials (LCF) have been shown to be suitable candidates as oxygen transport membranes in syngas

reactors due to the combination of excellent stability at high temperatures under reducing conditions and high oxygen flux rates.⁶

Lanthanum ferrite (LaFeO_3) has the orthorhombic, Pbnm, ABO_3 perovskite structure as shown in Figure 4.1.⁷ When Ca^{2+} is added it to lanthanum ferrite it forms a solid solution by occupying the La^{3+} A-site. In addition to the small difference in ionic radii (~3%), the difference in valence results in a charge imbalance.⁸ As a result, there are two possible charge compensating mechanisms: either an oxygen vacancy may form for every two Ca^{2+} ions added, or the valence state of iron may change from Fe^{3+} to Fe^{4+} . The extent to which each of these compensation mechanisms occurs has been shown to be affected by the thermal history and partial pressure of oxygen during synthesis or sustained annealing of the material. Synthesizing samples under low oxygen partial pressures will result in charge compensation primarily by the formation of oxygen vacancies as confirmed by Mossbauer spectroscopy^{9, 10} Previous studies have reported the simultaneous existence of both oxygen vacancies and tetravalent iron in LCF samples treated in air.^{11, 12} Ordered oxygen vacancies may also form with increasing calcium content and lower oxygen partial pressures.

When iron based perovskite materials are subjected to sufficiently reducing atmospheres at elevated temperatures, a large mass loss is observed as the material decomposes. A study by Nakamura *et al.*¹³ investigated the decomposition behavior of lanthanum ferrite at 1000°C and 1200°C and has shown that LaFeO_3 decomposes in the following reaction:

Despite great interest in syngas materials, decomposition partial pressures have not been reported for calcium substituted lanthanum ferrites near the expected operating temperatures of the membranes ($\sim 750\text{--}900^\circ\text{C}$). In this study, we synthesized LCF materials with 0, 10, 20, 30, and 40% calcium substitution and have investigated the decomposition behavior of each composition under reducing atmospheres at 800, 900, and 1000°C .

Figure 4.1 The LCF perovskite structure is composed of a large A-site cation shown at the center of the unit cell, a Fe cation located at the center of the octahedra, and oxygen atoms located at the vertices of the octahedra.

Figure 4.2 Hydrogen gas bubbler apparatus. H_2 at controlled pressure is bubbled through a thermally stable water bath in a beaker, which is contained in an insulated dewar, and insulated by an additional 2" of foam board. The water surrounding the beaker is actively chilled by an external cooling unit, which also pre-cools the stainless steel gas line.

4.2 Experimental Procedures

Lanthanum calcium ferrites were synthesized using the procedures discussed previously.¹⁴ The orthorhombic (Pbnm) structure of synthesized samples was verified using x-ray diffractometer (Bruker AXS D8, Madison, WI) with parallel beam geometry at room temperature. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to investigate the thermal stability of LCF compounds in reducing atmospheres. All thermal analysis studies were performed in a thermal analyzer (Netsch STA-449, Burlington, MA) equipped with a simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC/TG) carrier, silicon carbide furnace, alumina protective tube, and 85 μ l platinum rhodium (Pt/Rh) crucibles. Temperature

calibrations were performed by the melting of five pure metals. In order to remove background and noise from the sample signal, correction files were created prior to all thermal analysis experiments by running the DSC/TGA stage with empty crucibles using equivalent parameters as sample measurements. An empty Pt/Rh crucible was used as a reference for all sample measurements. All samples were ramped at 20° C/min with a total gas flow rate of 200 ml/min. Reducing atmospheres were achieved using certified H₂–Ar gas mixtures (2% or 6% H₂; balance Argon) with a measured moisture content of less than 10 ppm. The DSC/TGA has three internal mass flow controllers (MFC). Two of the MFCs are available for experiments and one is used to provide a continuous flow of 10 mL/min of high purity argon (99.999%) protective gas through the balance chamber. Each MFC was adjusted for the appropriate gas densities. The argon gas was passed through a gas purifier (Sigma-Aldrich Supleco 22398, St. Louis, MO) operating at 580°C to remove any residual oxygen. The resulting oxygen partial pressure was measured with a zirconia cell oxygen analyzer (Neutronics OA-1, Exton, PA) operating at 725°C. A nominal voltage reading of 570 mV was recorded correlating to approximately P_{O₂}=10⁻¹² bar. The P_{O₂} was calculated using the Nernst equation as follows:

$$\text{Electrical Potential (V)} = \frac{RT}{nF} \ln \left(\frac{0.209}{\text{Unknown } P_{O_2}} \right) \quad (1)$$

Reducing atmospheres with controlled oxygen partial pressure were achieved by controlling the volume ratio of experimental gases with mass flow controllers. The experimental gases were mixed in a manifold and passed through a section of stainless steel tubing to facilitate mixing prior to entering the experimental chamber. The certified H₂–Ar gas mixture was delivered to the MFC either directly from the tank or bubbled

through a water bath at controlled temperature and pressure. The pressure above the water bath was measured with a calibrated test pressure gauge with a $\pm 0.5\%$ accuracy (OMEGA Engineering PGT-30L-15, Stamford, CT) and controlled with a precision pressure regulator ($\pm 0.05\%$ precision) (OMEGA Engineering Omega PRG101-25, Stamford, CT). All gas lines and fittings were welded or fitted with stainless steel fittings (Swagelok, Solon, OH) to limit hydrogen or oxygen leakage. The hydrogen bubbler apparatus is shown in Figure 4.2. The bubbler water was contained in a glass beaker placed inside an insulated dewar, surrounded by a copper coil, and immersed in a circulated water bath, which was held at 0.5°C by an external cooling unit. The dewar was placed in a 2" foam lined box for added thermal stability. A K-type thermocouple was inserted directly into the bubbler water bath and the temperature was continuously monitored with a digital thermometer (OMEGA Engineering HH806AW, Stamford, CT). The stainless steel gas line feeding the bubbler was pre-cooled by a copper line from the external cooling unit and all cooling and gas lines were insulated.

The partial pressure of the system can be calculated using thermodynamic relationships for the following reaction:

The equilibrium constant, K , for the formation of water vapor can be calculated using the Gibbs free energy of formation ΔG as shown in the following two equations:

$$K = \frac{(P_{\text{H}_2\text{O}})^2}{(P_{\text{H}_2})^2 (P_{\text{O}_2})} \quad (2)$$

$$K = \exp\left(\frac{-\Delta G}{RT}\right) \quad (3)$$

Solving for the partial pressure of oxygen from equations (2) and (3) gives:

$$P_{O_2} = \left(\frac{P_{H_2}}{P_{H_2O}} \right)^{-2} \exp(\Delta G/RT) \quad (\text{bar}) \quad (4)$$

The Gibbs free energy of formation was taken from the JANAF tables for temperatures from 1000-1400K and a linear fit was applied to extrapolate intermediate values given in the following equation:

$$\Delta G_{H_2O(g)} = 112.522 (T) - 497790.8 \text{ (J/mol)} \quad (5)$$

The pressure of water vapor (P_{H_2O}) above the water bath was calculated from the ITS-90 formulations for vapor pressure using the following equation.¹⁵

$$\ln(e_s) = \sum_{i=0}^6 g_i T^{i-2} + g_7 \ln(T) \text{ (Pa)} \quad (6)$$

where,

$$\begin{array}{lll} g_0 = -2.8365744 \times 10^3 & g_3 = -2.737830188 \times 10^{-2} & g_6 = -1.8680009 \times 10^{-13} \\ g_1 = -6.028076559 \times 10^3 & g_4 = 1.6261698 \times 10^{-5} & g_7 = 2.7150305 \\ g_2 = 1.954263612 \times 10^1 & g_5 = 7.0229056 \times 10^{-10} & \end{array}$$

The partial pressure of hydrogen (P_{H_2}) above the water bath can be calculated as a function of the line pressure exerted by the pressure regulator (LP), the atmospheric pressure (ATM), the partial pressure of water vapor as a function of temperature from equation (6) ($e_s(T)$), the back pressure exerted by the water above the bottom of the submerged inlet tube (WBP), and the hydrogen concentration in the H_2 -Ar mixture as given in equation (7). Typically, the line pressure was held at 4 psi, the water head was 6 cm and the average daily atmospheric pressure was 92 kPa giving a total pressure of approximately 120 kPa.

$$P_{H_2}(T) = (ATM + LP - e_s(T) - WBP) * [H_2] \quad (\text{Pa}) \quad (7)$$

The water vapor partial pressure is equal to e_s from equation (6) for bubbled gases and can be directly calculated from the measured moisture content in the tank for dry gas. The total H_2/H_2O ratio of two mixed gases with predetermined MFC gas flow rates (P_1 and P_2) can be calculated from the following equation:

$$\left(\frac{P_{H_2}}{P_{H_2O}} \right)_{Total} = \frac{P_{H_2}(T1) \frac{P_1}{P_1+P_2} + P_{H_2}(T2) \frac{P_2}{P_1+P_2}}{P_{H_2O}(T1) \frac{P_1}{P_1+P_2} + P_{H_2O}(T2) \frac{P_2}{P_1+P_2}} \quad (8)$$

The total experimental partial pressure of oxygen in the unit bar can then be calculated by combining equations (5) and (9) giving the following equation:

$$P_{O_2} = \left(\frac{P_{H_2}(T1) \frac{P_1}{P_1+P_2} + P_{H_2}(T2) \frac{P_2}{P_1+P_2}}{P_{H_2O}(T1) \frac{P_1}{P_1+P_2} + P_{H_2O}(T2) \frac{P_2}{P_1+P_2}} \right)^{-2} \frac{754672.4}{e^{\frac{59873.8}{T}}} \text{ (bar)} \quad (9)$$

Table 4.1 lists the gas mixtures used and calculated achievable oxygen partial pressures at each experimental temperature.

Table 4.1 List of Experimental Gas Mixtures and Bath Temperatures

% H_2	Isothermal Temperature (°C)	Dry	Bubbled 0.5°C	Bubbled 22.5°C
Log[P_{O_2}] (bar)				
2%	800	-26.95	-19.5	-18.21
	900	-24.89	-17.43	-16.15
	1000	-23.15	-15.69	-14.47
6%	800	-27.91	-20.45	-19.17
	900	-25.84	-18.39	-17.1
	1000	-24.1	-16.65	-15.36

Figure 4.3 Fully decomposed samples in 6% H_2 at 1100°C. The mass lost was consistent with the formation of CaO, La_2O_3 , and metallic Fe, with a maximum deviation of less than 0.5%.

4.3 Results and Discussion

Previous studies have shown that pure $LaFeO_3$ decomposes into iron, lanthanum oxide, and oxygen in sufficiently reducing atmospheres.¹³ The data in Figure 4.3 show mass loss for the complete decomposition of our Ca substituted samples (0-40% Ca) isothermally treated in 6% H_2 at 1100°C. These mass losses are consistent with the formation of calcium oxide (CaO), lanthanum oxide (La_2O_3), and iron. Peaks associated with all three phases were present in x-ray diffraction data. Therefore, decomposition of LCF is given by:

The measured mass losses were within 0.25% of the theoretical value except for the 40% Ca substituted sample, which was within 0.5%. Previous studies have shown that a small percentage of ordered oxygen vacancies exist at this high Ca concentration, which would decrease the amount of available oxygen for decomposition.¹⁴

Examples of the typical decomposition curves are shown in Figure 4.4 for LCF samples treated at 1000°C. A typical thermal profile and gas flow rate scheme is also shown. The data contains three distinct mass loss regions labeled LR1, LR2, and LR3. All samples were chemically stable during the initial ramp to 500°C in 200 mL/min of purified Ar with a $P_{\text{O}_2} \approx 10^{-12}$ bar. At 500°C, the gas flow was switched to moist (0.5°C) 6% H_2 , resulting in mass loss. A 30 minute isotherm was evoked to ensure complete oxygen evolution at this stage, which will be referred to as loss region #1 (LR1). The furnace was then ramped to 1000°C while flowing moist gas. Calcium substituted samples rapidly lost mass when the furnace reached 1000°C at $P_{\text{O}_2} = 10^{-16.65}$ bar. The rapid mass loss continues for a short period of time, after which, the rate of decomposition slows, but does not stop. This part of the decomposition curve will be referred to as loss region #2 (LR2).

A dry 6H% gas stream is introduced and begins to decompose the sample in loss region #3 (LR3). The oxygen partial pressure was incrementally increased by decreasing the flow rate of dry 6% H_2 gas until the decomposition was reaction reversed resulting in oxidation and an observed increase in mass. Equilibrium decomposition oxygen partial pressures were calculated using gas flow rates at the onset of oxidation. Similar

experiments were performed at higher oxygen partial pressures and the decomposition in LR2 was discovered to also be reversible, where the decomposition oxygen partial pressure was measured at the onset of oxidation.

Figure 4.4 Decomposition behavior at 1000°C. The temperature profile ramps to 500°C to ensure complete oxygen disassociation in the first mass loss region (LR1). When the temperature is increased to 1000°C at a partial pressure of $10^{-16.64}$ bar a rapid decomposition is observed in the second mass loss region (LR2) followed by a slow linear mass loss for all Ca substituted samples. The oxygen partial pressure is then decreased to $10^{-17.30}$ bar and the all samples, including LaFeO_3 begin to decompose in the final mass loss region (LR3). The partial pressure is then increased in a stepwise fashion back to $10^{-16.64}$ bar and the reversible reaction begins to oxidize the materials at a partial pressure of $10^{-16.98}$ bar.

No mass loss was observed in LR1 and LR2 for pure LaFeO_3 . Furthermore, no mass loss was observed in LR2 for the 10% Ca substituted sample at 800°C or 900°C, but a small mass loss was observed at 1000°C. In the following, we attempt to give a physical explanation for the occurrence of mass loss in each of the three discrete regions.

The saturated mass loss observed in LR1 is wholly consistent with the formation of oxygen vacancies, assuming that calcium substituted samples initially are entirely charge compensated by Fe^{4+} , which is then reduced to Fe^{3+} . The ionic radius of the Fe^{3+} cation is 18% larger than Fe^{4+} .⁸ X-ray diffraction patterns of specimens treated at the 500°C isotherm in LR1 shift to lower angles, indicating increased lattice parameters, which is consistent with the expected chemical expansion due to the change in iron valance state. No calcium oxide or ordered oxygen vacancy structures were observed in the XRD data of samples reduced in LR1.

The reversible decomposition behavior of LaFeO_3 , which only occurs in LR3, is consistent with the findings of Nakamura *et al.*¹³ The equilibrium partial pressure of oxygen at 1000°C was calculated to be $10^{-16.98}$ bar using the double gas flow method described here. This is very close to the equilibrium oxygen partial pressure of $10^{-16.95}$ bar reported by Nakamura *et al.* Calcium substituted samples were allowed to reach the semi-steady state mass loss in LR2 prior to decomposition in LR3. Rather than a progressive shift, all samples were found to have the exact same equilibrium P_{O_2} in LR3.

Figure 4.5 X-ray diffraction data for $\text{La}_{0.7}\text{Ca}_{0.3}\text{FeO}_{3-\delta}$. The specimen was first reduced at 900°C with a $P_{\text{O}_2}=10^{-18.4}$ bar, resulting in mass loss from LR2, but not LR3. Both calcium oxide and metallic iron peaks are observed in the XRD spectrum of the reduced specimen. The specimen was then re-oxidized above the LR2 equilibrium P_{O_2} of $10^{-17.22}$ bar. The CaO and $\alpha\text{-Fe}$ peaks are not observed in the XRD spectrum of the oxidized sample. However, peaks indicative of an ordered oxygen vacancy structures have appeared.

Table 4.2 Calculated equilibrium P_{O_2} for the decomposition in LR1 and LR2. The data from Reference [20] gives the decomposition of brownmillerite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) for comparison. The standard Gibbs free energy, enthalpy, and entropy were calculated from equations (10-12).

	Isotherm	% H_2	Gas	Flow #1	Gas	Flow #2	Calculated	ΔG°	ΔH°	ΔS°
	($^\circ\text{C}$)		Stream #1	(mL/min)	Stream #2	(mL/min)	Log[P_{O_2}] (Bar)	(KJ/mol)		
Decomposition of $\text{Ca}_2\text{Fe}_2\text{O}_5$	800						-19.6	302		
	900						-17.3	291	425	-114
LR2	800	6%	0.5C	110	22.5 $^\circ\text{C}$	80.00	-19.5	301		
	900	6%	0.5C	30	22.5 $^\circ\text{C}$	160.00	-17.2	290	425	-116
	1000	2%	0.5C	145	22.5 $^\circ\text{C}$	45.00	-15.2	278		
LR3	800	6%	Dry	150	0.5C	40.00	-21.8	336		
	900	6%	Dry	110	0.5C	80.00	-19.1	322	474	-128
	1000	6%	Dry	60	0.5C	130.00	-17.0	310		

Table 4.3 Mass lost due to Ca decomposition in LR2. Estimated %Ca in solid solution after decomposition in LR2.

%Ca →	10	20	30	40	10	20	30	40
Temperature °C	Measured %Ca Decomposed to CaO				Estimated %Ca Left in Solution			
800°C	0.0	9.2	20.5	31.6	10.0	10.8	9.5	8.4
900°C	0.0	11.1	22.7	34.3	10.0	8.9	7.3	5.7
1000°C	5.3	15.2	26.0	36.6	4.7	4.8	4.0	3.4

The chemically invariant nature of the equilibrium oxygen partial pressure in LR3 indicates a single chemical reaction with a single value of standard free energy given by the following equation, where $\frac{3}{4}$ is the stoichiometric fraction of O_2 produced in the reaction.

$$\Delta G^\circ = -RT \ln(K) = -\frac{3}{4}RT \cdot 2.303 \log [P_{O_2}] \quad (\text{J/mol}) \quad (10)$$

The standard enthalpy and entropy can be estimated using the following equations:

$$\Delta H^\circ = \left(\frac{\Delta G_1^\circ}{T_1} - \frac{\Delta G_2^\circ}{T_2} \right) / \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (\text{J/mol}) \quad (11)$$

$$\Delta S^\circ = \frac{\Delta G_1^\circ - \Delta G_2^\circ}{T_1 - T_2} \quad (\text{J/mol K}^{-1}) \quad (12)$$

The measured equilibrium oxygen partial pressure for LR3 and thermodynamic estimations are listed in Table 4.2.

In LR2 the desired P_{O_2} was achieved by using a mixture of 2 moist gases (0.5°C and 22.5°C water baths). Similar to LR3, the decomposition behavior in LR2 was found to be reversible. The equilibrium P_{O_2} in LR2 was approximately two orders of magnitude higher than LR3 as indicated in Table 4.2. The measured equilibrium P_{O_2} in LR2 was also found to be chemically invariant; however, the 10% Ca sample did not show any signs of decomposition in LR2 at 800°C or 900°C, but did show a small decomposition in LR2 at

1000°C. The equilibrium P_{O_2} showed no dependence on degree of calcium substitution, but the amount of mass lost during the LR2 decomposition was found to be chemically dependent.

A 30% Ca substituted specimen was annealed below the equilibrium P_{O_2} of decomposition in LR2, but above the equilibrium P_{O_2} for decomposition in LR3 at 900°C for 8 hours, and cooled under reducing conditions. The x-ray spectrum in Figure 4.5 shows after decomposition the 30% specimen was composed of LCF perovskite, CaO, and iron. No La_2O_3 or ordered oxygen vacancy structures were found indicating nearly all mass loss observed in LR2 was due to the formation of CaO and Fe. The same 30% Ca sample was re-oxidized at 900°C above the LR2 equilibrium P_{O_2} but below the oxygen disassociation observed in LR1. The XRD spectrum of the re-oxidized sample shows the CaO and iron peaks disappeared, confirming the reversal of the decomposition. However, additional diffraction peaks are indicative of ordered oxygen vacancies were present in the spectrum.

The measured percentage of calcium converted to CaO is given in Table 4.3. The data show that a percentage of the calcium remains oxidized for all samples subjected to decomposition in LR2. The amount of non-decomposed Ca decreases with increasing temperature and increasing initial calcium content. The data shown in Table 4.3 indicate that all Ca compositions predict that less than 5% of calcium is stable at 1000°C in the perovskite structure, which is consistent with the decomposition behavior observed in LR2 for the 10% Ca.

The peculiar decomposition behavior of LCF compounds can be explained by considering the ordering of oxygen vacancies in the perovskite structure. The material

decomposes at two discrete oxygen partial pressures at every temperature, with discrete Gibbs formation energies, rather than a progressive shift, because the material is not single phase at the submicron scale under reducing conditions. There have been multiple studies that have reported the coexistence of brownmillerite with perovskite on this scale.^{16–18} These small domains can be difficult to observe in diffraction data due to the small coherent scattering domains.¹⁹ After the oxygen disassociation in LR1, there are enough oxygen vacancies to reduce all of the Ca in the material from CaFeO_3 to $\text{CaFeO}_{2.5}$, which is the composition of the vacancy ordered brownmillerite. The extent to which the material can be decomposed in LR2 at a given temperature is dependent on the ability of calcium ions to cluster and form domains of ordered oxygen vacancies. The probability of this occurring increases with increasing Ca content and increases with temperature because increased diffusion enables the delivery of calcium to ordered oxygen vacancy domains. This is consistent with the rapid decrease in mass shown in Figure 4.4 during the initial stages of LR2 due to statistical clustering of calcium, which saturates as those regions are decomposed. This is followed by a semi-linear decomposition at a substantially reduced rate, which could be the result of calcium migration to ordered vacancy clusters via a diffusion controlled process. It was shown in Figure 4.4 that when the 30% Ca specimen was re-oxidized, diffraction peaks correlating to ordered oxygen vacancies appeared. Furthermore, we have compared the equilibrium P_{O_2} for the decomposition of brownmillerite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) from literature to our values in measured in LR2.²⁰ As can be seen in Table 2, these equilibrium oxygen partial pressures for decomposition are nearly identical, supporting the claim that it is submicron domains of the brownmillerite structure that is being decomposed in LR2. This result indicates that

as long as Ca is randomly distributed throughout the structure, the stability will be nearly equivalent to that of LaFeO_3 as is the case with the 10% Ca substituted samples up to 900°C. Transversely, when calcium starts to cluster under reducing atmospheres in the perovskite structure, the thermodynamically favorable ordered oxygen vacancy state will form, which will then be susceptible to decomposition at two orders of magnitude higher oxygen partial pressures.

4.4 Conclusions

It has been shown that three mass loss regions occur in the calcium substituted lanthanum ferrites. The first region indicates the LCF materials synthesized in air are nearly entirely charge compensated by Fe^{4+} , which is then reduced to Fe^{3+} by the formation of oxygen vacancies. The decomposition data indicates two discrete decompositions in LR2 and LR3. Mass loss in LR2 is from the decomposition of small domains of brownmillerite, which exists in the perovskite matrix as small intergrowths. These brownmillerite domains are decomposed at substantially higher oxygen partial pressures than that of lanthanum ferrite. The stability of the calcium substituted perovskite structure under reducing conditions is dependent on the ability of the Ca to remain randomly distributed throughout the structure. This randomness is achieved by the 10% Ca substituted structure up to 900°C but is reduced to approximately 5% Ca at 1000°C. Greater than 10% calcium concentrations may be stable at lower temperatures. These materials have many potential applications as high temperature oxygen conducting membranes. The equilibrium oxygen partial pressures and decomposition behavior discussed here can be used to help design and determine the operation limitations of these materials. The material discussed here was developed under patent 6,492,290 B1.⁶

4.5 Author Justification

The research presented in this publication was carried out and authored by Patrick Price as a partial fulfillment of the requirements for a Doctoral degree in Materials Science and Engineering at Boise State University, under the advisement and supervision of Dr. Darryl P. Butt. Dr. Darryl P. Butt contributed greatly with financial support and technical guidance throughout the research and provided in-depth critical reviews of the article during the writing process.

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CHAPTER FIVE: MICRODOMAIN FORMATION, OXIDATION, AND CATION
ORDERING IN $\text{LaCa}_2\text{Fe}_3\text{O}_{8+y}$

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Microdomain Formation, Oxidation, and Cation Ordering in $\text{LaCa}_2\text{Fe}_3\text{O}_{8+y}$

Patrick M. Price¹

Nigel Browning²

Darryl P. Butt^{1,3}

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¹*Department of Materials Science & Engineering, Boise State University, 1910
University Dr., Boise, ID 83725*

²*Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory,
3335 Innovation Boulevard Richland, WA 99354*

³*Center for Advanced Energy Studies,
995 University Boulevard, Idaho Falls, ID 83401*

Abstract

The compound $\text{LaCa}_2\text{Fe}_3\text{O}_8$, also known as the Grenier phase, is known to undergo an order-disorder transformation (ODT) at high temperatures and oxidation has been observed when the compound is cooled in air after the ODT. In this study, we have synthesized the Grenier compound in air using traditional solid state reactions and investigated the structure and composition before and after the ODT. Thermal analysis showed that the material undergoes an order-disorder transformation in both oxygen and argon atmospheres with dynamic, temperature dependent, oxidation upon cooling. Results from scanning transmission electron microscopy (STEM) suggest that the Grenier phase has preferential segregation of Ca and La on the two crystallographic A-sites before the ODT, but a random distribution above the ODT temperature. Furthermore, STEM images suggest the possibility that oxygen excess may exist in La-rich regions within microdomains rather than at microdomain boundaries.

5.1 Introduction

There has been a great interest in lanthanum calcium ferrite LCF materials for potential applications as oxygen conducting membranes in high temperature electrochemical devices due to their excellent chemical and thermal stability.¹⁻⁶ Despite this interest, the LCF material system is not fully understood. This is due, in part, to limitations in the ability to adequately characterize these materials using diffraction techniques. The structural similarity of the multiple phases present in the system result in the convolution of peaks in diffraction patterns and an order-disorder transformation (ODT) in Ca-rich specimens result in a quenched microstructure, which deceptively gives a cubic diffraction pattern.⁷⁻¹⁶

Three distinct crystal structures exist in the LCF system: ABO_3 (perovskite), $\text{A}'\text{A}_2\text{B}_3\text{O}_8$ (Grenier), and $\text{A}'_2\text{B}_2\text{O}_5$ (brownmillerite). The Grenier and brownmillerite phases may be considered derivatives of the perovskite structure with ordered oxygen vacancies in the pseudo-cubic $[101]$ direction. The difference between the three structures (Figure 5.1) is illustrated in the stacking sequence octahedra (O) and tetrahedra (T) given as follows: OOO (perovskite), OOT (Grenier), and OTOT' (brownmillerite). Nearly identical planes of octahedra are common to all three crystal structures, allowing for the seamless stacking of multiple crystal structures, called intergrowths, by sharing of a common octahedral plane. Intergrowth structures in the LCF system were first observed in the early 1980's using high resolution transmission electron microscopy.^{7, 11, 15}

Figure 5.1 Relationship between the orthorhombic perovskite, Grenier, and brownmillerite crystal structures. The red squares represent ordered oxygen vacancies.

When quenched from 1400°C in air, the $\text{LaCa}_2\text{Fe}_3\text{O}_8$ compound gives cubic perovskite diffraction pattern and an increase in mass is observed, suggesting the transformation of tetrahedra to octahedra via the disordering of oxygen vacancies. However, high resolution transmission electron microscopy (TEM) revealed a more complicated microstructure, which suggested that microdomains of ordered oxygen vacancies persist in the material with sizes on the order of tens of nanometers.¹⁷ A model was proposed in which the axis normal to ordered oxygen vacancies of each microdomain could be permuted in three mutually orthogonal directions producing a structure that is metrically cubic.¹⁷ It was also suggested that the observed mass gain was due to the oxidation of domain walls upon cooling and that the structure observed in quenched phases was representative of the high temperature structure.¹⁷ In a separate investigation by Gibb¹⁸, $\text{LaCa}_2\text{Fe}_3\text{O}_8$ samples were quenched at different rates, resulting in different amounts of oxidation, with the least amount of oxidation with the fastest quench. Gibb also demonstrated that Mossbauer spectroscopy of quenched samples indicated the formation of microdomains; however, he suggested that this did not preclude the existence of a different structure at high temperatures.

In the work presented here, we have synthesized the $\text{LaCa}_2\text{Fe}_3\text{O}_8$ Grenier phase in air using solid state ceramic processing techniques. We have revisited the order-disorder transformation, oxidation, and microdomain structure using modern instruments. Simultaneous differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) was used for the *in situ* investigation of phase change energies and measurements of dynamic oxidation with sub-microgram resolution. Additionally, high resolution microscopy has progressed significantly since the time of earlier investigations.^{17,18}

Scanning transmission electron microscopes (STEM) equipped with aberration correction and high angle annular dark field (HAADF) detectors are capable of achieving sub-angstrom resolution, with z-contrast imaging and electron energy loss spectroscopy (EELS).^{19–23}

5. 2 Experimental Procedures

The $\text{LaCa}_2\text{Fe}_3\text{O}_8$ compound was synthesized using solid-state reactions. Stoichiometric portions of calcium carbonate (Puritronic® CaCO_3 , 99.99% pure metals basis), iron (III) oxide (Fe_2O_3 , 99.995% pure), and lanthanum (III) oxide (Reacton® La_2O_3 , 99.999% pure) were combined to achieve the desired composition. Lanthanum oxide is hygroscopic and reacts with moisture in the air to form $\text{La}(\text{OH})_3$.²⁶ The moisture content of each precursor powder was determined and corrected for by loss on ignition (LOI) measurements by thermogravimetric analysis (Netszch STA-449, Burlington, MA 01803) prior to mixing each batch. Precursor powders were then mixed with yttira-stabilized zirconia media and isopropyl alcohol (IPA) in nylon jars for 12 hours on a table top mixer, and subsequently calcined at 1000°C for 8 hours in a box furnace. The calcined powder formed a cake-like compact, which was crushed and then mixed as described above for an additional 10 hours. The calcined mixture was dried and isostatically pressed into green pellets. The pellets were sintered in air at 1250°C for 24 hours. The sintered pellets were then crushed, ground to a fine powder with a mortar and pestle, and then re-pressed and re-sintered for another 24 hours. The pellets were re-crushed, pressed, and sintered a total of 6 times to ensure homogeneity. The orthorhombic structure of synthesized samples was verified using x-ray diffractometer

(Bruker AXS D8, Madison, WI) with parallel beam geometry and was consistent with the indexed patterns of Hudspeth *et al.*²⁴

All thermal analysis experiments were performed in a STA-449 (Netsch STA-449, Burlington, MA) equipped with a simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC-TG) carrier, silicon carbide furnace, alumina protective tube, and 85 μ l platinum rhodium (Pt/Rh) crucibles. Temperature calibrations were performed via the melting of 5 pure metals. Correction files with empty crucibles were obtained prior to all DSC-TGA experiments in order to remove background and noise from the sample signal. An empty crucible was used as a reference for all measurements.

Scanning transmission electron microscopy was performed on a FEI Titan 80-300TM (FEI Hillsboro, OR) equipped with a CEOS hexapole spherical aberration corrector (Corrected Electron Optical Systems GmbH, Heidelberg, Germany) for the probe forming lens, high angle annular dark field detector, and a high resolution Gatan Imaging Filter (GIF) for EELS (Gatan, Pleasanton, CA). Samples for STEM were prepared on a FEI Quanta dual FIB/SEM.

5.3 Results and Discussion

The change in mass as a result of the oxidation after order-disorder transformation was measured in quenched specimens in previous investigations.^{17,18} In the work presented here, we have measured the change in mass with thermogravimetric analysis and found that the oxidation behavior during cooling is dynamically dependent on temperature and reversible upon heating. The thermogravimetric analysis data in Figure 5.2 shows the change in mass of the $\text{LaCa}_2\text{Fe}_3\text{O}_8$ Grenier compound before and after the order-disorder transition. There is a small mass loss (0.3%) when the sample is heated to

Figure 5.2 Thermogravimetric analysis (solid line) of the oxidation behavior before and after the order-disorder transformation. After quenching the temperature (dashed line) is cycled from 500°C to increasingly higher temperatures to illustrate the dynamic oxidation behavior and the stability of the microdomains at lower temperatures.

Figure 5.3 Thermogravimetric analysis of the oxidation behavior after treatment in argon. Clean air is introduced after quenching at 500°C resulting in oxidation of the sample.

Table 5.1 Order-Disorder transformation temperatures measured by DSC

Run	Type	DSC Onset (°C) $\pm 15^\circ\text{C}$	DSC Peak (°C) $\pm 5^\circ\text{C}$
Argon		1288	1318
Air Cycle #1	Heating	1285	1312
Air Cycle #2		1236	1291
Air Cycle #3		1236	1292
Argon		1163	1109
Air Cycle #1	Cooling	1083	1009
Air Cycle #2		1083	1013
Air Cycle #3		1083	1013

Figure 5.4 Thermogravimetric analysis of the oxidation behavior after repeated heat treatments above the order-disorder transition temperature.

Figure 5.5 Comparison of endothermic DSC signals during the order-disorder transformation and the exothermic peaks suggesting a structural rearrangement during cooling.

1360°C due to the increase in thermally created oxygen vacancies. When the sample undergoes the endothermic order-disorder transformation, there is a characteristic 0.06% increase in mass that always occurs when heated in air. As the sample is cooled to 500°C there is a comparatively large increase in mass. When the ramp is halted in the isothermal region at 500°C, oxidation stops. Likewise, when the specimen is heated to 600°C, the oxygen gained during cooling is released as indicated by a proportional mass loss. This same behavior is observed when the temperature is reduced back to 500°C and then back up to 700°C. The temperature dependent oxygen uptake and release behavior suggests that the situation is more complicated than a simple oxidation of domain walls. An alternative explanation is the formation of a material with a larger equilibrium concentration of thermally activated oxygen vacancies when the $\text{LaCa}_2\text{Fe}_3\text{O}_{8+y}$ compound is quenched. When the temperature is cycled from temperatures 800°C or higher, there is a systematic decrease in the amount of oxidation of the material when the temperature is returned to 500°C, indicating a restructuring of the material back to the starting $\text{LaCa}_2\text{Fe}_3\text{O}_8$ compound.

Previous investigations have focused on the oxidation after the ODT in samples treated in air. The thermogravimetric data in Figure 5.2 indicates that there is little to no gain in mass at the ODT temperature and that oxidation does not begin until the sample is cooled. Since no oxygen is required during the ODT, it suggests that Grenier compounds treated in oxygen deficient atmospheres may also undergo the ODT. The ODT and oxidation behavior of the $\text{LaCa}_2\text{Fe}_3\text{O}_{8+y}$ compound treated in an oxygen deficient atmosphere are shown in the TG/DSC data in Figure 5.3. The Grenier specimen was heated to 1360°C and then cooled to 500°C in high purity argon. An endothermic peak at

in the DSC signal at approximately 1300°C confirms that the ODT also occurs in oxygen deficient atmospheres. An exothermic peak is present in the DSC signal during cooling, indicative of a structural reconfiguration. At 500°C, oxygen is introduced for the first time in the form of clean air, resulting in the immediate oxidation of the Grenier compound to a mass above that of the starting material. The temperature is then increased to 700°C and then decreased to 200°C, resulting in the same temperature dependent oxygen uptake and oxygen release observed in Grenier specimens treated in air. This suggests that Grenier specimens treated in oxygen-deficient atmospheres result in a similar microdomain structure as those treated in air and that oxidation is a result of the microdomain structure, rather than the formation of the microdomain structure as a result of oxidation.

The temperature dependent oxidation of the Grenier compound is evident in the TG/DSC data presented in this study and previous studies have shown the existence of ordered oxygen vacancies and microdomain texture¹⁷; however, it remains unclear if this is representative of the Grenier compound above the ODT temperature. In order to gain insight into this question, the starting $\text{LaCa}_2\text{Fe}_3\text{O}_8$ Grenier compound was heated above the ODT temperature in air, quenched, and reheated above the ODT temperature in two subsequent cycles as shown in the TG/DSC data in Figure 5.4. In the first cycle, the characteristic endothermic peak is present in the DSC signal with the small characteristic increase in mass shown in the TG signal during the ODT. On cooling, there is also an exothermic peak in the DSC signal indicative of restructuring. On both of the subsequent heating and cooling cycles, both the endothermic and exothermic peaks are present in the DSC signal and the oxidation behavior is nearly identical to the initial heating and

cooling cycle. This suggests that the high temperature structure is not retained and that the microdomain structure must reorder during the ODT.

The DSC signals from both Figures 5.3 (argon) and 5.4 (air) are plotted as a function of temperature in Figure 5.5 and tabulated in Table 5.1. The order-disorder transition temperature was found to be slightly higher in argon atmospheres than in air. The ODT temperature measured from the second and third cycles in air were slightly lower than the first. The lowering of the phase transition temperature may be due to the lowering of the energy barrier due to the presence of available oxygen. The DSC signals in the upper region of Figure 5.5 show an exothermic peak observed during cooling, indicative of a reconstructive transformation. There is a large difference in the exothermic peak shape and position between samples treated in air and argon. The exothermic peak of the argon treated sample has a sharper peak and occurs at a temperature $\approx 100^\circ\text{C}$ higher than air treated samples, indicating the presence of excess oxygen may act to impede the phase transition during cooling.

It is evident in the DSC and thermogravimetric data that:

1. The room temperature microdomain structure is not likely representative of the high temperature ($<1320^\circ\text{C}$) structure based on exothermic peaks observed in the DSC data upon cooling and the endothermic peaks of the quenched microdomain structure on subsequent re-heating.
2. The quenched microdomain structure is oxidized upon cooling resulting in an increase in the oxygen stoichiometry above that of the starting material.

3. The microdomain structure is likely present in Grenier compounds treated in both oxidizing and oxygen deficient atmospheres above the ODT temperature, based on the oxidation behavior shown in Figures 5.2-5.4.
4. The oxidized microdomain sample can be returned to the starting oxygen stoichiometry by annealing the material above 700°C.

In order to help elucidate the cause of the dynamic temperature-dependent oxidation behavior, aberration corrected scanning transmission electron microscopy (STEM) was used to investigate the structure of the $\text{LaCa}_2\text{Fe}_3\text{O}_{8+y}$ Grenier phase treated above and below the order-disorder transformation temperature. The STEM image of the low temperature Grenier compound with a pseudo cubic [100] zone axis is shown in Figure 5.6a. While the oxygen atoms cannot be visualized directly in this image, the iron atoms located in the tetrahedra planes are physically offset as shown in the superimposed crystal structure, allowing for the distinction between planes octahedrally and tetrahedral coordinated iron. There are two unique crystallographic A-sites in the orthorhombic $\text{P2}_1\text{ma}$ space group.²⁴ Broadening of peaks in Mossbauer studies of the Grenier compound led Gibb to conclude that different coordination states of iron atoms were present and that the Ca and La A-site cations were randomly distributed throughout the structure.¹⁸

Figure 5.6 STEM images used for the comparison of the structure before (left) and after (right) the order-disorder transformation. The two micrographs are situated so that tetrahedral planes are lined up as indicated by the horizontal white lines at the top of the image. The z-contrast seen in the Grenier compound on the left indicates A-site cation ordering where the bright A-site positions (green spheres) are preferentially substituted by La and the darker A-site positions (blue spheres) are preferentially occupied by Ca. The z-contrast seen in the image on the right (microdomain structure) indicates the random occupation of La and Ca on the A-sites based on the random contrast of A-site positions. The smaller brown spheres indicate the position of the iron atoms.

Figure 5.7 STEM image of Grenier phase with overlaid EELS core-loss signal. The EELS data show that the bright columns are preferentially occupied by lanthanum while the A-site locations on either side of the tetrahedra are preferentially occupied by calcium.

A STEM image of the starting Grenier compound is shown in the left side of Figure 5.6. The two crystallographic A-sites are indicated by the green and blue spheres in the superimposed crystal structure in the top-left corner. The green A-site sits between two planes of octahedra and the blue A-site sit between a plane of octahedra and a plane of tetrahedra. The STEM image of the left has a bright row of atomic columns on the green site and darker atomic columns on all of the blue sites. The z-contrast afforded by the high angle annular dark field (HAADF) detector suggests that the green A-site located between octahedral planes is preferentially substituted by the larger lanthanum ($Z=57$) over the calcium cation ($Z=20$). The z-contrast can be extended to show that the intensity of the iron cations ($Z=26$) are, on average, brighter than the adjacent A-sites believed to be preferentially occupied by calcium. If the larger lanthanum cation was randomly on the blue A-site, the average intensity would be predicted to be periodically higher than adjacent iron columns. The preferential occupation of lanthanum between octahedral planes is also confirmed in the electron energy loss spectroscopy (EELS) superimposed over the Grenier phase shown in Figure 5.7.

A STEM image of the quenched microdomain structure is shown on the right hand side of Figure 5.6, which is also oriented with a pseudo cubic [100] zone axis. For ease of comparison, the tetrahedral planes of the two STEM images in Figure 5.6 are lined up. It is evident from the random distribution of z-contrast across the two A-sites in the STEM image, that lanthanum and calcium are randomly distributed on the two crystallographic sites in the quenched microdomain structure.

The STEM image shown in Figure 5.8 is that of a single microdomain oriented with a pseudo cubic [100] zone axis. The white tick marks on the top and bottom identify

the planes of tetrahedra in the structure. There are no stacking faults or disruption of the periodicity of the spacing of the tetrahedral planes horizontally; however, the characteristic offset of the iron cations in the tetrahedral plane disappear in a domain on the right side of the image. The FFT for this region is shown on the right, indicating cubic symmetry. In contrast, the FFT from the left side of the image indicates the characteristic tetragonal symmetry of the cations in the Grenier compound. The images on the lower left and right side of Figure 5.8 are of the original z-contrast STEM image with a threshold subtraction adjusted so pixels equal to or less than the intensity of iron cations are removed from the image. The remaining atomic areas of bright contrast are representative of atomic columns that have an average z-contrast greater than iron and therefore contain higher concentrations of lanthanum. The quantity of remaining bright pixels in the image was quantified with digital micrograph. There are approximately 20% more bright pixels on the right side of the image. While this analysis is semi-qualitative, it suggests that the region with cubic symmetry in the otherwise uninterrupted periodicity of tetrahedral planes of a single microdomain has a higher lanthanum concentration than the area on the left. This suggests that oxidation may occur at lanthanum rich regions throughout the material. This is supported by the fact that no ordered oxygen vacancies have been observed in lanthanum ferrite compounds. It has been demonstrated that lanthanum ferrite will maintain the perovskite structure in extremely reducing atmospheres, and will decompose prior to the formation of ordered oxygen vacancies.²⁵

It was originally proposed by previous authors that the oxygen excess observed in quenched microdomain samples was located in the domain wall.¹² Other authors have analyzed microdomain boundaries in other systems with STEM and EELS and found no

evidence of oxidation at domain boundaries.²⁶ The STEM image in Figures 5.6-5.8 clearly demonstrate the transition from a preferentially occupied state of A-site cations, with lanthanum stabilized between two octahedral planes, to a random distribution of the two A-site cations in the microdomains structure. It is unlikely that clusters of lanthanum will be able to stabilize the ordered oxygen vacancies at room temperature and offer an alternative explanation as to where oxidation occurs in the microdomains texture of quenched Grenier compounds.

Figure 5.8 A STEM image of a single microdomain with a [100] view direction. The region on the right side has a cubic symmetry as indicated by the FFT on the right. The FFT from the left side of the image gives the expected tetragonal symmetry of the cations in the Grenier structure. The white tick marks at the top and bottom illustrate the periodicity of the tetrahedral planes. The results of a threshold subtraction are shown on the sides. Image analysis reveals a 20% increase in the number of bright pixels on right side of the STEM image, indicating a higher concentration of lanthanum.

The oxidation as a result of lanthanum clustering is supported by two other observations. First, the thermogravimetric data in Figure 5.2 shows that the oxidation behavior is stable until the sample is annealed at temperatures greater than 700°C. Oxygen is mobile well below 700°C, suggesting that the reconstruction of the low temperature Grenier compound is likely limited by cation diffusion. Second, if the La^{3+} cations are randomly distributed, then 1/3 would be expected to reside between octahedral planes and 2/3 would be expected to reside in between octahedral and tetrahedral planes. Therefore, clusters of La^{3+} cations residing on the Ca^{2+} sites would need to be locally stabilized by excess oxygen. One oxygen anion (O^{2-}) will compensate for the local charge difference created by every two La^{3+} cations. This would result in a minimum expected oxidation stoichiometry increase of $y=0.33$ giving $\text{LaCa}_2\text{Fe}_3\text{O}_{8.33}$. The measured mass gain from thermogravimetric data in samples quenched in air was 1.29%, suggesting an estimated stoichiometry increase to $\text{LaCa}_2\text{Fe}_3\text{O}_{8.41}$, which is in good agreement with the expected value. The re-distribution of lanthanum clusters to an ordered state gives a phenomenological explanation as to the reason for the oxidation in the microdomain structure. It is important to note that this domain structure is a result of the reconstruction of the high temperature phase upon cooling.

The STEM imaging technique was also used to investigate microdomain boundaries. The high resolution STEM image in Figure 5.9a shows a typical microdomain texture reminiscent of those reported by previous authors.¹⁷ The authors suggested that the microdomain texture was the result of the permutation of the OOT stacking sequence of the Grenier phase in three mutually orthogonal directions. The atomic resolution micrograph shown in Figure 5.9b shows an additional level of

complexity. The tetrahedral planes in the two microdomains at the top and bottom of the image are oriented in the same direction, but are offset by a single plane as indicated by the arrows. Rather than the tetrahedral planes converging to form a stacking of two consecutive tetrahedra, a small microdomain forms orthogonally between the two. This was representative of most of the area of the microdomains when viewed from the [100] type direction. Most of the tetrahedral planes were oriented in one direction with only small domains oriented orthogonally separating mismatched tetrahedral planes.

A view of microdomain formation with a pseudo cubic [101] zone axis is shown in Figure 5.10. Unlike the [100] zone axis, which is equivalent when rotated 90 degrees, the [101] zone axis changes Fe-Fe bond lengths when rotated. Ordered oxygen vacancies are located parallel to the [101] direction and the iron spacing alternates between long and short bond lengths. When rotated 90 degrees to the [-101] direction, the Fe-Fe distance is equal. Both of these variations are seen in the STEM image with the (a) variant located in the bottom-left corner and the (b) variant located in the top-right corner. A mismatch of tetrahedral planes is also commonly found in this image and throughout the structure. However, there was no orthogonal formation of oxygen vacancies visible in this direction. The simultaneous presence of the two variants suggests that when the high temperature phase undergoes the exothermic reconstructive transition during cooling, there is equal likelihood of formation of different crystallographic orientations next to each other. The random occurrence of similar crystallographic orientations further illustrates that the microdomain structure is not representative of the high temperature phase and suggests that the microdomain texture

Figure 5.9 STEM image of the [100] zone axis of (a) typical microdomain structure and (b) a stacking mismatch of tetrahedral planes in the microdomain texture. Ordered oxygen vacancies form orthogonally to compensate for the mismatched stacking of the vertical ordered vacancies.

Figure 5.10 Crystallographic representation of the crystal structure (a) viewing down the pseudo cubic [101]. The Fe-Fe distance alternates between long and short as shown in the planes indicated by the arrows. (b) viewing down the [-101] zone axis. The Fe-Fe distance is fixed (c) STEM image showing microdomains in the [101] type orientation with both crystallographic variations present. The bimodal iron separation can be seen on the lower left and the equally spaced iron cations are located in the upper-right corner.

may result, at least partially, from the mismatch of tetrahedral planes during the reconstructive transformation.

5.4 Conclusions

Thermogravimetric analysis and DSC has revealed that the $\text{LaCa}_2\text{Fe}_3\text{O}_{8+y}$ Grenier compound undergoes a reconstructive phase transformation that is not retained in quenched samples with the microdomain structure. During the quenching process, a dynamic temperature dependent oxidation was observed, even in samples initially treated in oxygen deficient atmospheres. High resolution STEM images revealed the preferential occupation of lanthanum between octahedral planes and calcium between the octahedral and tetrahedral planes the Grenier compound. In contrast, the A-site cations were observed to be disordered in the microdomain structure after quenching from above the ODT temperature. We propose that the disordering of the lanthanum cations may be the cause for the oxidation behavior. Evidence has been presented to support the possibility of oxidation of lanthanum clusters within microdomains rather than oxidation segregated to domain walls. We observed misalignment in the stacking of tetrahedral planes that may also give rise to the microdomain texture seen at lower magnifications. The oxidized microdomain structure appears to release and uptake oxygen very rapidly at temperatures as low as 400°C and is metastable at temperatures below 700°C, indicating that this material may be worth investigating as a low temperature oxygen conductor. The structure of the high temperature phase is still unknown and is the subject of future work.

5.5 Author Justification

The research presented in this publication was carried out and authored by Patrick Price as a partial fulfillment of the requirements for a Doctoral degree in Materials Science and Engineering at Boise State University, under the advisement and supervision of Dr. Darryl P. Butt. Nigel Browning generously donated STEM time, gave electron microscopy advice and training, and contributed to Patrick's education via an internship at Pacific Northwest National Laboratory. Dr. Darryl P. Butt contributed greatly with financial support and technical guidance throughout the research and provided in-depth critical reviews of the article during the writing process.

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CHAPTER SIX: CONCLUSIONS

Calcium substituted lanthanum ferrites are an important technological material, especially in the use of syngas reactors. These materials offer good chemical stability with good chemical selectivity and high oxygen flux. Phase transformations including structural, chemical, and magnetic changes need to be characterized to better understand the performance and failure of LCF materials in engineering applications. In this study, we have discovered and characterized phase transformations in the LCF system as a function of calcium composition, temperature, and atmosphere with a variety of techniques. In addition, we have investigated the effect of these transformations and calcium substitution on changes in expansion behavior, which is relevant in choosing appropriate operating temperatures, thermal cycling, and co-material selection of syngas reactors.

In Chapter One, we investigated phase transformations and changes in expansion behavior in calcium doped lanthanum ferrites synthesized in air by solid state reactions. The Grenier phase ($\text{LaCa}_2\text{Fe}_3\text{O}_8$) was found to undergo an order-disorder transition at approximately 1320°C . As previously reported by Grenier *et al.*, LCF materials cooled in air after exceeding the order disorder transition temperature have a complicated microdomain structure, which falsely appear to be cubic perovskite by diffraction methods.¹⁻³ Since materials synthesized above the order-disorder transformation temperature will likely contain small domains of ordered oxygen vacancies, which can

only be observed by high resolution microscopy techniques, the LCF specimens in this study were synthesized well below this temperature.

Rietveld refinement of XRD data indicates the solubility limit of calcium in the perovskite structure is 38% in samples synthesized by solid state reactions in air at 1250°C. Grain sizes were substantially decreased in 10, 20, and 30% Ca substituted samples. A large increase in grain size was observed in the 40% sample, possibly indicating small amounts of secondary phases or intergrowths may enhance the grain growth.

Calcium doped lanthanum ferrites were found to undergo an orthorhombic to rhombohedral transition at elevated temperatures, which is first order in nature. The orthorhombic to rhombohedral transition temperature decreases with increasing calcium concentration and decreasing partial pressure of oxygen. Increasing the temperature further will result in a second order transition to the cubic structure, which was observed in the $\text{La}_{0.6}\text{Ca}_{0.4}\text{FeO}_{3-\delta}$ specimen. The coefficient of thermal expansion is increased after the phase transition for all compositions. The increase in expansion coefficients after the orthorhombic to rhombohedral transition is increased with larger calcium concentrations.

In Chapter Two, the relationship between a nonlinear thermal expansion, measured Néel temperatures, and structural variations were explored in calcium, strontium, and barium substituted lanthanum ferrites. Non-linear thermal expansion behavior of $\text{La}_{0.9}\text{R}_{0.1}\text{FeO}_3$ (R=Ca, Sr, Ba) was correlated with antiferromagnetic to paramagnetic phase transformation at the Néel temperature consistent with the findings of Selbach *et al.* in the investigation of undoped LaFeO_3 .⁴ Néel temperatures determined through dilatometry, XRD, and VSM were in agreement and were consistent with values

available in literature.⁵⁻⁷ This is the first such study that has used a combination of these three techniques to measure the both the Néel temperature and expansion behavior for alkaline-doped perovskites. The results confirm the results of Selbach *et al.* that the thermal expansion behavior has contributions from magneto-static coupling.

Differences between observed Néel temperatures in LF, LCF, LSF, and LBF specimens were attributed to both the nature of the charge compensation mechanism and the effect of the substituent on the Fe-O1-Fe bond angle involved in the super-exchange interaction. For divalent calcium-substituted LaFeO₃, the coupling is significantly disrupted by the presence of tetravalent iron from charge compensation and a smaller Fe-O1-Fe bond angle. For strontium and barium-substituted LaFeO₃, it is suspected that charge compensation was accomplished by both the reduction of iron and the formation of oxygen vacancies, the latter of which would offset the disruption to the long range magnetic ordering caused by the reduction of iron cations compared to the calcium doped samples. In addition, this disruption is mitigated by an increase in both the bond angle and the strengthening of the Fe-O1-Fe super-exchange interaction. The correlation between calculated bond angles from neutron diffraction data and Néel temperatures suggest that the super-exchange still occurs along the c-axis of the Pbnm unit cell for divalent doped samples. The directions of the antiferromagnetic moment in LCF, LSF, and LBF were ambiguous in our neutron diffraction data, but likely remained slightly canted along the a-axis, as is suggested in literature for the case of pure LF.⁸

In Chapter Three, we investigated the decomposition of calcium substituted lanthanum ferrites in reducing atmospheres. Three mass loss regions were found to occur in LCF materials heated in reducing H₂-Ar gas mixtures. The mass loss in the first region

scales with calcium substitution. Measured mass changes in LR1 values are almost exactly equal to the mass associated with the loss of one oxygen anion for every two calcium cations in each composition suggesting that the starting material was nearly fully oxidized prior to the treatment in reducing atmospheres. This indicates LCF materials synthesized in air are nearly entirely charge compensated by Fe^{4+} , which is then reduced to Fe^{3+} via the formation of oxygen vacancies.

The mass losses observed in the other two regions are due to oxygen evolution from decomposition reactions. Rather than a progressive shift in value, the measured decomposition oxygen partial pressures in LR2 were exactly the same for all calcium compositions at every temperature. No mass loss was observed in LR2 for the pure LaFeO_3 material. The decomposition proceeded to a point of near saturation where minimal changes in mass were observed. The measured mass loss in LR2 was found to scale with calcium content, but was always less than expected for total decomposition of calcium in the material. Furthermore, fraction of calcium decomposed in LR2 for a given composition increased with increasing temperature. Further decomposition was achieved by decreasing the oxygen partial pressure roughly two orders in magnitude until the third mass loss region, LR3, was observed. Pure lanthanum ferrite also began to decompose in this region. Again, rather than a progressive shift in value, the measured decomposition oxygen partial pressure in LR3 was nearly the same for all calcium compositions, including LaFeO_3 . All samples decomposed completely in LR3.

The behavior of the two discrete singular decomposition oxygen partial pressures for all compositions is explained in the following. The decomposition in LR3 goes to completion and is clearly a result of the decomposition of lanthanum ferrite. The

measured decomposition oxygen partial pressures in LR3 are consistent with those found in literature for LaFeO_3 .⁹ The decomposition in LR2 is clearly related to presence of calcium. The decomposition oxygen partial pressures measured in LR2 are consistent with those found in literature for pure brownmillerite ($\text{Ca}_2\text{Fe}_2\text{O}_5$).¹⁰ It is likely that the oxygen vacancies created in LR1 order in calcium clusters to form localized nanodomains of $\text{Ca}_2\text{Fe}_2\text{O}_5$, which are then decomposed in LR2. The stability of calcium under reducing atmospheres is increased if calcium is maintained in the randomly distributed perovskite state, free of oxygen vacancy ordering. This randomness is achieved by the 10% Ca substituted structure up to 900°C but is reduced to approximately 5% randomly distributed Ca at 1000°C. Once oxygen vacancy ordering begins, the stability of the material in reducing atmospheres is substantially reduced by nearly two orders of magnitude.

Increasing the calcium content in oxygen conducting membranes manufactured from LCF materials has the advantage of increasing oxygen flux. However, increasing the calcium content will eventually result in oxygen vacancy ordering, substantially decreasing the stability of the membrane in reducing atmospheres. The research here has shown that the maximum amount of randomly distributed calcium increases with decreasing temperatures. The 10% calcium composition was shown to be stable up to 900°C but higher stable calcium concentrations can likely be achieved at lower operating temperatures. These membranes can be optimized to achieve the greatest flux by simultaneous control of the operating temperature and maximum stable calcium concentration without compromising chemical stability.

In Chapter Five, the peculiar oxidation and complicated microstructure of the $\text{LaCa}_2\text{Fe}_3\text{O}_{8+y}$ Grenier compound has been investigated. Thermogravimetric analysis and DSC has revealed that the Grenier compound has a reconstructive phase transformation that is likely not retained in the quenched microdomain samples. During the quenching process, a temperature dependent dynamic oxidation is observed, even in argon treated samples not exposed to oxygen until 500°C. High resolution STEM images have revealed the preferential occupation of lanthanum between octahedral planes and calcium between the octahedral and tetrahedral planes in the low Grenier compound. In contrast, the A-site cations are found to be disordered in the quenched microdomain structure. We have proposed that the disordering of the lanthanum cations is the driving force behind the oxidation behavior. Evidence has been presented to support the possibility of oxidation of lanthanum clusters in microdomains rather than oxidation segregated to domain walls as previously speculated.^{1, 11} We observed a common misalignment in the stacking of tetrahedral planes that may also give rise to the microdomain texture seen from wider fields of view. The oxidized microdomain structure appears to release and uptake oxygen very rapidly at temperatures as low as 400°C and is metastable at temperatures below 700°C, indicating that this material may be worth investigating as a low temperature oxygen conductor. The structure of the high temperature phase is still unknown and is the subject of future work.

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