

IMPROVING SOLID OXIDE FUEL CELL CATHODE
STABILITY WITH CHEMICAL SUBSTITUTIONS

BY

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B.S. ALFRED UNIVERSITY 2013

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This work represents over four thousand hours of controlled atmosphere furnace time, five hundred hours of instrument time, Rietveld analysis on one hundred and fifty seven x-ray patterns with up to five phases in each, dozens more supporting data sets without full refinements, four DOE reports, two posters, and an unquantifiable amount of time reviewing literature. Naturally, this could not have been done without the people in my life that have supported me and continue to do so.

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ABSTRACT

The chemical flexibility of the perovskite structure allows enormous opportunity to modify lanthanum strontium manganite (LSM), a material that has been demonstrated to be a practical and efficient solid oxide fuel cell cathode. Calcium and nickel substitutions on the A and B sites, respectively, have been identified as potentially stabilizing substitutions on the basis of thermodynamic stability in the perovskite structure and compatibility with other materials in the fuel cell. In this study, the phase stability of YSZ-LSM composites is evaluated experimentally.

LSM materials with chemistries $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM-20), $\text{La}_{0.8}\text{Sr}_{0.1}\text{Ca}_{0.1}\text{MnO}_{3-\delta}$ (LSM+Ca), $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ (LSM+Ni), and $\text{La}_{0.8}\text{Sr}_{0.1}\text{Ca}_{0.1}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ (LSM+Ca+Ni), were annealed at 850°C and 1350°C in a compact with 8 mol% yttria stabilized zirconia (YSZ) to evaluate potential reactions between the two materials. Substituting calcium for A-site strontium transformed more than half of the zirconia to a cubic calcia stabilized phase. Nickel substitutions to B-site manganese stopped this transformation, but encouraged precipitation of up to 12 weight percent lanthanum zirconate, versus about 5 weight percent for calcium modified LSM and 3 percent for the base chemistry. SEM analysis shows that the zirconate crystallizes with a fine grained microstructure, and is especially prominent in samples intentionally depleted of manganese. Formation of the zirconate phase trends closely with an expansion of the LSM unit cell, suggesting the material becomes lanthanum deficient as the reaction takes place. CO_2 enriched air was shown to be the most reactive atmosphere, and incorporating 3% H_2O into the atmosphere limited zirconate formation, especially for the nickel substituted sample.

All LSM materials assumed R-3c symmetry after synthesis, however, calcium containing samples tended to form a Pnma phase as the material was annealed. Similarly to the observations on zirconate formation, CO_2 enriched air encouraged this development and humid air slowed transformation. The samples annealed in humidified atmospheric air all adopted and remained in the R-3C phase, with no other reactions taking place. The space group symmetry is closely related to the Goldschmidt Tolerance Factor, which changes with chemical substitutions, including hydroxide from humid air, and the oxidation and spin state of transition metals in the structure.

INTRODUCTION

A. Background on Solid Oxide Fuel Cells

Solid state energy conversion devices (solar cells, fuel cells) have garnered recent attention because of the increase in efficiency over conventional power generation. Without moving parts or an intermediate combustion step, potentially all of the energy contained in an energy source can be converted to usable DC electricity. A fuel cell refers specifically to a device that converts potential energy from chemical sources (i.e. hydrogen, methane, ethanol, or other hydrocarbons) directly to electricity.

Fuel cells have existed in several forms over the years. The technology was initially developed for defense and space applications,¹ but the recent interest in more efficient and less polluting technologies has directed developmental resources into “green” technology. Most generations of fuel cell technology are still in use today because advantages and disadvantages to each design may suit some applications better than others.

1. Past generations of fuel cell technology

The first fuel cell type device was invented in the early 19th century, when Sir William R. Grove (1811-1896) reported his “gas voltaic battery”. Grove had successfully designed a wet cell battery that was used in the American telegraph system, but like other batteries in this era, it necessitated frequent replacement of both the electrolyte and electrodes as the chemical energy is spent. Diminished potential as the battery was depleted emphasized the necessity for an energy source that could operate on a continuous supply of fuel. Using platinum electrodes with and a sulfuric acid electrolyte, Grove was able to demonstrate reverse electrolysis of water, (i.e. recombination of hydrogen and oxygen to generate electricity) with his second cell design. The Grove fuel cell was never a commercial source of electricity generation, and remained a proof of concept design for research programs. Research into fuel cells slowed for the next 100 years, in

part due to the commercial development of the internal combustion engine (ca. 1860).

The term fuel cell was coined in 1889 when Ludwig Mond and Charles Langer attempted to create a gas battery fueled by industrial coal gas and air.^{2,3} Impurities in the coal gas quickly poisoned the platinum black catalyst and the high cost of replacing this material proved prohibitive to further development.³ The Mond-Langer design was revisited in 1930 by Francis Bacon, who improved the fuel cell with a potassium hydroxide electrolyte and nickel electrode. After years of development, Bacon created a 6kW stack, enough to power a forklift, welding equipment and a circular saw as a demonstration.⁴ The Bacon design was licensed by the United Technologies Corporation and eventually evolved into the first commercial success of this technology, the alkaline fuel cell (AFC).³

The AFC design was first used in 1960 to provide on-board electric power to the Apollo space vehicle. The electrolytes high sensitivity to CO and CO₂ has limited terrestrial deployment, but remains the standard for aerospace. The highest performing fuel is pure H₂, but the elevated temperature (~250°C) allows for some other fuels to be utilized through internal reforming reactions. Reforming other fuels in an AFC comes at a cost to efficiency. Despite the flexibility of the cell with respect to electro-catalysts (Ni, Ag, metal oxides, and noble metals), other materials in the fuel cell are particularly hazardous, especially the electrolyte, which is concentrated potassium hydroxide (KOH) and the matrix housing the catalyst, which is typically asbestos.

Changing the electrolyte to a concentrated phosphoric acid addresses the sensitivity to CO and CO₂, allowing air to be used as an oxidant at the cathode⁵ but the highly corrosive nature limits construction materials to silicon carbide and graphite coated with a fluorinated polymer. Platinum is required for the catalyst because cathode side oxygen reduction is slower than in an AFC. Phosphoric acid

fuel cells (PAFCs) are the most developed and have largely replaced the AFC design. Efficiency is around 37-42%.⁶

Molten carbonate fuel cells (MCFCs) operate at high temperature ($>T_m$ of carbonate salts, around 650°C), allowing internal reforming of hydrocarbons. At elevated temperatures, nickel is sufficient to promote a reaction, mitigating costs associated with precious metal catalysts. In addition to this, Poisoning by CO and CO₂ is of no concern, and efficiencies have been demonstrated up to 60% with a bottoming cycle.³ The corrosive electrolyte presents similar challenges to the AFC and PAFC designs, but materials are still cheaper than in earlier generations.⁶

Low temperature polymer exchange membrane (PEM, PEFC) fuel are simple to operate and are constructed of relatively safe materials. There is a narrow window of operating conditions in which a PEM type fuel cell may function. The fluorinated sulfonic acid polymer membrane must be hydrated to conduct protons efficiently, so the temperature cannot exceed 100°C. The anode and cathode are of higher catalyst (precious metal) loading than other fuel cells, driving costs up. These catalysts are responsible for facilitating the oxidation of fuel and are extremely sensitive to fuel impurities (sulfur, ammonia, and/or carbon monoxide) necessitating significant fuel pretreatment. Ideally, pure hydrogen produced from electrolysis of water is used as an energy source, but producing hydrogen in this fashion is not cost-effective. The efficiency for PEM type fuel cells is around 35%.⁶ The low temperatures make this technology particularly attractive for small scale and portable applications, and some low voltage stacks are even available to consumers.

A solid oxide fuel cell (SOFC) is more specifically a cell constructed of high temperature ceramic materials. SOFCs offer several advantages over established fuel cell technology:

- High temperatures enable internal reforming of otherwise incompatible fuels into smaller and more easily oxidized hydrogen (H₂) or carbon monoxide (CO).
- Coupled with a system to recover wasted heat energy, SOFCs offer high efficiency (>70%) compared to other designs.
- Precious metal catalysts (platinum, rhodium, or palladium) can potentially be replaced by carefully engineered oxide materials with similar properties. Rare earth metals are cost prohibitive and are an obstacle in widespread deployment of fuel cell technology.
- Modular construction provides the opportunity to scale technology from very small (personal electronics) to very large (power plant) sizes.
- Production of by-products is minimized over other fuel cell types.
- The solid electrolyte is non-corrosive and can be constructed with traditional ceramic processing techniques.

A small SOFC power plant can be located on site for facilities that necessitate backup power or are in an area lacking infrastructure for reliable electricity delivery. Currently, this market is dominated by diesel or propane generators, which are noisy, polluting, and of relatively low efficiency.

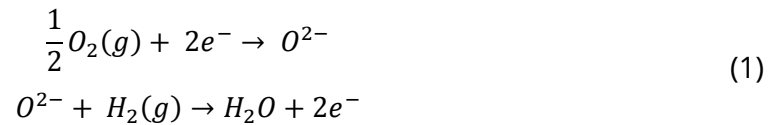
The unique operating conditions of SOFCs present several challenges to development:

- Operating temperatures necessitate refractory materials with a similar thermal expansion coefficient to minimize stresses in the material
- Gastight seals are difficult at high temperatures. The most common approach is to use a glass material that is viscous under operating conditions.
- The anode and cathode experience very different partial pressures of oxygen and can be difficult to process together.

High temperatures are necessary because SOFC operation relies on an electrolyte between the cathode and anode that conducts either oxygen or protons. Currently, materials utilized for this include yttria stabilized zirconia (YSZ) and gadolinium doped ceria (GDC), which are both ionic conductors at appropriate temperatures via oxygen vacancy diffusion. Current efforts in fuel cell research are focused on maximizing power density and phase compatibility of materials.

2. Thermodynamics and operation of an SOFC

Fuel cells are advantageous over conventional generation of electricity because they are not subject to losses in mechanical inefficiency or the limitations of the Carnot cycle. A modern SOFC consists of a yttria doped zirconia (YSZ) electrolyte that conducts oxygen ions from the cathode side, made from strontium doped lanthanum manganite (LSM), to the anode side, traditionally constructed of a nickel oxide-YSZ composite. Oxygen at the anode reacts with the fuel and electrons are released. The electrons are returned to the cathode through a circuit to ionize oxygen from the air such that they can be accepted and conducted by the YSZ electrolyte. A schematic SOFC is drawn in Figure 1. The open circuit potential of an SOFC is determined by the free energy of the fuel oxidation reaction, ie. $E = \Delta G/nF$, where n is the number of electrons transferred and F is the faraday constant.¹ The half cell reactions for a SOFC running on oxygen and hydrogen are:



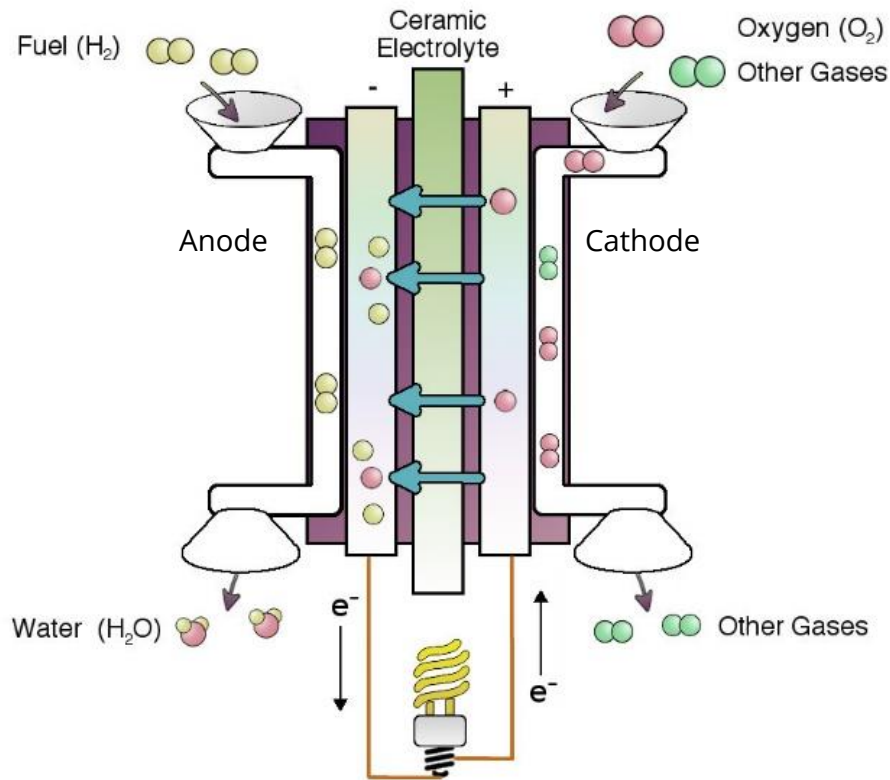


Figure 1: A schematic of a SOFC running on hydrogen and air.

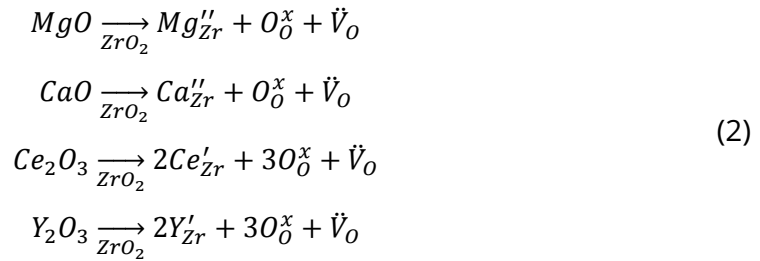
B. Crystallography of Zirconia

Zirconia (ZrO_2) is a very well understood ceramic material. Its naturally occurring phase is monoclinic, but phase transformations to tetragonal or cubic forms occur at 1200°C and 2500°C , respectively (Figure 2). This phase transformation is associated with a volume change, which complicates sintering of pure zirconia. Consequently, zirconia stabilized to either the tetragonal or cubic forms is preferred for functional ceramics. Common stabilizing oxides are CaO , MgO , Y_2O_3 , and Ce_2O_3 .⁷⁻¹⁰

For structural applications, zirconia is partially stabilized such that all of the material is converted the tetragonal phase at sintering temperatures. On cooling, this structure persists in a metastable state because of compression within the body. A crack that is propagating through the ceramic body relieves this

compression, which is immediately reintroduced by the transformation of a single crystallite at the crack tip to the monoclinic phase. This effectively stops the crack from further propagation and the entire ceramic body is stronger as a whole. This is called transformation toughening.

Electrical applications rely on the materials ability to conduct charge through an oxygen vacancy mechanism. In addition to stabilizing higher symmetry crystal structures, cations of a lower valence state substituting for zirconium in the crystal force the system to charge compensate with oxygen vacancies.



The maximum in conductivity occurs at the dopant concentration necessary to fully stabilize the cubic phase (~8 mol% in the case of Y_2O_3).¹¹ Additional adulterants in the structure are detrimental to conductivity because of defect ordering, vacancy clustering, or electrostatic interaction.¹² A transformation to either of the other two phases would be detrimental to the ionic conductivity of the YSZ phase and ultimately compromise the efficiency of the system.¹³

In efforts to better understand the stabilization mechanism of zirconia, x-ray absorbance spectroscopy experiments carried out by Li, et. al. in the early 1990s studied the oxygen coordination in doped zirconia.⁷⁻¹⁰ The researchers took into consideration valence state, ionic radius, and electronegativity of dopant ions during their investigation, and made several interesting observations.

The XAS studies have a clear advantage over x-ray diffraction techniques in that the local environment around a given cation can be studied without the dependence on long range order. XAS can also distinguish between yttrium and zirconium ions because of the difference in band edge for the k-shell x-ray. These

two capabilities allow us to learn about the difference in oxygen coordination for two cations sharing the same site in a given crystal.

The strongly covalent Zr-O bond favors seven fold coordination about the Zr^{+4} cation,⁷ observed in the undoped, monoclinic polymorph. In addition to introducing oxygen vacancies, oversized dopant cations (like Y) have an increased tendency to adopt an eight fold-coordination with the anions, leaving the vacant oxygen site to preferentially associate with zirconium ions. This vacant site completes a cubic polyhedron around each zirconium ion, creating a network of edge sharing cubes in the highest symmetry zirconia polymorph (Figure 3).

1. Destabilization of YSZ under SOFC operating conditions

It is generally well accepted that cathode derived degradation in SOFCs is the result of Mn diffusion into the fluorite structure of YSZ.^{12, 14} There are two detrimental reactions that take place as the manganese enters the YSZ:

- To compensate for positively charged manganese ions, YSZ will fill its oxygen vacancies. This is detrimental to SOFC operation because YSZ requires oxygen vacancies to conduct charge.
- The perovskite becomes unstable at the interface, provoking reactions between the leftover A-site ions and YSZ.¹⁵

Several strategies exist for limiting the reactions taking place at the interface of these two phases. To prevent zirconate formation with the A-site ions, the perovskite can be formed slightly non-stoichiometric, driving equilibrium away from the zirconate phase. By providing excess B ions, the leftover A ions diffuse into vacant sites in the perovskite. While this is favorable to forming the insulating zirconate phase, it does not address the mobility of the manganese ion. Yokokawa et al. note that there exists a tradeoff between the two reactions when controlling reactivity in this fashion.¹⁶

Waller et al. determined the diffusion coefficients of manganese in single crystal and polycrystalline YSZ within the temperature range of 1100 to 1400°C and found that the diffusion is much higher for polycrystalline YSZ than single crystal sample. This suggests that the manganese diffuses along the grain boundary in polycrystalline electrolytes.¹⁷ The authors also note that upon entering the YSZ, the manganese ions exist almost exclusively in the +2 oxidation state.

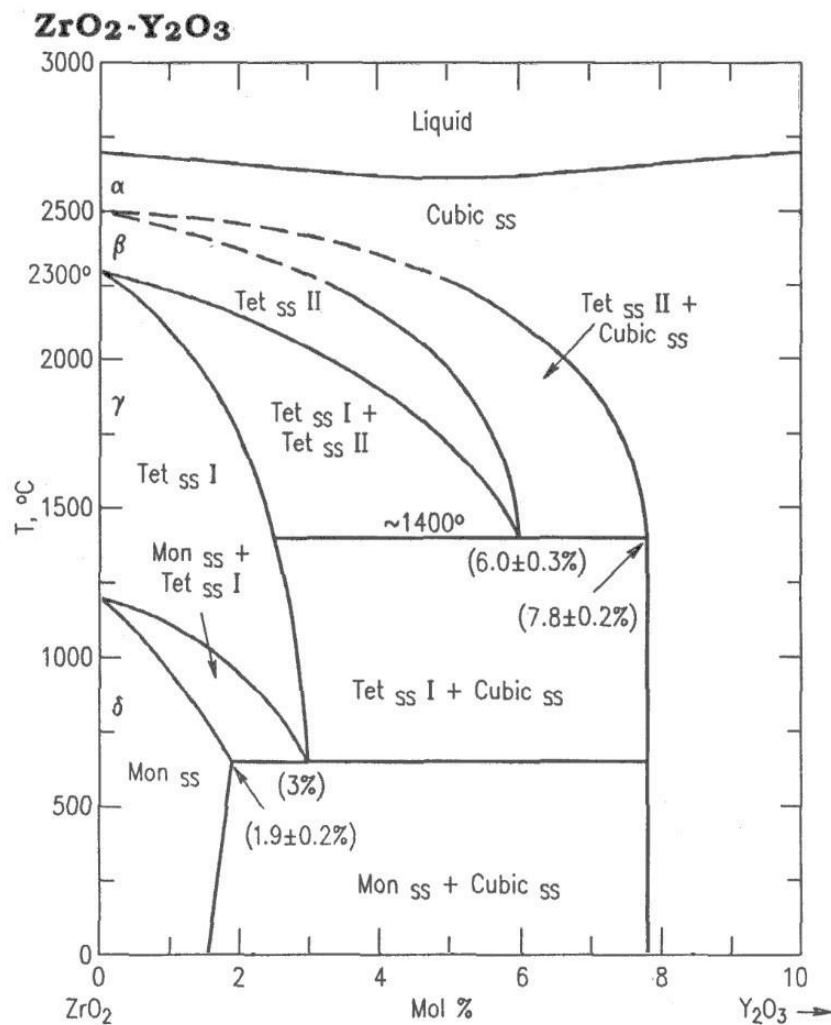


Figure 2: $\text{ZrO}_2\text{-Y}_2\text{O}_3$ Phase diagram. Adapted from¹⁸.

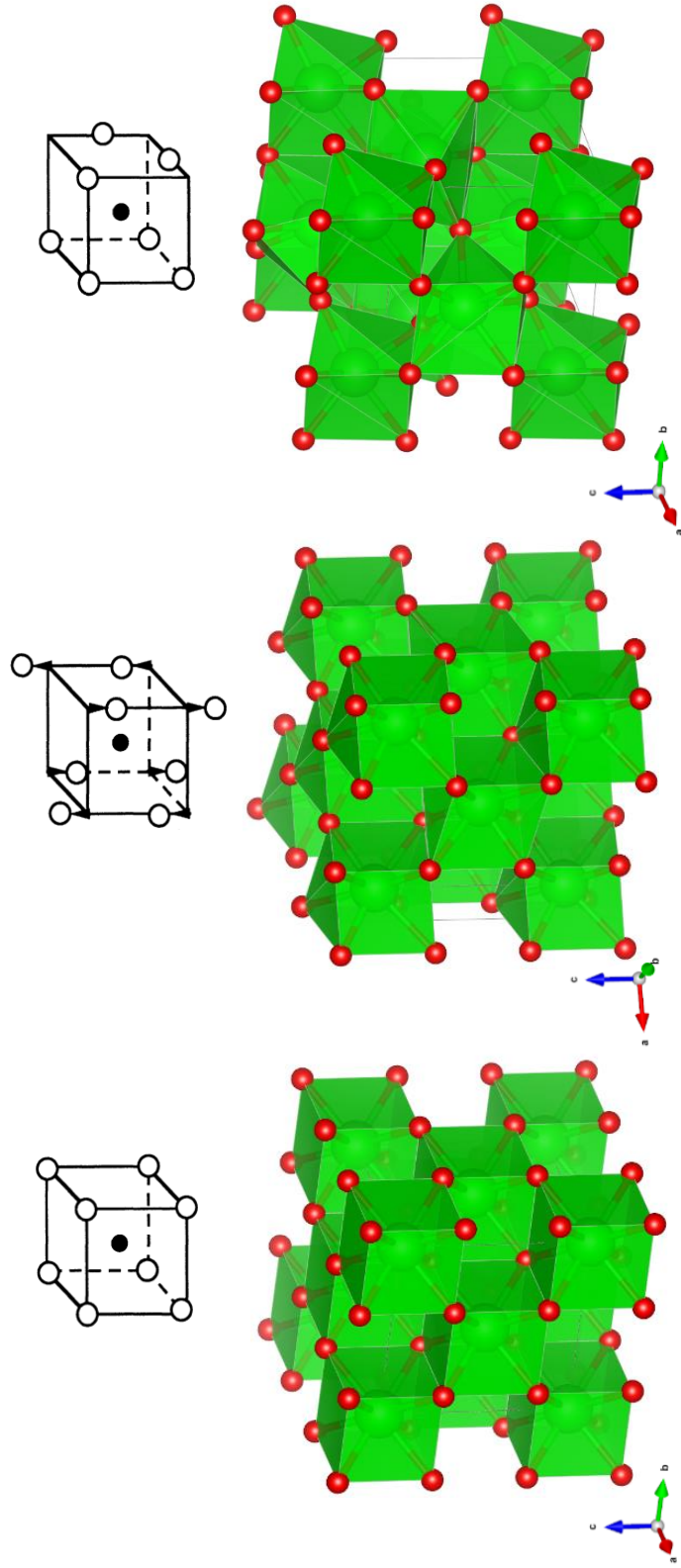


Figure 3: Pseudocubic projections of three zirconia polymorphs. From left to right: cubic, tetragonal, and monoclinic. Drawings of the polyhedra adapted from ⁷

C. Crystallography of Perovskite Materials

Materials of the chemistry ABO_3 may form the perovskite structure. This structure consists of a close packed array of the anions and the A cation, in a 3:1 ratio¹⁹ while the B cations occupy sites octahedrally coordinated with oxygen anions. The B cations are 6-fold coordinated in corner sharing octahedral, and the A cations occupy sites between the polyhedra, in 12-fold coordination. Considering the polyhedral construction of these materials reveals interesting relationships between their structures. In the three perovskite structures drawn in Figure 4, all of the B site cations are coordinated in corner sharing octahedra. For the highly symmetric cubic structure (e.g. $BaTiO_3$), the B – O – B angle is perfectly straight, i.e. 180° . As the structure departs from the ideal case, the space group symmetry shifts first to rhombohedral ($R-3c$) and then to orthorhombic ($Pnma$), with an associated reduction in the B – O – B angle. This distortion also results in a periodic displacement of the A ion. This ion acts as a strong scattering site in diffraction experiments, so this displacement presents in the diffraction pattern as splitting of a characteristic peak from the high symmetry phase.

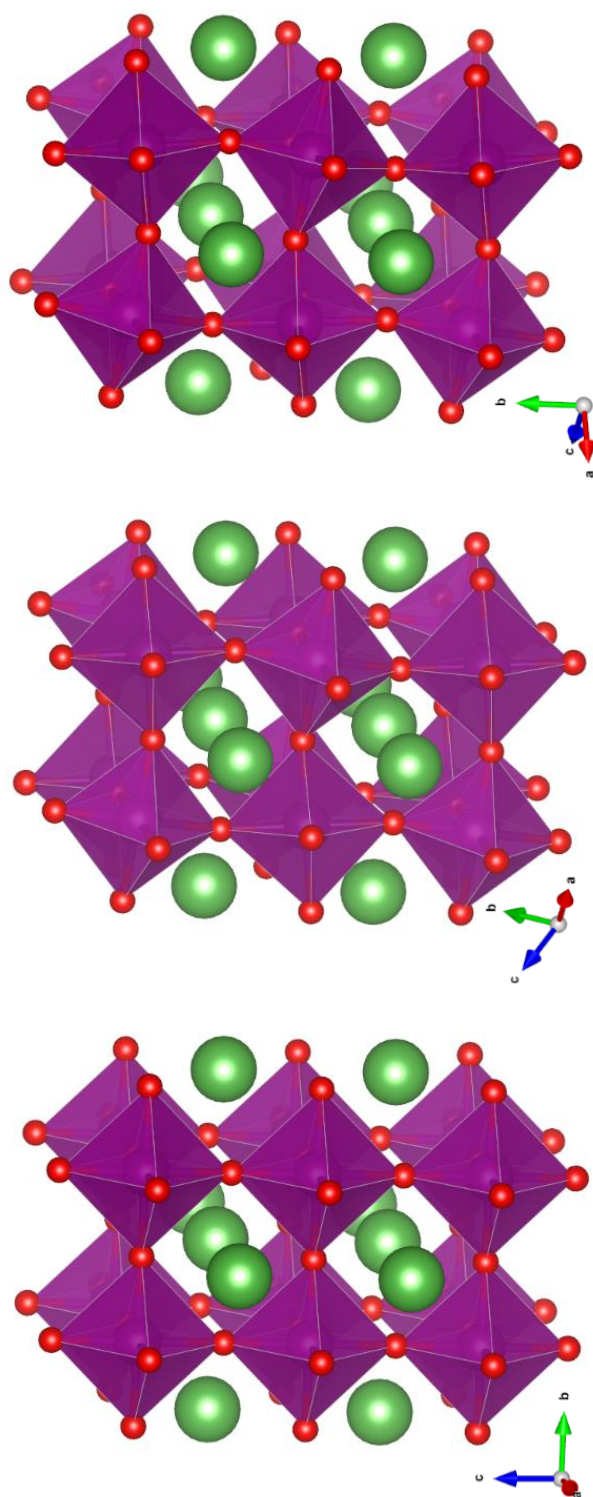


Figure 4: Pseudocubic projections of three perovskite space groups. From left to right: $Pm\bar{3}m$ (cubic), $R\bar{3}c$ (rhombohedral), $Pnma$ (orthorhombic). Depending on radii ratios, the BO_6 octahedra may need to distort to accommodate the interstitial A cation. Each step away from the highest symmetry cubic structure is an incremental increase in octahedral tilting.

1. Goldschmidt Tolerance Factor (GTF)

It is well established that ionic radii ratios have an influence on space group symmetry adopted by the perovskite. This was investigated in 1926 by V. Goldschmidt²⁰, who developed the following formula:

$$T = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \quad (3)$$

The formula is derived from a model of rigid sphere packing in a perovskite structure. This presents a number of implicit assumptions:

For a structure in which the radius of A equals the radius of the anion, these ions form a cubic close packed structure. Any r_A smaller than r_O results in a diminished contribution to lattice parameter from the A cation. If we continue with the assumption of a close packed oxygen octahedron, the interstitial space will only accept an ion with radius smaller than $(\sqrt{2} - 1)r_O$ without distorting. A high Goldschmidt tolerance factor (~ 1.0) predicts the highly symmetric rhombohedral (R-3c) crystal structure, but as the tolerance factor decreases (i.e. either r_O becomes smaller or the ratio $r_A:r_B$ decreases) the crystal decreases in symmetry to orthorhombic (Pnma).^{20, 21}

2. Thermodynamic Stability of Perovskites

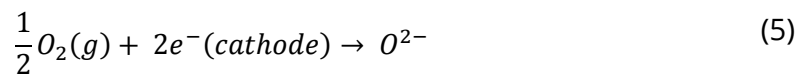
A more general concept of material stability is the change in energy associated with a given phase transformation.²² For example, synthesizing LSM perovskites from the constituent oxides demonstrates that the perovskite phase is thermodynamically favorable under the conditions of synthesis. Yokokawa, et al. performed thermodynamic calculations on several perovskite compounds in 1991.²³ In this paper, the stabilization energy, δ , of a perovskite is defined as the enthalpy change for formation from the constituent binary oxides. This can be written as:

$$\delta(AMO_3) = [\Delta H_f(AMO_3) - \{\Delta H_f(AO_n) + \Delta H_f(MO_m)\}] \quad (4)$$

The stabilization energy trends closely with the Goldschmidt tolerance factor, described in part 1 of this section. Highly stable perovskites typically have higher stabilization energy, i.e. there is a correlation between ionic radius and thermodynamic stability of perovskites. Finding binary oxides with higher formation energies could result in a less reactive material. Perovskites are very flexible in terms of chemical substitutions which opens up several opportunities in engineering material functionality and stability.

D. Fuel Cell Cathodes

In addition to conducting charge to the electrolyte, an important function of fuel cell cathodes is to provide high activity and sufficient reaction sites for the oxygen reduction reaction (ORR) to take place.^{24, 25} The cathodes for the low temperature PEM and PAFC fuel cells are platinum based (AFC designs have higher oxygen reduction kinetics than both these designs), but at high temperatures necessary for SOFCs, ceramics engineered to have high activity in the ORR can replace precious metal catalysts. The oxygen reduction reaction is written in Equation (5)



1. Lanthanum Manganite Perovskite

Strontium doped lanthanum manganite (LSM) is popular as a SOFC cathode because of its high electrical conductivity and activity as a catalyst in oxygen reduction reactions.²⁶⁻²⁹ To date, LSM remains the most investigated cathode material for SOFCs. Strontium substitutions enhance the p-type electronic conductivity of LSM by oxidizing the manganese to the 4+ valence.^{1, 12} The ionization potential for manganese is very low, allowing electron holes to move easily between manganese ions.³⁰ $LaMnO_3$ adopts an orthorhombic perovskite structure, as described in Section C of this chapter, but with increasing Sr content, the

rhombohedral and cubic structures become stable.²⁹ The strontium ion is smaller than the lanthanum it replaces,³¹ which has two consequences:

- Shifting the radii ratios such that the Goldschmidt Tolerance Factor predicts the rhombohedral distortion observed by most researchers.^{28, 29, 32-34}
- Reduction in the unit cell parameters²⁹

Similarly to zirconia doping, high concentrations of dopants or substitutions can result in oxygen vacancy ordering and precipitation of brownmillerite or pyrochlore phases.^{27, 29} For this reason, strontium concentration is typically kept below 0.3 for LSM in SOFC cathode applications

2. LSCF, BSCF, and other Cathode Materials

LSM is not the only candidate material for SOFC cathodes. By changing the B-site occupancy in the ceramic to iron-cobalt, the bond between oxygen and the B cation is weakened and oxygen becomes mobile through the lattice.²² Mobile oxygen enables mixed ionic electronic conductivity (MIEC), which is responsible for high power density in SOFC cathodes with this chemistry.³⁵⁻³⁹ $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ is the direct translation of LSM to the chemistry with MIEC. In 2004, Shao and Haile reported also a $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) perovskite cathode that maintained high power density at reduced temperatures. This activity is attributed to the high anion mobility through the perovskite.²⁷ BSCF was developed as a high temperature oxygen permeation membrane and its mixed ionic and electronic conductivity is by design. Its activity in the oxygen reduction reaction is also higher than LSM.³⁹ The thermal expansion coefficient of perovskites with Co-Fe or Ni-Fe at the B site is significantly higher than manganese based materials, which can potentially present thermomechanical instabilities during processing or operation.²⁵ The thermodynamic stabilities of these materials is also inferior.²⁵

MIEC cathodes have also been developed with the chemistry $\text{La}_x\text{Sr}_{1-x}\text{Ni}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$.^{25, 40, 41} These materials are attractive as cathodes because of their extremely

high electrical conductivity at lower temperatures and activity in the ORR. The material has been shown to be very reactive with YSZ, so this particular material is intended primarily for SOFCs with ceria electrolytes, which has also been shown to be very active at lower temperatures.²⁵ Ni and Co have been shown to enable MIEC in many other chemistries because of its relatively low bonding energy with oxygen (See Appendix B: Selected properties of ions in LSM perovskite) and so may be a good candidate for substitution in LSM.

Calcium has been investigated as a potential substitution for strontium in LSNF and BSCF perovskites and has been found to decrease the thermal expansion coefficient without sacrificing electrical conductivity.^{42, 43}

E. Reaction products of LSM and YSZ

Yokokawa et al. calculated the thermodynamic stabilities of the phases at the interface of YSZ and LSM.¹⁶ The calculations suggested that in the LaMnO_3 -YSZ system, both lanthanum zirconate formation and Mn dissolution into YSZ will occur independently of each other, and as these reactions progress, the system will move to a triple phase point representing the junction of $\text{La}_{(1-x)}\text{MnO}_{(3-\delta)}$ - $\text{La}_2\text{Zr}_2\text{O}_7$ -YSZ. The generated phase equilibria further suggest that the critical stoichiometry for the perovskite phase is $\text{La}_{0.86}\text{MnO}_{(3-\delta)}$. With a higher stoichiometry of La, zirconate formation is favorable, and lower, Mn diffusion is favorable. It should be noted that the authors performed these calculations on non-substituted lanthanum manganite, not the strontium substituted variants studied for SOFC applications.

F. Instrumentation Background

1. X-Ray Diffraction (XRD)

The laboratories at Alfred University are well equipped to evaluate phase compatibility. The x-ray diffraction lab has several instruments capable of generating high quality data, from which crystal structures and quantification of included phases may be refined. This technique relies on the relative scattering strength of ions included in the crystalline phases, and as such, its capabilities are limited in cases where the signal is dominated by a strongly scattering ion (like lanthanum) or when similarly weighted elements need to be distinguishable (like yttrium and zirconium). The relative ability of an ion to scatter x-rays is represented by the atomic scattering factor, which trends with atomic number, z . The atomic scattering factor is plotted in Figure 5 with respect to both Q and diffraction angle. To overcome this particular limitation, neutron scattering experiments are often used to compliment x-ray scattering experiments, though this necessitates a neutron diffractometer, typically available only at large national labs, and remains inaccessible to most researchers.

2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy provides a convenient alternative to transmission electron microscopy when high magnifications are unnecessary and preparation of a thin section is impractical. Imaging with backscattered electrons can show contrast between different phases provided a difference in the average atomic number between the phases. For this study, quantification of results were provided primarily by XRD and data collected with the electron microscope did not contribute directly to conclusions.

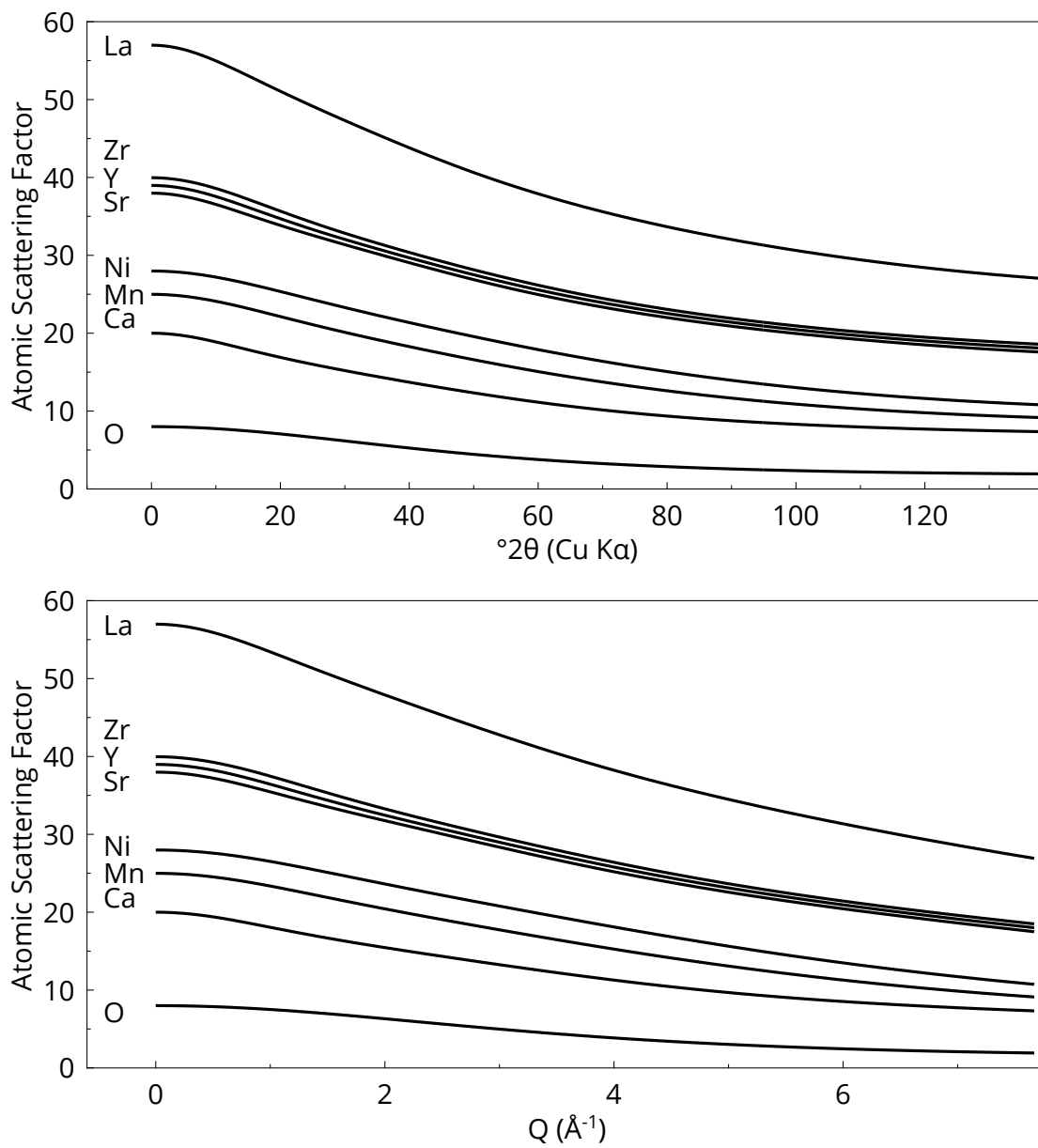


Figure 5: Atomic scattering factors for all ions in the YSZ-LSM system, including substitution cations studied in this work.

EXPERIMENTAL PROCEDURE

A. Synthesis of Perovskite

The base LSM-20 is commercially available from Praxair and was used as a control in the experiment. The bulk modified perovskites of chemistries $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM-20), $\text{La}_{0.8}\text{Sr}_{0.1}\text{Ca}_{0.1}\text{MnO}_{3-\delta}$ (LSM+Ca), $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ (LSM+Ni), and $\text{La}_{0.8}\text{Sr}_{0.1}\text{Mn}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ (LSM+Ca+Ni) were synthesized in-house via a solid state process as follows: stoichiometric amounts of the precursors, La_2O_3 (Alfa Aesar), $\text{Ca}(\text{CO}_3)$ (Acros Organics), $\text{Sr}(\text{CO}_3)$, NiO (Fisher Sci), and $\text{Mn}(\text{CO}_3)$ were ball milled in dilute nitric acid to aid in carbonate dissolution. The slurry was dried in air at 95°C, deglomerated with a mortar and pestle, and heat treated in air at 1500°C for 16 hours, with an intermediate grinding step after 8 hours. Phase purity was evaluated via XRD with special attention towards oxides of the precursors.

B. Annealing

To ensure a homogeneous distribution of phases as well as similar particle size and morphology, the LSM and YSZ (TOSOH TZ8Y) were milled together in deionized water with a McCrone Micronizing mill for 15 minutes. The slurry was covered with a porous membrane to minimize contamination and dried in an oven at 95°C. The resulting powder was deglomerated with a mortar and pestle and pressed into 4.1 g pellets at 138 MPa (20,000 psi). Leftover powder was used to create a powder bed, limiting chemical interactions with the refractory.

Compacts were annealed in four atmospheres, at two different temperatures, 850°C, and 1350°C. Alumina tube furnaces were used for controlled atmosphere experiments. Humidifying the atmosphere was accomplished with a gas washer/sparger type device (Figure 6). Samples were removed at 50, 100, 250, and 500 hours. The experimental matrix is tabulated in Table .

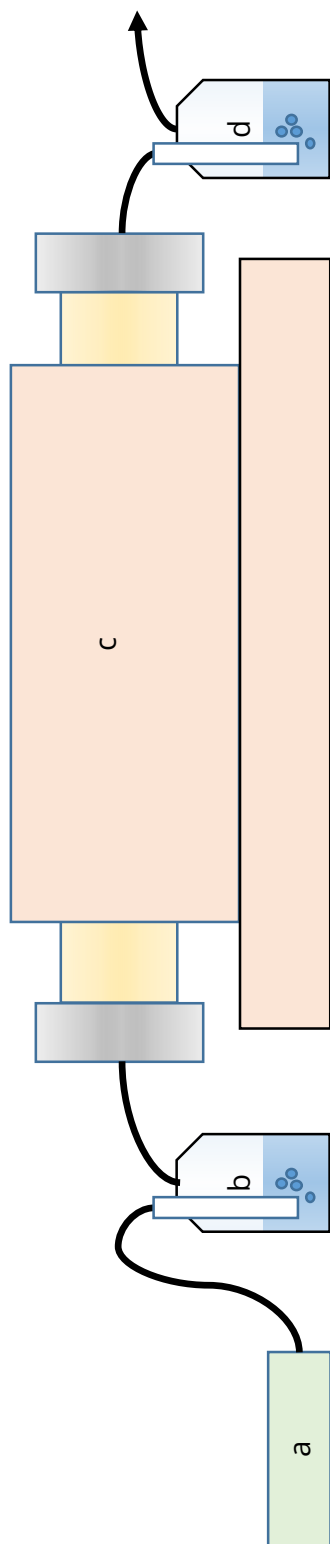


Figure 6: Schematic of the humid air assembly. An aquarium pump (a) forces air through a sparger in water (b). The humidified air is pushed through a tube furnace (c). To check system integrity, exhaust air also moves through water (d) so that the operator can ensure integrity of the gas line. To incorporate water into the CO₂-enriched air, the aquarium pump is replaced with a gas cylinder of appropriate chemistry.

Table I: Experimental Matrix for Phase Compatibility Experiments. Table II Shows Qualitative Data on Extraneous Phases after Annealing.

Atmosphere / Temperature		Air		Air + 3% H ₂ O		90% Air 10% CO ₂		90% Air 10% CO ₂ + 3% H ₂ O	
		850°C	1350°C	850°C	1350°C	850°C	1350°C	850°C	1350°C
Time (hours)	Chemistry								
	LSM-20								
	LSM+Ca								
	LSM+Ni								
50	LSM+Ca+Ni								
	LSM-20								
	LSM+Ca								
	LSM+Ni								
100	LSM+Ca+Ni								
	LSM-20								
	LSM+Ca								
	LSM+Ni								
250	LSM+Ca+Ni								
	LSM-20								
	LSM+Ca								
	LSM+Ni								
500	LSM+Ca+Ni								
	LSM-20								
	LSM+Ca								
	LSM+Ni								
500	LSM+Ca+Ni								
	LSM-20								
	LSM+Ca								
	LSM+Ni								

C. Characterization

The observed reactions are best measured with bulk techniques, so after annealing, the sintered compacts were crushed in a mortar and pestle to a fine powder. The solid-atmosphere interactions were kept constant by controlling carefully the size of the compact, so internal reactions should be the only source of observable differences in these data.

1. X-Ray Diffraction (XRD)

All XRD patterns were collected on a 1600W Bruker D8 diffractometer with Cu K α ($\lambda=1.54\text{\AA}$) radiation and a Ni filter. To gather sufficient data demonstrating transformation of YSZ to the tetragonal or monoclinic phase (observable at high q) and well defined peaks for standardless quantification, a large 2θ range was measured from 10-135 $^{\circ}2\theta$. The count time per 0.02 $^{\circ}2\theta$ step was 1.5 seconds. Variable divergence slits (15mm fixed sample illumination) and a sample spinner were used. The detector was a Lynxeye position sensitive detector covering 3.0 $^{\circ}2\theta$.

2. Scanning Electron Microscopy (SEM)

Samples unsuitable for bulk analysis because of chemical interactions with refractory were prepared for SEM by mounting in epoxy small pieces of the sintered, dense material. Only four samples from the most reactive atmosphere were selected for SEM analysis because results are better quantified via XRD. All images are of cross sections, polished with silicon carbide paper and colloidal diamond suspension, down to 0.6 μm . After polishing, the samples were removed from the epoxy and thermally etched at 1350 $^{\circ}\text{C}$ for 30 minutes. The etched samples were again mounted in epoxy and sputter coated with gold-palladium to assist in charge mitigation during SEM analysis.

All images were collected on an FEI Quanta 200F scanning electron microscope under high vacuum conditions.

RESULTS

A. $\text{La}_2\text{Zr}_2\text{O}_7$ Formation

Previous work has shown unambiguously that zirconate formation occurs at the interface of LSM-YSZ.¹⁵ Both lanthanum and strontium zirconate have been observed by other researchers, but only the lanthanum containing phase was detected in this work.

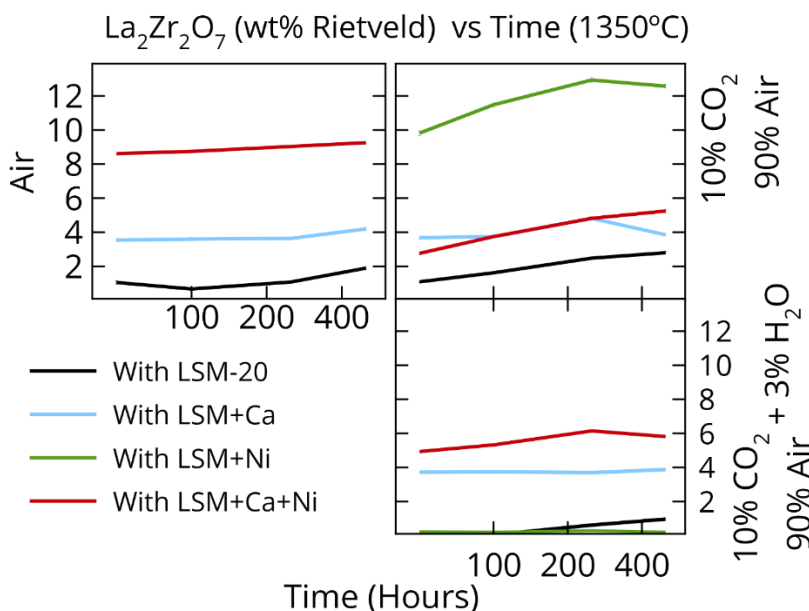


Figure 7: Zirconate formation in three different atmospheres, for the four LSM chemistries. The data on the left was collected after annealing in air, and the data on the right was 10% CO_2 | 90% Air. The plot on the lower right is also CO_2 enriched air, but with 3% H_2O incorporated into the atmosphere. No zirconate was detected in the humid air atmosphere.

Both base LSM and Ni-substituted LSM show a response to water vapor in that $\text{La}_2\text{Zr}_2\text{O}_7$ formation is limited. About the same amount of zirconate formed in air as in the CO_2 rich air, but none was observed for the experiment performed in humidified air. The evolution of this phase is associated with a change in LSM cell parameters, discussed in Part B of this section. It is well established that the conductivity of the zirconate phases is small compared to LSM and YSZ¹⁵, and so, we should work towards limiting this reaction.

B. LSM Phase Changes and Cell Parameters.

As noted in the previously, a change in LSM cell parameters has been observed under most cases. There is a correlation with the formation of lanthanum zirconate, with the extreme cases in 3% humidified air and 10% CO₂ enriched air. Humidified air contracts the unit cell and CO₂ enriched air expands the unit cell.

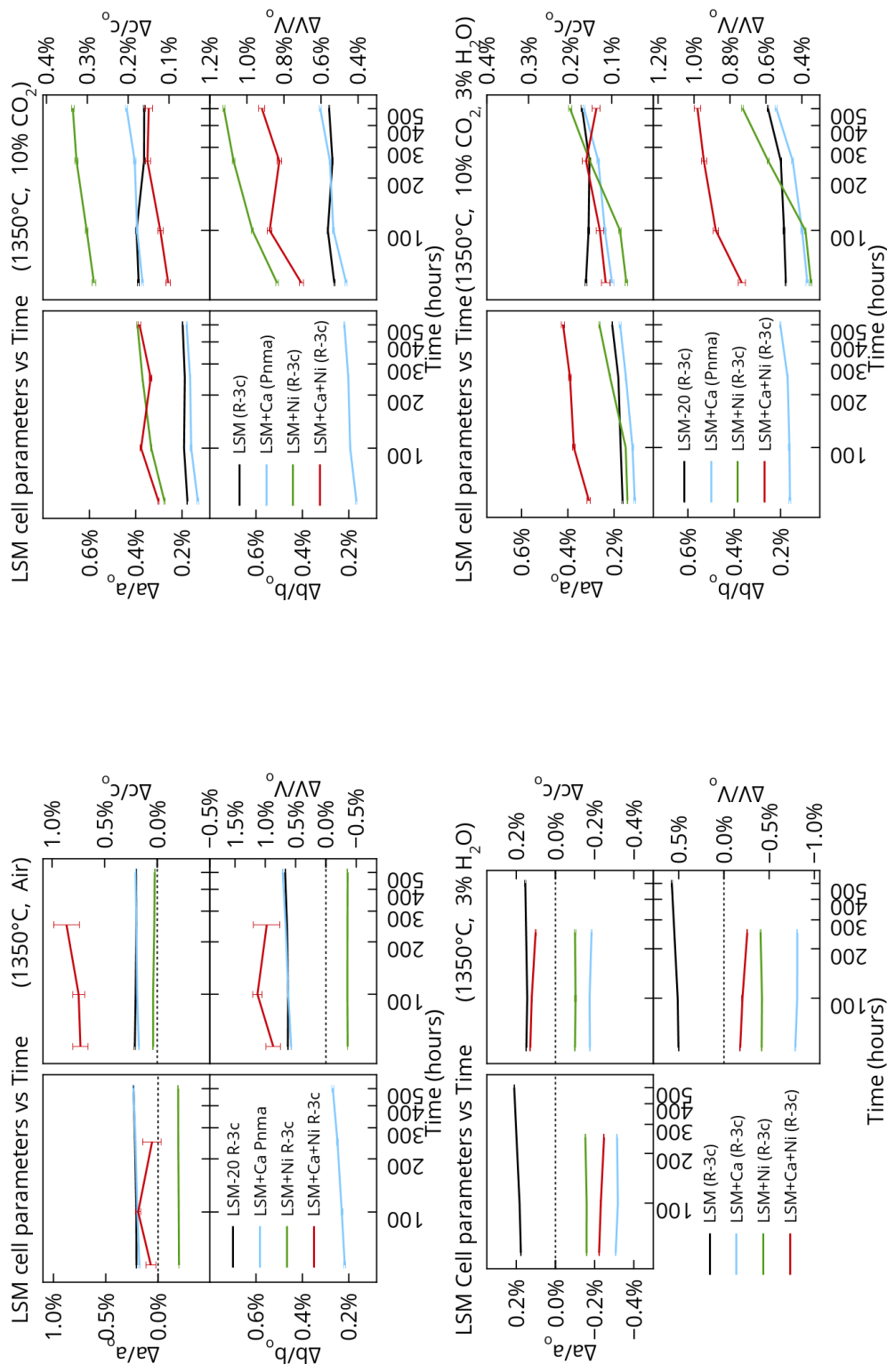


Figure 8: Cell parameters of LSM change as the experiment is carried out. In general, the cell expanded, and an upward trend was still observed after 500 hours for CO₂ rich atmospheres. The LSM contracted in the humid atmosphere, and again, the combined additions had an intermediate effect. The data for LSM+Ca+Ni in air is of low confidence because the phase was minor compared to the orthorhombic polymorph, of which there is no initial data (only R-3C phase after synthesis).

Annealing the material provoked formation of an orthorhombic perovskite phase for calcium containing samples in all atmospheres except for the humidified air, in which R-3c remained the dominant polymorph for all chemistries. The sample doped with both calcium and nickel seemed to be on the threshold of both polymorphs, providing interesting insight into the evolution of the two phases. Comparing results from the CO₂ enriched experiments (both dry and humid atmospheres) demonstrates the changes provoked for this particular chemistry:

- CO₂ encourages formation of the orthorhombic phase, with an upward trend for this polymorph observable even after 500 hours.
- H₂O discourages formation of the orthorhombic phase. Similar trends are clear, but with slower kinetics versus the dry CO₂ enriched atmosphere.

The slowest transformation occurred in the control atmosphere (air), suggesting that being in intimate contact with zirconia can provoke slight changes that result in evolution of the crystal structure of the material. These results are discussed in the next chapter.

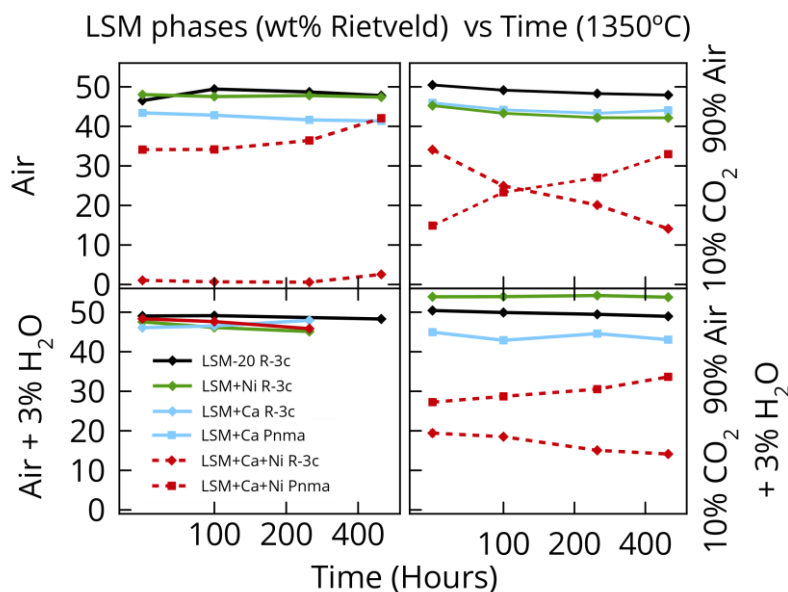


Figure 9: Weight percent of LSM in the annealed compacts. The least reactive atmosphere, 3% H₂O in air, also had the least change in LSM phase content. There was no orthorhombic phase detected.

C. Results from SEM analysis

SEM analysis provides qualitative information about the phases present after annealing and complements results from the x-ray diffraction analysis. In all images collected, the following phases are identifiable by considering the z (atomic number)-contrast. Average z is calculated for the three major phases:

Phase	Average Z
8YSZ	18.89
LSM	20.08 – 20.62
$\text{La}_2\text{Zr}_2\text{O}_7$	22.72

Two images are shown for each chemistry (Appendix A: SEM Photomicrographs). The bulk of the sample shows a dense microstructure with an even distribution of phases, but the lanthanum zirconate precipitates primarily at the interface with the refractory. The crystallites present as a bright phase (because of the high average z) with sub-micron crystallites. This observation is supported by x-ray peak broadening for this particular phase and qualitative XRD on both sides of the compact supports the observation that more $\text{La}_2\text{Zr}_2\text{O}_7$ forms on the Mn deficient side. The peaks for lanthanum zirconate are significantly stronger for the side in contact with the refractory, which pales in color through the anneal (Figure 10).

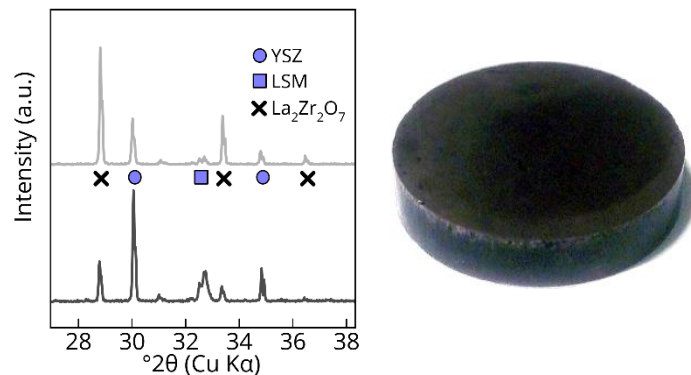


Figure 10: Qualitative XRD shows clearly the manganese deficient side has formed more zirconate phase.

SEM analysis also showed enormous grain size in the zirconia phase (Figure 13). XRD identified a Ca-stabilized zirconia phase, but cannot provide information on crystallite size above about 1000 nm.¹⁹

D. YSZ Destabilization

Oxygen ion conductivity is a critical property in functional SOFC cathodes. The maximum in conductivity occurs at the dopant concentration necessary to fully stabilize the cubic phase (~8 mol% in the case of Y_2O_3). Additional adulterants in the structure are detrimental to conductivity because of defect ordering, vacancy clustering, or electrostatic interaction.¹²

There are two transitions observed in the material after annealing: cubic YSZ $\rightarrow$ tetragonal YSZ or cubic YSZ $\rightarrow$ cubic CSZ. The calcium-stabilized zirconia was identified by formation of a similar cubic phase with a slightly smaller lattice parameter and formed only with the LSM+Ca perovskite. Destabilization to the tetragonal phase presents with a similar pattern to the cubic phase, but with peak splitting at higher angles. Incorporating nickel into the LSM halted both reactions.

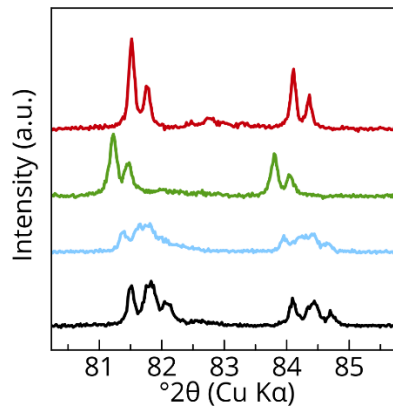


Figure 11: Peak splitting at high angles occurred after long term annealing and indicate either formation of a cubic Ca stabilized zirconia, or formation of a tetragonal phase. The patterns were collected after annealing at 1350°C in air for 500 hours. The four samples (from bottom to top) are base LSM, LSM+Ca, LSM+Ni, and LSM+Ca+Ni.

Similarly to the other described reactions, CO_2 accelerates the degradation while H_2O slows down the reaction. The atmosphere with both additions presents an intermediate case. The results are summarized qualitatively in Table II.

Table II: Qualitative Results from Phase Identification Performed on LSM-YSZ Samples Annealed at 1350°C;
Only Phases of at Least 5 Weight Percent are Considered,
Except La₂Zr₂O₇, in Which the Threshold is 1 Weight Percent.

▲ = R-3c perovskite △ = Pnma Perovskite
■ = Cubic YSZ □ = Cubic CSZ ◆ = Tetragonal YSZ
● = Lanthanum Zirconate

Initial composition (All atmospheres)	LSM-20	▲■
	LSM+Ca	▲△■
	LSM+Ni	▲■
	LSM+Ca+Ni	▲■

Time (hours)	Atmosphere / Temperature		Air		Air + 3% H ₂ O		90% Air 10% CO ₂		90% Air 10% CO ₂ + 3% H ₂ O	
	Chemistry		Initial phases still present	Evolved phases	Initial phases still present	Evolved phases	Initial phases still present	Evolved phases	Initial phases still present	Evolved phases
50	LSM-20		▲■	●	▲■		▲■	●	▲■	
	LSM+Ca		△■	□●	■		△■	□●	△■	□●
	LSM+Ni		▲■		▲■		▲■	●	▲■	
	LSM+Ca+Ni		▲■	△●	▲■		▲■	△●	▲■	△●
100	LSM-20		▲■	◆●	▲■		▲■	◆●	▲■	
	LSM+Ca		△■	□●	■		△■	□●	△■	□●
	LSM+Ni		▲■		▲■		▲■	●	▲■	
	LSM+Ca+Ni		■	△●	▲■		▲■	△●	▲■	△●
250	LSM-20		▲■	◆●	▲■		▲■	◆●	▲■	●
	LSM+Ca		△■	□●	■		△■	□●	△■	□●
	LSM+Ni		▲■		▲■		▲■	●	▲■	●
	LSM+Ca+Ni		■	△●	▲■		▲■	△●	▲■	△●
500	LSM-20		▲■	◆●	▲■		▲■	◆●	▲■	●
	LSM+Ca		△■	□●	■		△■	□●	△■	□●
	LSM+Ni		▲■		▲■		▲■	●	▲■	●
	LSM+Ca+Ni		■	△●	▲■		▲■	△●	▲■	△●

DISCUSSION

The observed reactions are interrelated in that ionic mobility is a limiting factor. The smallest radius ion in the YSZ-LSM system is manganese, which has a radius between 0.53Å and 0.58Å in six-fold coordination depending on its oxidation state, assumed to be between +2 and +4.³¹ This small radius contributes to its high mobility in the system. Water vapor present in the atmosphere has been shown to promote oxygen mobility in ceramics⁴⁴, presumably by the substitution of hydroxide on an oxygen site. The hydroxide ion is both smaller³¹ and more polarizable,⁴⁵ contributing to its overall higher mobility in a crystal.

A. Hydroxide incorporated into LSM

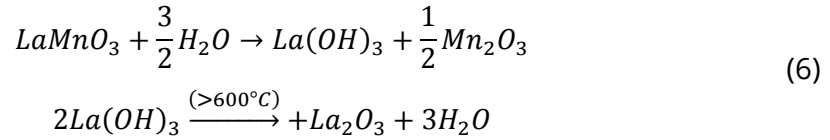
Water vapor in the atmosphere will dissociate into H^+ and OH^- ions. Incorporating hydroxide ions into the structure at a site typically populated by oxygen has potential consequences with respect to observed reactions:

1. A reduction in lattice cell parameters associated with the smaller ionic radius of OH^- compared to O^{2-}
2. Charge compensation by manganese via transition to a lower oxidation state.
3. Change of the effective radius of the anion or the B-site cation, which may shift the observed crystal structure (see Section C)

The effect of (2) will increase the radius of the manganese cation, reducing its mobility. A larger B-cation will also contribute to the lattice parameters, counteracting the effects of (1), but only slightly because the close packed sublattice of perovskite is formed by the A cation (La, Ca, or Sr) and the anion (O or OH) in a 3:1 ratio.¹⁹

In 2011, Liu et al carried out experiments on durability of LSM and LSCF under humid air conditions.⁴⁶ The accelerated failure of both LSM and LSCF cathode materials was clearly demonstrated above 3 vol% atmospheric water. At low concentrations of water (~3%), cell degradation is diminished. The current study

confirms the findings of Liu, et al. and demonstrates 3% water vapor in air can mitigate material degradation for other chemistries as well. The extraneous phases identified at higher and lower concentrations of water were MnO_x and La_2O_3 which have been shown to evolve after annealing the samples in reducing conditions.^{15, 47} It is likely that at very high water vapor concentrations, the degradation mechanism is as follows:



LSCF showed relatively poorer tolerance to water vapor than LSM.⁴⁶ The identified mechanism for degradation was likewise different: For the LSCF cathode, there was identified a Sr rich layer at the interface of the atmosphere, assumed to be SrO. Annealing the sample at a higher temperature prevented the formation of the insulating SrO layer.

B. Intermediate Carbonate formation

CO_2 may accelerate the reactions degrading the LSM-YSZ system by provoking formation of intermediate carbonate species. These have not been detected via XRD, so it is proposed that this is a surface reaction that creates a single layer of carbonate bonds without long range order necessary for diffraction, CO_2 facilitates the extraction of A-site cations from the LSM and the intermediate carbonate subsequently reacts with YSZ to form the respective zirconate phase. This process also destabilizes the perovskite by driving the chemistry away from the ideal stoichiometric balance. The unstable material is rich in manganese, which has been shown to provoke reactions with YSZ.¹⁶ Thermodynamic calculations or in-situ spectroscopy to identify carbonate groups may support or disprove this hypothesis.

C. Goldschmidt Tolerance Factor (GTF)

All synthesized materials assumed the perovskite structure with Goldschmidt tolerance factors close to unity. The radii (in Å) used for La, Sr, Ca, Mn, Ni, and O were 1.36, 1.44, 1.34, 0.58, 0.56 and 1.35 respectively.³¹ For this calculation, the +3 oxidation state was assumed for Mn and Ni. It is likely that other oxidation states are present, as noted in Part A of this section, so calculated numbers are for reference only.

Table III: Observed Crystal Structure and Goldschmidt Tolerance Factor (GTF) for LSM Chemistries Studied.

Material	Space Group(s)	GTF estimate [†]
La _{0.8} Sr _{0.2} MnO _{3-δ}	R-3c	0.999
La _{0.8} Sr _{0.1} Ca _{0.1} MnO _{3-δ}	R-3c + Pnma	0.995
La _{0.8} Sr _{0.2} Mn _{0.7} Ni _{0.3} O _{3-δ}	R-3c	1.00
La _{0.8} Sr _{0.1} Ca _{0.1} Mn _{0.7} Ni _{0.3} O _{3-δ}	R-3c + Pnma	0.998

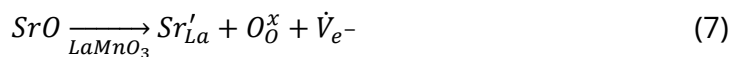
The two chemistries with potential for adopting orthorhombic symmetry (Ca-containing) have the lowest tolerance factors, suggesting they are close to the threshold for the orthorhombic → rhombohedral transition. This threshold is commonly accepted to be around 0.9.^{20, 37}

In 2001, Rørmann, et al. showed that a higher oxidation state (lower radius) of Mn in LSM encouraged the rhombohedral phase.³⁴ Coupling results of differential thermal analysis and iodometric titration allowed the researchers to calculate oxygen stoichiometry and make assumptions about the valence of transition metal elements in the material.

[†]Absolute determination of the GTF is dependent on quantification of Mn and Ni valence and spin states, which is non-trivial.

D. Conductivity and Thermodynamic Stability of Modified LSM Perovskites

In this study, only two substitutions were considered: Ca replacing Sr, and Ni replacing Mn. Sr improves conductivity of LSM by introducing more charge carrying electron vacancies according to the following reaction:



The electron hole is associated with the transition metal in the B-site, which in base LSM, is manganese.⁴⁸ Calcium maintains this balance because it is also in the 2+ valence state, and in theory provides a slightly more thermodynamically stable perovskite (ΔH_f is 151.6 kcal/mol for CaO vs 144.2 kcal/mol for SrO).⁴⁹ This study has shown that Ca-modified LSM is in fact more reactive. The difference in radius ratio encourages formation of a Pnma phase and CaO has been shown to be reactive with YSZ. Abnormally large crystallites are also observable, without magnification in the most extreme cases. Substituting Ni on a Mn site moves the Goldschmidt tolerance factor back towards the starting point (~ 0.991 , see Section C) and does not inhibit electronic conductivity because Ni has similarly low ionization potential.³⁰ If we assume that the thermodynamic stability of a perovskite trends with the stability of its constituent binary oxides as suggested by Yokokawa,^{16, 23} then another criterion for a B-site substitution should be enthalpy of formation, which for NiO, is significantly lower than MnO (57.5 kcal/mol vs 92.0 kcal/mol) suggesting poor thermodynamic stability of a nickel substituted LSM.

CONCLUSIONS

Long term annealing studies highlight:

- LSM will destabilize YSZ to the tetragonal phase in air
- Ca in LSM can react with the YSZ to form a Ca-containing zirconia phase
- Addition of Ni to LSM or LSM+Ca eliminates YSZ degradation in all atmospheres
- H₂O slows or eliminates all observed reactions
- CO₂ encourages all observed reactions

But:

- Ni additions cause up to 12% La₂Zr₂O₇ formation
- (Ni+Ca) additions cause up to 5% La₂Zr₂O₇ formation vs. 3% for base LSM
- Ca additions can cause formation of a Ca-stabilized cubic phase
- Ca additions can also provoke grain growth

These results are tabulated below:

Table IV: A stability summary of all LSM and atmospheres tested

	La _{0.8} Sr _{0.2} MnO _{3-δ}	La _{0.8} Sr _{0.1} Ca _{0.1} MnO _{3-δ}	La _{0.8} Sr _{0.2} Mn _{0.7} Ni _{0.3} O _{3-δ}	La _{0.8} Sr _{0.1} Ca _{0.1} Mn _{0.7} Ni _{0.3} O _{3-δ}
Air	Unstable (T - YSZ)	Unstable (Forms CSZ)	Stable	Stable but with La ₂ Zr ₂ O ₇
Humid air (+3% H ₂ O)	Stable	Stable	Stable	Stable
10% CO ₂ 90% Air	Unstable (T - YSZ)	Unstable (Forms CSZ)	Stable but with La ₂ Zr ₂ O ₇	Stable but with La ₂ Zr ₂ O ₇
10% CO ₂ 90% Humid Air	Stable	Unstable (Forms CSZ)	Stable	Stable but with La ₂ Zr ₂ O ₇

Based on these conclusions, the authors recommend Ni or Ni+Ca substituted LSM for long term electrochemical testing. To mitigate evolution of all phases, it is

also advisable to sinter cathode material onto button cells under humid air. This has been shown to effectively halt all phase evolution taking place in this system.

FUTURE WORK

To fully evaluate viability for application in SOFC, electrochemical testing is required. To be an effective cathode, electrical conductivity must be high. Operating under load may also change the equilibrium of the system, encouraging or discouraging observed reactions. An option for an A-site substitution not explored in this study is silver (Ag). XPS studies on silver substituted LSM carried out by Machocki et al. in 2004 demonstrated that silver substituted into LaMnO_3 perovskites adopts the +2 oxidation state and provokes formation of Mn^{4+} , similarly to Sr^{2+} or Ca^{2+} substitutions.⁵⁰ Silver substituted LaMnO_3 materials are studied for methane oxidation catalysts⁵⁰⁻⁵², but may have properties desirable for SOFC cathodes. Ag is unreactive with YSZ, but may vaporize if present in its metallic form.

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Appendix A: SEM Photomicrographs

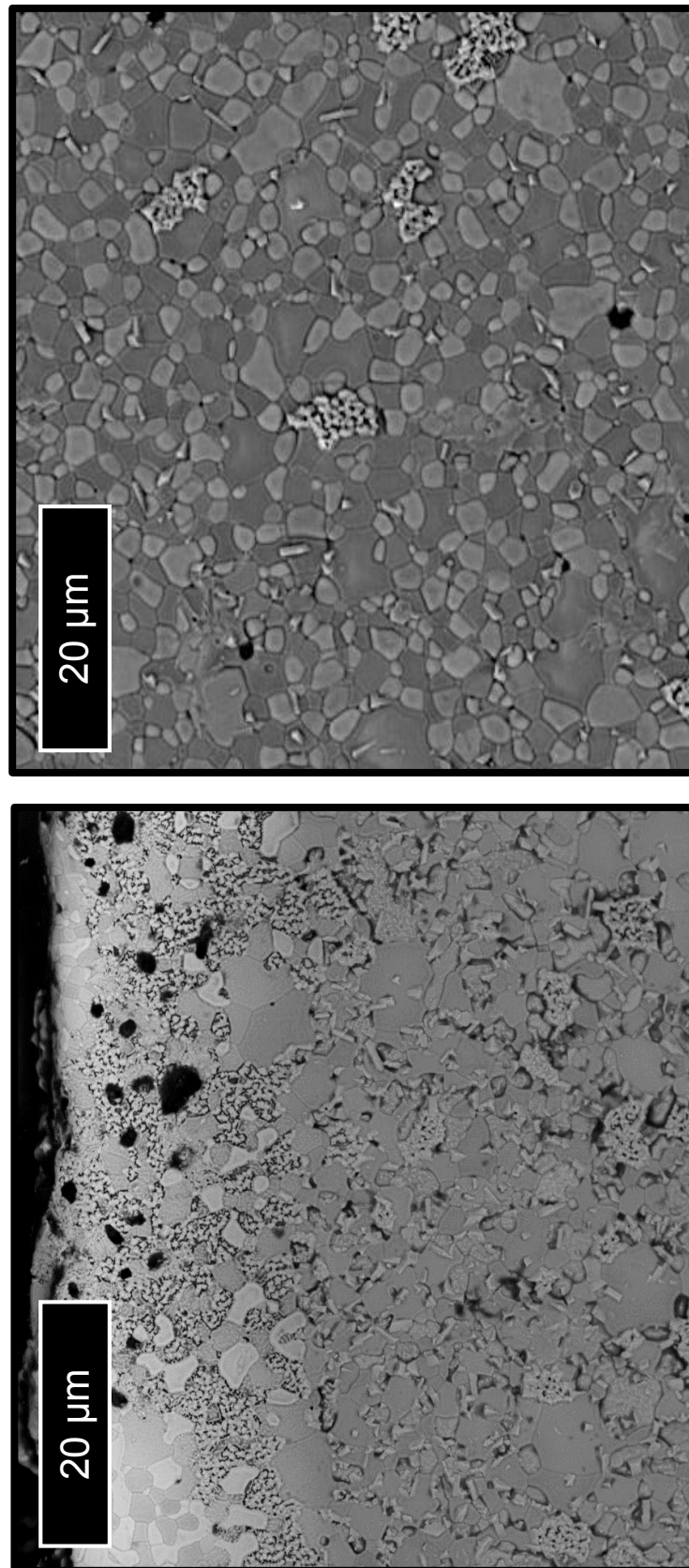


Figure 12: Backscattered electron images of LSM20 - YSZ composites after 500 hours at 1350°C in 10% CO₂ enriched air. At least three phases are distinguishable: YSZ, LSM, and La₂Zr₂O₇

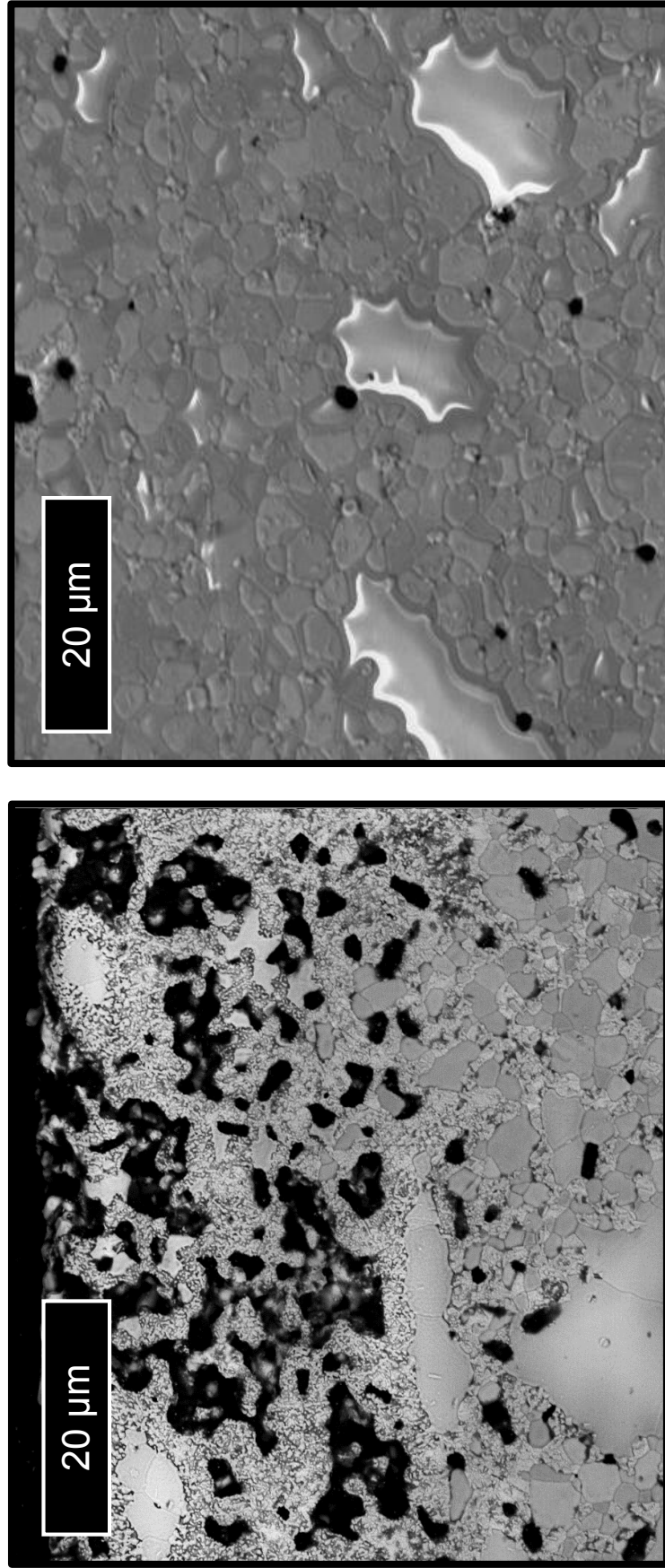


Figure 13: Backscattered electron photomicrographs of the calcium substituted LSM-YSZ composites after 500H at 1350°C in 10% CO₂ enriched air. The zirconate formation at the sample-refractory interface is more extensive than in base LSM. Also interesting to note is the formation of large zirconia grains both at the surface and in the bulk of the material.

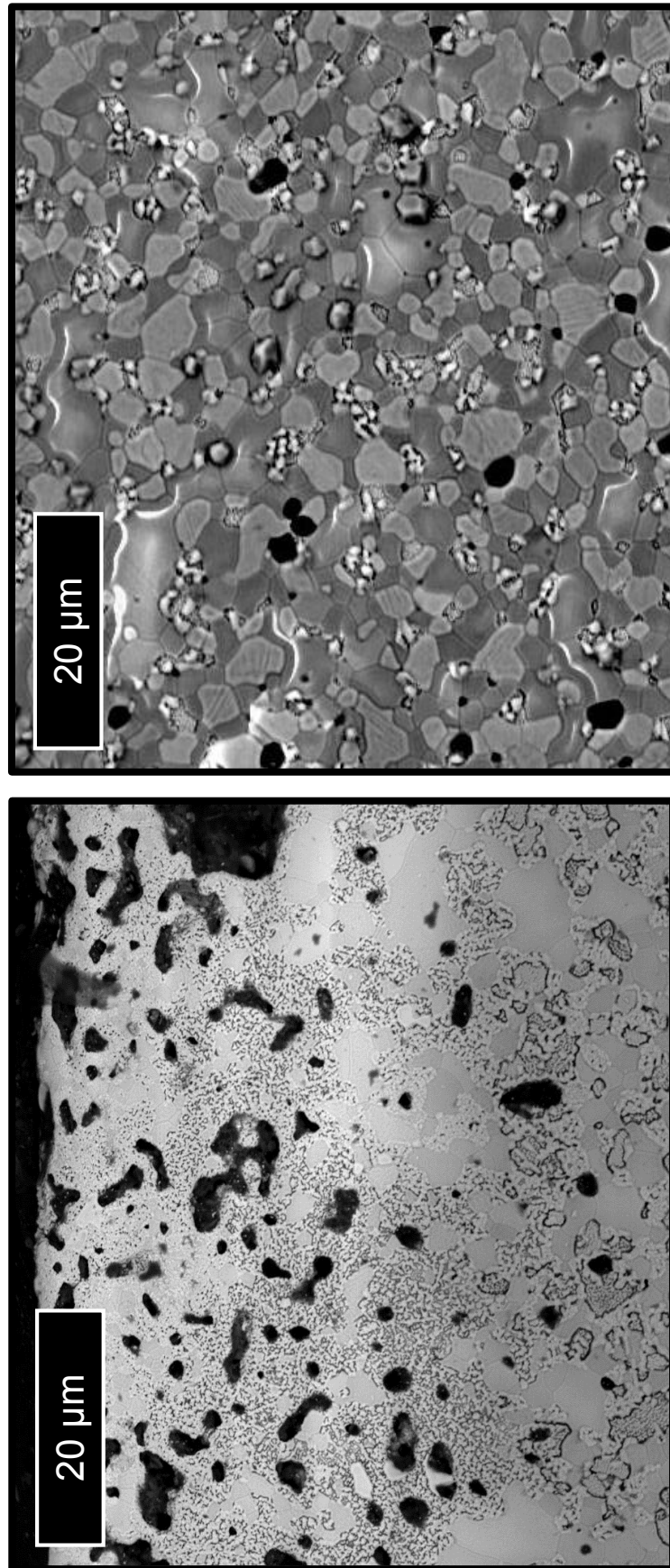


Figure 14: Backscattered electron photomicrograph of the nickel substituted sample after 500 hours at 1350 °C in 10% CO₂ enriched air. For this atmosphere, the nickel substituted sample formed the most lanthanum zirconate, observable especially at the interface with the refractory. Faceting can be seen on the LSM phase in the bulk.

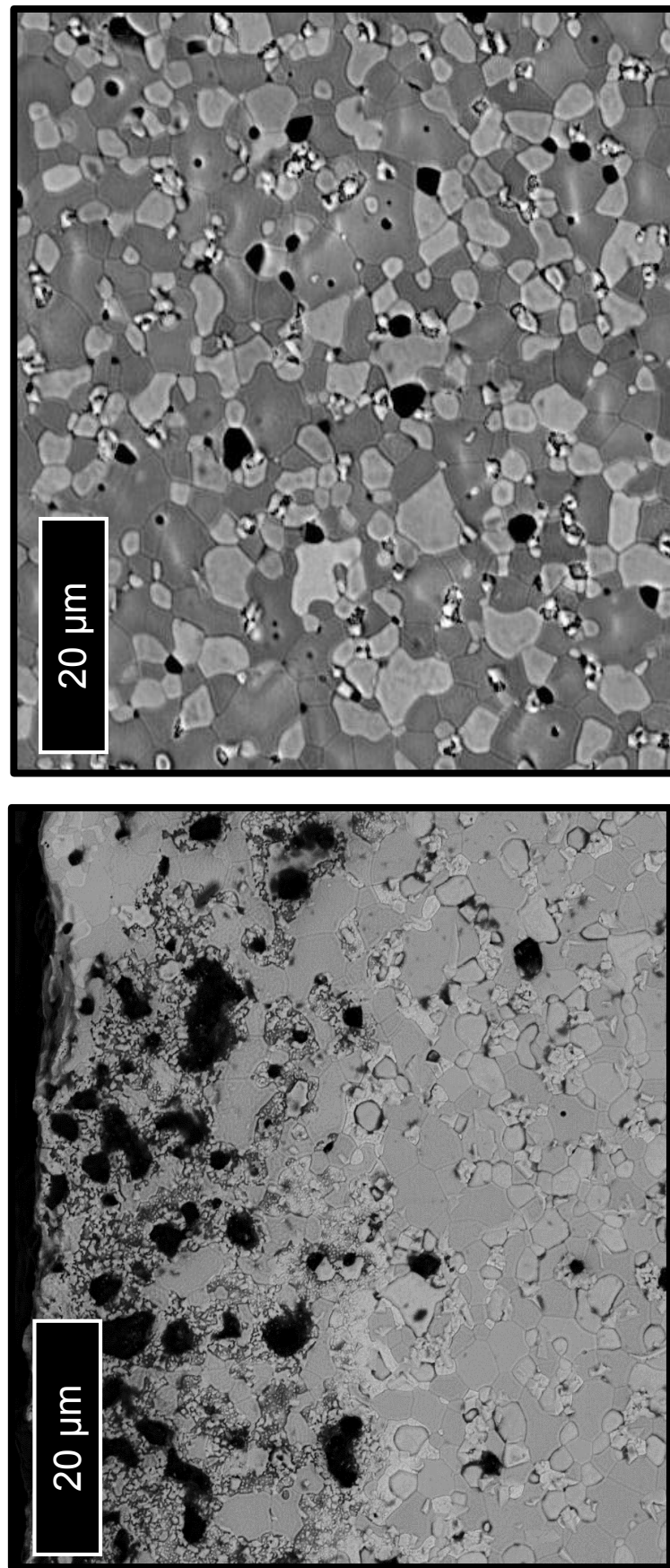


Figure 15: Backscattered electron photomicrograph for the sample substituted with both calcium and nickel.

Appendix B: Selected properties of ions in LSM perovskite

Ion	Valence	Radius (Å) [†] (from ³¹)	Ionization potential (eV) ³⁰	$\Delta H_{f,298}$ (kcal/mol) MO, M ₂ O ₃ , MO ₂ (from ⁴⁹)
La	+3	1.35		430±3.0
Sr	+2	1.44		144.2±1.5
Ca	+2	1.34		151.6±0.4
Ag	+1	1.22		
Mn	+2	0.67 / 0.83 ^{††}	-	92.0±0.5
	+3	0.58 / 0.645 ^{††}	33.667	228.7±1.2
	+4	0.53	51.2	124.3±0.5
Ni	+2	0.55 / 0.49 ^{††}	-	57.5±0.5
	+3	0.56 / 0.60 ^{††}	35.17	
	+4	0.48	54.9	
Co	+2	0.65 / 0.745 ^{††}	-	57.1±0.5
	+3	0.545 / 0.61 ^{††}	33.5	
	+4	0.41	51.3	
Mo	+3	0.69	-	
	+4	0.61	46.4	140.0±0.9
	+5	0.59	61.2	
O	-2	1.35		
OH	-1	1.32		

[†]12-fold coordination for A-site cations, 6-fold coordination for B-site cations. Anions are 2 fold coordinated.

^{††} Ionic radii for low spin / high spin states

Appendix C: Example Rietveld Refinements

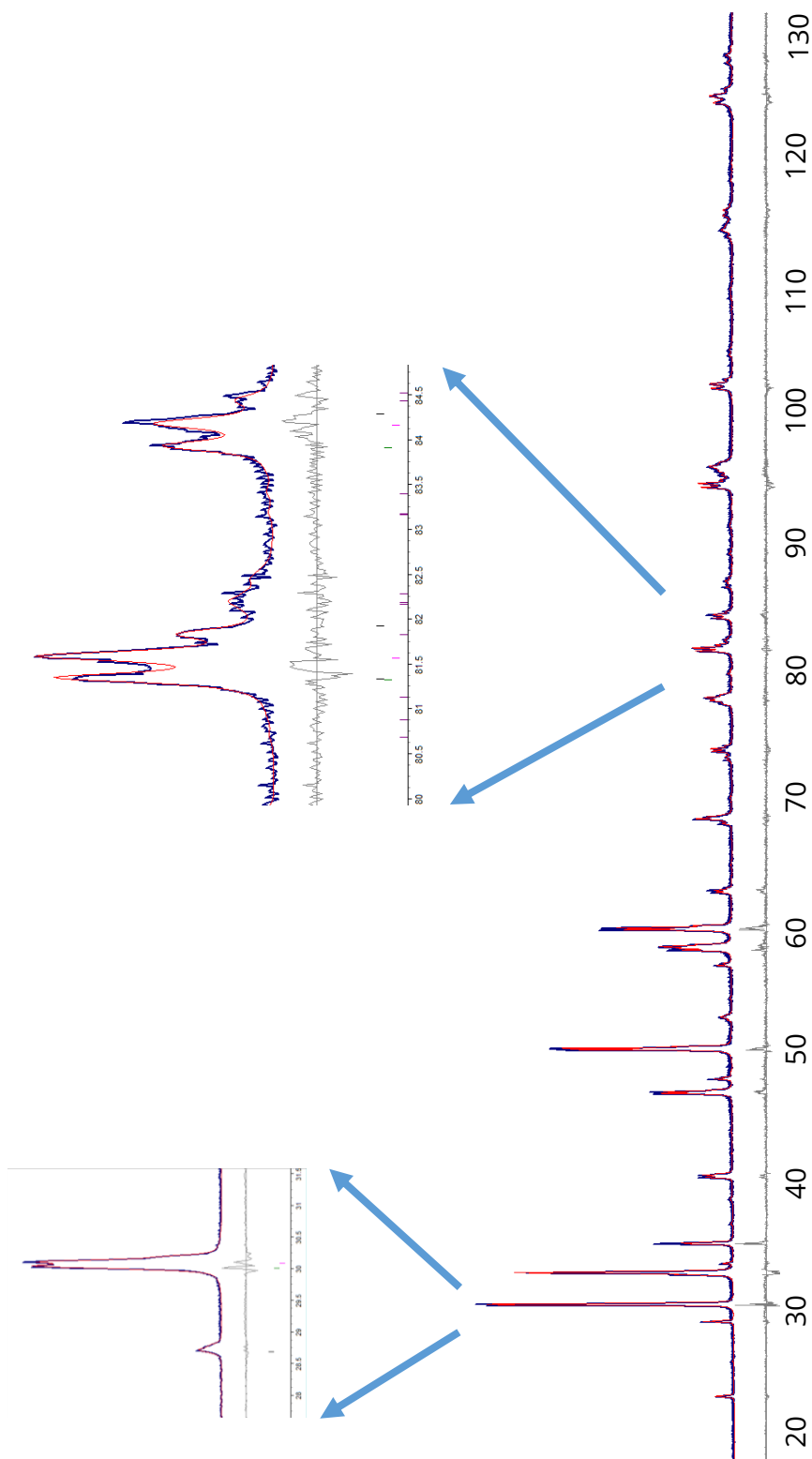


Figure 16: Rietveld refinement of LSM+Ca-YSZ composite after annealing at 1350°C in 10% CO₂ 90% Air for 500 Hours. Details show two features characteristic of destabilization. A) Development of the $\langle 222 \rangle$ La₂Zr₂O₇ peak at $\sim 28.7^\circ 2\theta$ and B) splitting of the higher angle YSZ peaks $\langle 331 \rangle$ and $\langle 042 \rangle$ in the detail.

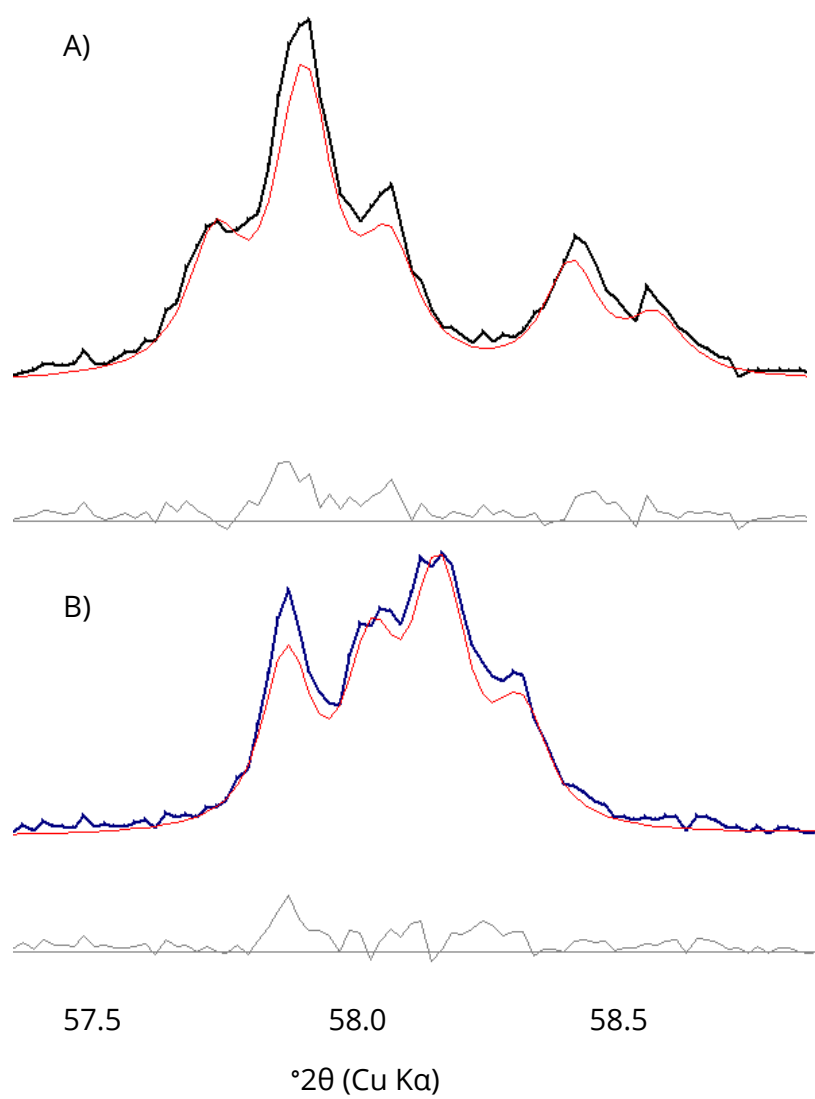


Figure 17: Example perovskite peaks showing the difference between R-3c (A) and Pnma (B) perovskite peaks.

Appendix D: Tabulated XRD data

Appendix D is the tabulation of refined XRD data presented in the results chapter. This includes cell parameters in the various LSM phases through the anneals as well as quantification of all detected phases

Table 5: LSM Cell Parameters Measured for the As-Synthesized Materials.

<i>Initial Parameters</i>	<i>a (Å)</i>	<i>b (Å)</i>	<i>c (Å)</i>	<i>vol (Å³)</i>
LSM-20				
	5.518(4)		13.361(4)	352.3(8)
LSM+Ca (R-3c)				
	5.499(2)		13.320(8)	348.8(7)
LSM+Ca (Pnma)				
	5.480(9)	7.751(2)	5.517(3)	234.3(9)
LSM+Ni				
	5.497(4)		13.310(2)	348.3(6)
LSM+Ca+Ni				
	5.493(6)		13.297(6)	347.5(5)

Table 6: LSM Cell Parameters Measured for the As-Synthesized Materials.

Hours	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	vol (Å ³)
LSM-20 1350 °C Air				
50	5.529(8)		13.389(8)	354.5(9)
100	5.529(9)		13.388(8)	354.5(8)
250	5.530(6)		13.387(9)	354.6(4)
500	5.531(4)		13.388(2)	354.7(5)
LSM+Ca 1350 °C Air				
50	5.490(7)	7.768(1)	5.526(9)	235.7(3)
100	5.491(8)	7.769(0)	5.527(8)	235.8(5)
250	5.492(7)	7.770(5)	5.528(2)	235.9(5)
500	5.493(8)	7.772(0)	5.528(7)	236.0(6)
LSM+Ni 1350 °C Air				
50	5.486(4)		13.315(4)	347.1(1)
100	5.486(6)		13.315(4)	347.1(3)
250	5.486(8)		13.313(9)	347.1(2)
500	5.486(9)		13.313(4)	347.1(1)
LSM+Ca+Ni (R-3c) 1350 °C Air				
50	5.497(4)		13.394(6)	350.5(7)
100	5.504(1)		13.396(9)	351.4(8)
250	5.496(8)		13.412(3)	350.9(5)
500	5.523(6)		13.432(9)	354.9(4)
LSM+Ca+Ni (Pnma) 1350 °C Air				
50	5.485(5)	7.764(4)	5.525(5)	235.3(4)
100	5.485(4)	7.763(5)	5.525(5)	235.3(1)
250	5.485(4)	7.763(4)	5.525(6)	235.3(1)
500	5.485(7)	7.763(4)	5.507(2)	234.5(4)

Table 7: Measured LSM Cell Parameters Through Anneal in Humid (3% H₂O) Air at 1350°C.

<i>Hours</i>	<i>a (Å)</i>	<i>b (Å)</i>	<i>c (Å)</i>
LSM-20 1350 °C 3% H₂O			
50	5.528(2)		13.381(2)
100	5.528(5)		13.380(6)
500	5.530(1)		13.381(9)
LSM+Ca (R-3c) 1350 °C 3% H₂O			
50	5.482(3)		13.297(3)
100	5.481(7)		13.297(5)
250	5.481(9)		13.296(2)
LSM+Ni 1350 °C 3% H₂O			
50	5.488(7)		13.296(9)
100	5.488(6)		13.296(5)
250	5.489(0)		13.296(9)
LSM+Ca+Ni 1350 °C 3% H₂O			
50	5.485(2)		13.314(6)
100	5.484(7)		13.313(7)
250	5.483(8)		13.311(0)

Table 8: Measured LSM Cell Parameters Through Anneal in 10% CO₂ 90% Air at 1350°C.

Hours	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	vol (Å ³)
LSM-20 1350 °C 10% CO₂ 90% Air				
50	5.528(2)		13.384(6)	354.2(4)
100	5.529(0)		13.385(3)	354.3(7)
250	5.528(8)		13.382(9)	354.2(8)
500	5.529(3)		13.382(8)	354.3(4)
LSM+Ca 1350 °C 10% CO₂ 90% Air				
50	5.488(1)	7.764(1)	5.526(4)	235.4(8)
100	5.489(7)	7.766(2)	5.527(1)	235.6(4)
250	5.450(0)	7.766(9)	5.527(4)	235.6(9)
500	5.490(8)	7.768(2)	5.528(5)	235.8(1)
LSM+Ni 1350 °C 10% CO₂ 90% Air				
50	5.512(6)		13.348(0)	351.2(8)
100	5.515(7)		13.350(3)	351.7(4)
250	5.517(8)		13.353(6)	352.1(0)
500	5.519(0)		13.354(8)	352.2(8)
LSM+Ca+Ni (R-3c) 1350 °C 10% CO₂ 90% Air				
50	5.510(2)		13.311(1)	350.0(1)
100	5.514(3)		13.313(7)	350.6(0)
250	5.512(0)		13.317(9)	350.4(2)
500	5.514(7)		13.317(4)	350.7(5)
LSM+Ca+Ni (Pnma) 1350 °C 10% CO₂ 90% Air				
50	5.467(6)	7.740(3)	5.509(1)	233.1(5)
100	5.477(1)	7.747(4)	5.510(2)	233.8(2)
250	5.477(6)	7.749(4)	5.521(1)	234.3(6)
500	5.477(5)	7.751(0)	5.521(3)	234.4(1)

Table 9: Measured LSM Cell Parameters Through Anneal in Humidified (3% H₂O) 10% CO₂ 90% Air at 1350°C.

Hours	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	vol (Å ³)
LSM-20 1350 °C 3% H₂O 10% CO₂ 90% Air				
50	5.527(4)		13.383(0)	354.1(1)
100	5.527(9)		13.382(2)	354.1(4)
250	5.528(4)		13.381(9)	354.2(0)
500	5.529(9)		13.384(2)	354.4(6)
LSM+Ca 1350 °C 3% H₂O 10% CO₂ 90% Air				
50	5.487(0)	7.763(5)	5.522(7)	235.2(6)
100	5.487(5)	7.763(7)	5.523(7)	235.3(3)
250	5.489(1)	7.764(3)	5.524(6)	235.4(5)
500	5.490(4)	7.766(8)	5.526(5)	235.6(6)
LSM+Ni 1350 °C 3% H₂O 10% CO₂ 90% Air				
50	5.505(2)		13.318(8)	349.5(8)
100	5.505(6)		13.320(9)	349.6(9)
250	5.509(3)		13.330(5)	350.4(1)
500	5.511(9)		13.336(8)	350.9(0)
LSM+Ca+Ni (R-3c) 1350 °C 3% H₂O 10% CO₂ 90% Air				
50	5.510(6)		13.312(8)	350.1(0)
100	5.514(2)		13.314(7)	350.6(1)
250	5.515(1)		13.319(0)	350.8(4)
500	5.516(7)		13.315(8)	350.9(6)
LSM+Ca+Ni (Pnma) 1350 °C 3% H₂O 10% CO₂ 90% Air				
50	5.467(2)	7.740(0)	5.510(6)	233.1(9)
100	5.468(1)	7.742(5)	5.508(7)	233.2(2)
250	5.473(0)	7.746(8)	5.513(1)	233.7(4)
500	5.474(0)	7.749(0)	5.512(9)	233.8(5)

Table 10: Quantitative Phase Analysis of Materials Annealed at 1350° C in Air

Hours at 1350°	Phase Name	Wt% Rietveld	Wt% (ESD)	Wt% Rietveld	Wt% (ESD)
		With LSM-20		With LSM+Ni	
50	LSM R-3c	48.742	0.291	48.036	0.280
	LSM Pnma				
	Cubic YSZ	50.078	0.291	51.964	0.280
	La ₂ Zr ₂ O ₇	1.18	0.116		
100	LSM R-3c	49.429	0.279	47.53	0.298
	LSM Pnma				
	Cubic YSZ	49.898	0.279	52.47	0.298
	La ₂ Zr ₂ O ₇	0.673	0.057		
250	LSM R-3c	48.707	0.266	47.79	0.276
	LSM Pnma				
	Cubic YSZ	50.212	0.266	52.21	0.276
	La ₂ Zr ₂ O ₇	1.081	0.073		
500	LSM R-3c	47.761	0.296	47.385	0.303
	LSM Pnma				
	Cubic YSZ	49.692	0.295	52.615	0.303
	La ₂ Zr ₂ O ₇	1.897	0.093		
		With LSM+Ca		With LSM+Ca+Ni	
50	LSM R-3c			1.056	0.147
	LSM Pnma	43.404	0.396	42.524	0.317
	Cubic YSZ	24.238	0.431	47.699	0.312
	Cubic CSZ	28.821	0.431		
	La ₂ Zr ₂ O ₇	3.537	0.104	8.72	0.150
100	LSM R-3c			0.675	0.133
	LSM Pnma	42.813	0.356	42.682	0.310
	Cubic YSZ	22.239	0.381	47.863	0.306
	Cubic CSZ	31.346	0.382		
	La ₂ Zr ₂ O ₇	3.602	0.100	8.78	0.152
250	LSM R-3c			0.655	0.129
	LSM Pnma	41.635	0.336	42.175	0.291
	Cubic YSZ	21.737	0.362	48.073	0.287
	Cubic CSZ	32.988	0.361		
	La ₂ Zr ₂ O ₇	3.639	0.095	9.097	0.145
500	LSM R-3c			5.628	1.693
	LSM Pnma	41.354	0.375	36.935	1.314
	Cubic YSZ	19.893	0.410	48.259	1.238
	Cubic CSZ	34.556	0.408		
	La ₂ Zr ₂ O ₇	4.198	0.114	9.177	0.274

Table 11: Quantitative Phase Analysis of Materials Annealed at 1350° C in Humidified (3% H₂O) Air

Hours at 1350°	Phase Name	Wt% Rietveld	Wt% (ESD)	Wt% Rietveld	Wt% (ESD)
		With LSM-20		With LSM+Ni	
50	LSM R-3c	49.033	0.171	47.552	0.187
	Cubic YSZ	50.967	0.171	52.448	0.187
100	LSM R-3c	49.133	0.169	46.126	0.251
	Cubic YSZ	50.867	0.169	53.874	0.251
250	LSM R-3c			45.104	0.247
	Cubic YSZ			54.896	0.247
500	LSM R-3c	48.28	0.263		
	Cubic YSZ	51.72	0.263		
		With LSM+Ca		With LSM+Ca+Ni	
50	LSM R-3c	46.079	0.192	48.328	0.181
	Cubic YSZ	53.921	0.192	51.672	0.181
100	LSM R-3c	46.522	0.18	47.621	0.277
	Cubic YSZ	53.478	0.18	52.379	0.277
250	LSM R-3c	47.929	0.275	45.841	0.269
	Cubic YSZ	52.071	0.275	54.159	0.269

Table 12: Quantitative Phase Analysis of Materials Annealed at 1350° C in 10%CO₂ 90% Air

Hours at 1350°	Phase Name	Wt% Rietveld	Wt% (ESD)	Wt% Rietveld	Wt% (ESD)
		With LSM-20		With LSM+Ni	
50	LSM R-3c	50.459	0.333	45.243	0.374
	LSM Pnma				
	Cubic YSZ	48.449	0.328	44.937	0.326
	La ₂ Zr ₂ O ₇	1.093	0.063	9.82	0.130
100	LSM R-3c	49.145	0.214	43.297	0.219
	LSM Pnma				
	Cubic YSZ	49.233	0.213	45.217	0.213
	La ₂ Zr ₂ O ₇	1.622	0.069	11.487	0.128
250	LSM R-3c	48.289	0.213	42.186	0.214
	LSM Pnma				
	Cubic YSZ	49.23	0.212	44.878	0.209
	La ₂ Zr ₂ O ₇	2.481	0.077	12.936	0.133
500	LSM R-3c	47.915	0.208	42.156	0.212
	LSM Pnma				
	Cubic YSZ	49.284	0.207	45.267	0.207
	La ₂ Zr ₂ O ₇	2.801	0.079	12.577	0.130
		With LSM+Ca		With LSM+Ca+Ni	
50	LSM R-3c			34.091	0.670
	LSM Pnma	45.939	0.390	14.904	0.613
	Cubic YSZ	34.367	0.337	48.243	0.584
	Cubic CSZ	16.006	0.321		
	La ₂ Zr ₂ O ₇	3.687	0.084	2.763	0.088
100	LSM R-3c			24.947	0.640
	LSM Pnma	44.172	0.299	23.307	0.663
	Cubic YSZ	34.337	0.309	47.915	0.572
	Cubic CSZ	17.747	0.329		
	La ₂ Zr ₂ O ₇	3.745	0.088	3.745	0.088
250	LSM R-3c			20.095	0.577
	LSM Pnma	43.308	0.289	27.024	0.534
	Cubic YSZ	35.333	0.300	47.953	0.490
	Cubic CSZ	16.54	0.316		
	La ₂ Zr ₂ O ₇	4.818	0.099	4.818	0.099
500	LSM R-3c			14.101	0.551
	LSM Pnma	44.049	0.282	32.975	0.487
	Cubic YSZ	35.421	0.290	47.674	0.456
	Cubic CSZ	16.679	0.311		
	La ₂ Zr ₂ O ₇	3.851	0.086	5.249	0.110

Table 13: Quantitative Phase Analysis of Materials Annealed at 1350° C in Humid (3% H₂O) 10%CO₂ 90% Air

Hours at 1350°	Phase Name	Wt% Rietveld	Wt% (ESD)	Wt% Rietveld	Wt% (ESD)
		With LSM-20		With LSM+Ni	
50	LSM R-3c	50.424	0.329	53.897	0.339
	LSM Pnma				
	Cubic YSZ	49.540	0.332	45.874	0.335
	La ₂ Zr ₂ O ₇	0.036	0.020	0.231	0.061
100	LSM R-3c	49.921	0.205	53.935	0.210
	LSM Pnma				
	Cubic YSZ	50.020	0.207	45.851	0.209
	La ₂ Zr ₂ O ₇	0.044	0.023	0.203	0.042
250	LSM R-3c	49.459	0.212	54.222	0.191
	LSM Pnma				
	Cubic YSZ	49.926	0.214	45.485	0.189
	La ₂ Zr ₂ O ₇	0.615	0.061	0.292	0.044
500	LSM R-3c	48.95	0.251	53.789	0.261
	LSM Pnma				
	Cubic YSZ	50.084	0.251	46.007	0.260
	La ₂ Zr ₂ O ₇	0.966	0.066	0.204	0.060
		With LSM+Ca		With LSM+Ca+Ni	
50	LSM R-3c			19.444	0.917
	LSM Pnma	44.951	0.468	27.214	0.771
	Cubic YSZ	30.762	0.392	48.412	0.731
	Cubic CSZ	20.573	0.388		
	La ₂ Zr ₂ O ₇	3.714	0.098	4.93	0.124
100	LSM R-3c			18.506	0.712
	LSM Pnma	42.891	0.309	28.706	0.694
	Cubic YSZ	31.509	0.330	47.466	0.607
	Cubic CSZ	21.855	0.350		
	La ₂ Zr ₂ O ₇	3.744	0.087	5.322	0.117
250	LSM R-3c			15.055	0.63
	LSM Pnma	44.579	0.324	30.536	0.597
	Cubic YSZ	32.284	0.338	48.267	0.538
	Cubic CSZ	19.445	0.362		
	La ₂ Zr ₂ O ₇	3.692	0.092	6.141	0.124
500	LSM R-3c			14.166	0.718
	LSM Pnma	43.056	0.343	33.605	0.683
	Cubic YSZ	32.765	0.362	46.424	0.604
	Cubic CSZ	20.301	0.386		
	La ₂ Zr ₂ O ₇	3.878	0.095	5.806	0.133

