Microwave-Assisted Hydrothermal Synthesis of Fine Grained La$_{0.77}$Sr$_{0.20}$Al$_{0.90}$Mn$_{0.10}$O$_{3-\delta}$

THESIS

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Abstract

Lanthanum strontium manganese oxide (LSM) is an appealing choice for use as the internal reference electrode in an yttria-stabilized zirconia sealed internal reference high temperature oxygen sensor because its mechanical stability, thermal expansion coefficient, and electronic conduction are compatible with the conditions described in previous studies. Doping of the perovskite b-site of LSM with aluminum has been proposed to limit side reactions which impede electrical conduction and complete sealing. It has been shown previously that lanthanum strontium aluminum manganese oxide (LSAM) can be joined with yttria-stabilized tetragonal zirconia polycrystal by plastic deformation. Two micron grain size LSAM was synthesized by the solid state method.

The current work examined the microwave-assisted hydrothermal synthetic method with the goal of producing fine grained La$_{0.77}$Sr$_{0.20}$Al$_{0.90}$Mn$_{0.10}$O$_{3-\delta}$ at low temperature with a shorter reaction time. X-ray diffraction, Fourier-transform infrared spectroscopy, and Raman spectroscopy were used to characterize the powder. It was found that microwave heating for 6 hours in basic aqueous solution with citric acid as a complexing agent followed by calcination in air produced the cubic perovskite phase of La$_{0.77}$Sr$_{0.20}$Al$_{0.90}$Mn$_{0.10}$O$_{3-\delta}$ with a grain size of 25 nm. Scanning electron microscopy showed that the La$_{0.77}$Sr$_{0.20}$Al$_{0.90}$Mn$_{0.10}$O$_{3-\delta}$ sample formed a dense joint with yttria-stabilized tetragonal zirconia polycrystal by the grain boundary sliding method.
Dedication

To my husband, Jason

For his continuing love and patience while I’ve worked on this

And to my parents, Nancy and Richard, and sister, Amanda

For their encouragement and support through all of my school
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Chapter 1: Introduction

A. High Temperature Oxygen Sensing

With rising fuel prices and increasing environmental awareness, the past several years have seen a huge amount of interest in alternative energy sources as well as methods of optimizing fuel use. One important factor in optimizing use of fossil fuels is to adjust the air to fuel ratio in combustion reactions. Wasted fuel costs the energy industry billions of dollars each year. The importance of the air to fuel ratio is apparent in Figure 1.1, which shows the optimal operating conditions for an energy plant. The ability to accurately regulate the amount of oxygen being supplied to the combustion reaction would greatly improve the efficiency of fuel burning processes. While the best known use of combustion is in the burning of fuel to produce electricity, this type of reaction is ubiquitous in modern society. Combustion is necessary for factories that produce food, paper, and steel, to name a few. From the largest industrial boiler to the engine in a car, fuel burning conditions are vital. A variety of oxygen sensors are readily available for optimizing these diverse combustion processes. The main types of oxygen sensors are based on amperometric, semiconductor, and potentiometric measurements.

Amperometric sensors operate based on the measurement of current passing through the sensing device as oxygen electrochemistry is occurring (Ramamoorthy, Dutta, & Akbar, 2003). An electrochemical reaction at one or both electrodes is driven
by an applied electrical current. The kinetics of this reaction are controlled by
temperature, gas pressure, and applied potential.

Semiconductor sensors measure changes in electrical conductivity due to the
chemisorptions of oxygen by the semiconducting material (Ramamoorthy, Dutta, &
Akbar, 2003). These devices use metal oxides, most often WO₃, SnO₂, TiO₂, SrTiO₃ and
Ga₂O₃ (Spirig J. V., 2007). Although semiconducting materials have been used in high
temperature oxygen sensors in the literature, they lack specificity, making it difficult to
determine whether oxygen is truly the cause of conductivity changes.

The most common type of potentiometric high temperature oxygen sensor is
known as the lambda sensor, pictured in Figure 1.2, and is composed of a hollow “finger”
of yttria-stabilized zirconia (YSZ) with platinum electrodes (Ramamoorthy, Dutta, &
Akbar, 2003). An electromotive force signal is detected when there is a difference in
partial pressures between the sample environment and the standard 21% oxygen
atmosphere. The potential difference exists due to the defect chemistry of YSZ. The
yttria doping of zirconia leads to aliovalent vacancies in the zirconia structure, as is
indicated by the Kroger-Vink notation:

\[
\text{ZrO}_2 + \text{Y}_2\text{O}_3 \rightarrow 2\text{Y}'\text{Zr} + \text{V}_{\text{oo}} + 3\text{O}_3 \quad (1)
\]

Doping with yttria causes an oxygen vacancy (V_{oo}) where yttrium replaces the
zirconium (Y'Zr) in the crystal structure. This creates openings for oxygen ions to move
through the lattice. Oxygen dissociates at the platinum/zirconia interface as:

\[
\frac{1}{2}\text{O}_2 + 2e^- + \text{V}_{oo} \leftrightarrow \text{O}_o^x \quad (2)
\]
The oxygen ions at the surface can then move through the vacancies in the material. The junction between the electrode, zirconia, and gas is known as the triple point boundary (TPB) (Spirig J. V., 2007). The movement of the oxygen ions produced by the defect chemistry creates a potential difference between the two oxygen environments, which is measured as a voltage potential (Ramamoorthy, Dutta, & Akbar, 2003). The voltage is related to oxygen partial pressure by the Nernst equation:

\[ E = \left( \frac{RT}{nF} \right) \ln \left( \frac{P_{O_2, \text{reference}}}{P_{O_2, \text{sensor}}} \right) \]  

where \( E \) is the measured voltage, \( R \) is the gas constant, \( T \) is temperature in Kelvin, \( n \) is the number of electrons involved in the reduction of \( O_2 \), \( F \) is Faraday’s constant, and \( \frac{P_{O_2, \text{sensor}}}{P_{O_2, \text{reference}}} \) is the ratio of the partial pressures of oxygen at the two electrodes. The materials are chosen based on their behavior at high temperatures; platinum has a very high melting point and YSZ is a much better oxygen ion conductor than electronic conductor at 400-1000°C.

There has also been some interest in the use of an internal reference for high temperature oxygen sensors (Spirig, Ramamoorthy, Akbar, Routbort, Singh, & Dutta, 2007). This is ideal in situations where air is not readily available for use as a reference. It would also eliminate the need for bulky plumbing currently used to carry reference gas into coal boilers and automobile engines. The design of such a sensor has been plagued by difficulty in finding a suitable reference material and forming a hermetic seal in the casing which will survive high temperatures. A recent study demonstrated such a sensor using a casing of yttria-stabilized tetragonal zirconia polycrystal (YTZP) and a
palladium/palladium oxide reference (Spirig, Ramamoorthy, Akbar, Routbort, Singh, & Dutta, 2007). This research produced a functional sensor up to a temperature of 800°C. However, this sensor showed a leak above 800°C due to melting of the glass frit needed to fill in a gap in the seal surrounding the platinum reference electrode. Preliminary studies were done to establish the suitability of lanthanum strontium aluminum manganese oxide (LSAM) as an internal reference electrode (Spirig J. V., 2007). A wafer of LSAM was sandwiched between the YTZP and deformed by a grain boundary sliding process, creating a dense, complete seal.

B. Superplastic Joining of LSAM with Yttria-stabilized Zirconia Polycrystal

Micron-sized particles of LSAM have been joined to yttria-stabilized tetragonal zirconia polycrystal (YTZP) by superplastic flow (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008). Superplastic flow is a type of grain boundary sliding (GBS), a creep process defined as boundary offsets which occur in response to the diffusion of stress-induced vacancies (Lifshitz, 1963). In this case, the definition of GBS can be simplified as the sliding of polycrystalline ceramic grains past one another along grain boundaries without changing shape. Figure 1.3 shows a schematic of this behavior (Langdon, 2006). Creep is the general class of the phenomenon and GBS is only one type of creep. Creep is generalized in the equation:

\[
\frac{ds}{dt} = \left(\frac{\sigma - \sigma_m}{\alpha}\right)^n \dot{\varepsilon}_{\text{creep}}
\]  

(4)
Where $\frac{d\varepsilon}{dt}$ is the plastic strain rate, $C$ is a material constant, $\sigma$ is the applied stress, $d$ is the grain size, $m$ and $b$ are exponents dependent on creep mechanism, $Q$ is the activation energy for creep to occur, $k$ is the Boltzmann constant and $T$ is temperature in Kelvin.

The specific form of creep used to model GBS is known as Coble creep and described by the following equation:

$$\frac{d\varepsilon}{dt} = \left(\frac{A\mu D_{gb}}{\sigma^m d^n}\right)\left(\frac{N^b}{d^b + N^b}\right)$$ (5)

where $\frac{d\varepsilon}{dt}$ is the plastic strain rate, $A$ includes all normalization factors in one parameter, $D_{gb}$ is the material-specific grain boundary diffusion coefficient, $\sigma$ is the applied stress, $d$ is the grain size, and $N$ is the number of dislocations in a single boundary wall (Lifshitz, 1963). Since creep is dependent on the inverse cube of grain size, decreased grain size greatly increases the allowable plastic strain rate. While the Coble creep model is sufficient in systems where grains change shape to allow for rearrangement, it is unsatisfactory in light of observed phenomena when grains do not change size. At this time, no complete model for GBS in a polycrystalline material has been established.

Although grain boundary sliding has been difficult to model due to the fact that the grains do not change shape, the stability of the grain shape has made it appealing for ceramic to ceramic joining (Spirig J. V., 2007). Plastic flow by GBS occurs at one half the melting temperature of the materials to be joined. It creates a homogeneous and complete joint between the two materials, eliminating issues with solid oxide fuel cells and oxygen sensors caused by the use of adhesives and bonding materials.
Superplastic deformation of YTZP has been the subject of rigorous study and characterization (Dominguez-Rodriguez, Gutierrez-Mora, Jimenez-Melendo, Routbort, & Chaim, 2001). Yttria-stabilized zirconia is of special interest due to its wide-spread use as a solid electrolyte in high temperature oxygen gas sensors and solid oxide fuel cells. Joining studies have been published for a wide variety of grain sizes, microstructures, purities, and percent yttria. Interestingly, the conclusions of these various studies were conflicting and produced some controversy. These opposing conclusions were caused by dynamic grain growth during the deformation process. This is elucidated when the creep equation is rearranged to solve for steady-state strain rate, $\dot{\varepsilon}$:

$$X = A \varepsilon^n \frac{1}{\dot{\varepsilon}^{p/2}}$$

(6)

where the parameter $A$ includes all normalizing factors and all other variables remain as defined previously. When $\dot{\varepsilon}$ is plotted logarithmically, as shown in Figure 1.4, against $\sigma$, the graph indicates changes in slope, the relationship between $n$ and $\sigma$, the activation energy, and $p$ with increased or decreased stress. These changes in the graphical relationship would not be identified in a narrow study, leading to controversy.

With the advent of nano-YTZP powders, the data surrounding deformation was further complicated by questions about improvements in desirable properties versus possible detracting phenomena that could occur with smaller particles and contradicting studies due to lack of knowledge about proper processing. Fully dense nano-YTZP was not initially available, making it difficult to compare studies. It was eventually concluded that deformation of these powders occurred by GBS. Superplastic flow has been achieved for fine-grained YTZP (Dominguez-Rodriguez, Gutierrez-Mora, Jimenez-Melendo, Routbort, & Chaim, 2001).
Very small grain sizes between 0.3 and 1.6 μm plastically deform between at 1350°C.

The joining of non-similar materials by superplastic flow has been documented. Extensive work has been done to characterize the joining of zirconia ceramics with hydroxyapatite and alumina compounds. Hydroxyapatite ceramic is of interest because it is well suited to biomedical applications (Singh, Lorenzo-Martin, Gutierrez-Mora, Routbort, & Case, 2006). The calcium phosphate structure, Ca₁₀(PO₄)₆(OH)₂, is highly compatible with human tissue and displays the long-term chemical durability that is desirable in biomedical applications. Zirconia has been investigated as a mechanically strong, bio-inert reinforcement for hydroxyapatite devices and plastic deformation is one method of joining the two materials. Homogeneous joining of the two materials has been achieved at 1300°C and a strain rate of 5 x 10⁻⁵/s (Singh 2006). Alumina and yttria-stabilized zirconia (YSZ) are both common electrical components in a variety of fields such as transportation and energy and the development of cost-effective, reliable components is a priority. One obstacle in producing completely joined samples of the desired dimensions was the unusual shapes needed for these applications (Goretta, Gutierrez-Mora, Picciolo, & Routbort, 2003). This was originally overcome through the use of an Al₂O₃ tape-cast layer, but the porous tape did not fully densify in the joining process, leaving some porosity in the joint (Chaim & Ravi, 2000). In search of a fully dense joint, Goretta, et al., used an aerosol spray of 50/50% volume Al₂O₃ and YSZ between the layers to be joined (2003). This was found to form a fully dense joint with superplastic deformation at 1200-1350°C and strain rates on the order of 10⁻⁵/s.
Despite the uses of lanthanum metal perovskites in conjunction with YSZ and its nanometer scaled sibling, YTZP, the use of superplastic joining in this system is a relatively recent idea. This process became of interest in high temperature oxygen sensors, but could also be applied to solid oxide fuel cells. Lanthanum strontium aluminum manganate (LSAM), \( \text{La}_{0.77}\text{Sr}_{0.20}\text{Al}_{0.90}\text{Mn}_{0.10}\text{O}_{3-\delta} \), compounds were of interest as an electrical conductor in the place of a platinum wire penetrating a joined YTZP packaging for the sensor (Spirig, Ramamoorthy, Akbar, Routbort, Singh, & Dutta, 2007). The small hole around the platinum internal reference electrode had to be plugged with a glass frit, stable to only 800˚C, decreasing the temperature ceiling of the sensor, as seen in Figure 1.5. To remove this leak, it is necessary to create an internal electrode that can be joined with the YTZP using GBS.

C. Fuel Cells

Another area of interest to reduce fossil fuel usage which also uses LSAM is the fuel cell. A fuel cell is a device which is designed to convert a fuel and an oxidant to electrical energy. These devices are generally small and significantly more efficient than fossil fuel burning processes. Each individual fuel cell is composed of an electrolyte sandwiched between fuel and oxidant electrodes. The individual cells are usually linked together to create various types of “stacks”. Several common types of fuel cells are polymer electrolyte membrane (PEM), phosphoric acid (PAFC), alkaline (AFC), carbonate, and solid oxide (SOFC) (Farooque & Maru, 2001). Each type of fuel cell is appropriate for different applications based on operating temperature, corrosion, and
poisoning due to fuel components. The stability of each fuel cell in various fuels is listed in Table 1.1 (Farooque & Maru, 2001). As indicated in the table, many of the components are poisoned by common fuel components. Because of these sensitivities, it is necessary to process most fuels before they reach the fuel cell. The basic fuel cell system includes the fuel supply, power output, and recovery of waste heat as shown in Figure 1.6 (Farooque & Maru, 2001). The waste heat can be used to produce hot water and steam or to run steam and gas turbines among other things depending on the operating temperature of the fuel cell. For example, a PEM fuel cell, which operates at only 80°C, produces enough waste heat to heat water, but not enough to create steam. The hottest operation is the SOFC at 800-1000°C, which can produce heat for steam and gas turbines, hot water, organic Rankine cycles, and steam.

Several types of fuel cells are characterized in Table 1.2 (Song, 2002). As is indicated in the table, each type of fuel cell has a different operating temperature, different fuel capabilities, and different components. The cell efficiencies all fall between forty and sixty percent. The efficiencies can be compared to the coal boiler, at 36-48% efficiency, and the gasoline internal combustion engine, at an average of 18-20% efficiency. Fuel cells as a group also offer the advantage of a wide range of operating temperatures, from below the boiling point of water to extremely hot. While all of these devices can operate using ordinary fuel sources such as gasoline, diesel, and jet fuel, they also offer a variety of other options. This flexibility should be taken into consideration when choosing an appropriate fuel cell for a given application.
The diversity of environments to which each fuel cell is exposed impacts the appropriate packaging and electrode materials. The solid oxide fuel cell generally uses a Ni/YSZ electrode. This type of electrode leaves the device vulnerable to Ni coarsening, sulfur poisoning, carbon deposition, redox instability, and a variety of other problems (Fu, Tietz, & Stoever, Synthesis and electrical conductivity of Sr- and Mn-substituted LaAlO3 as a possible SOFC annode material, 2006). The use of an oxide-based electrode material was proposed by Irvine (Tao & Irvine, 2003). Based on the work by Tao and Irvine, another group researched the use of b-site manganese-doped La_{0.8}Sr_{0.2}AlO_{3} due to its improved conductivity over LSC (Fu, Tietz, & Stoever, Synthesis and electrical conductivity of Sr- and Mn-substituted LaAlO3 as a possible SOFC annode material, 2006).

D. Lanthanum-based Perovskites

Lanthanum metal oxide perovskites have been studied extensively for a variety of uses because they make good solid electrolytes. These compounds have been used in solid oxide fuel cells, suggested for oxygen sensors and documented for several catalysis processes for hydrogen transfer between organic materials. The generalized perovskite crystal structure is shown in Figure 1.7 (Woodward, P.M., private communication). The perovskite structure is characterized by three different sites- A, B, and O (oxygen). Octahedrons with oxygen at the center and metal atoms at the vertices (b-site) are arranged in cubic or nearly cubic layers. A second metal occupies the openings between the octahedral layers, which are identified as the a-site. In lanthanum metal oxides, the b-
site of the perovskite is filled with chromium, aluminum, manganese, iron, or cobalt. As solid electrolytes, research has been focused on optimizing the electron transfer while minimizing reactivity with oxygen and yttria-stabilized zirconia, often used as an ion conductor in this type of system. To accomplish this, lanthanum manganates and aluminates have both been doped with strontium.

**D.1. Lanthanum Metal Oxide Synthesis**

Lanthanum metal oxide (LaMO₃) perovskites have been synthesized by almost every conventional inorganic synthesis method, including solid state, hydrothermal, and sol gel (Bernard, Laberty, Ansart, & Durand, 2003) (Ifrah, Kaddouri, Gelin, & Leonard, 2007) (Junliang, Wei, Cuijing, & Yanwei, 2009) (Taguchi, Matsu-ura, & Nagao, 1997) (Wang, Tao, Shao, & Wang, 2009) (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008). The generalized perovskite crystal structure is shown in Figure 1.7 (Woodward, P.M., private communication). Microwave-assisted syntheses have been published for the solid state and sol gel methods. This section will detail each method and its benefits and detractors.

**D.1.1. Solid State**

Spirig, et. al., published a solid state synthesis for La₀.₇₇Sr₀.₂₀Al₀.₉Mn₀.₁O₃ (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008). Stoichiometric ratios of lanthanum, strontium, and aluminum nitrate salts and manganese chloride were mixed by grinding and the use of a Spex mill. The ground samples were then heated in air in a platinum
crucible to 1000°C for 4 hours and 1200°C for 50 hours in 3 segments, with additional grinding between heating segments.

Characterizations of the reacted powders included elemental analysis, X-ray diffraction, and scanning electron microscopy. Elemental analysis showed that the reaction ratios were maintained through the reaction process. The X-ray powder diffraction patterns indicated a pure, cubic phase of LSAM. Scanning electron microscope images indicated approximately 2 μm grains.

D.1.2. Sol Gel Synthesis

Lanthanum manganate (LM) and lanthanum strontium manganate (LSM) have been synthesized using the conventional sol gel and Pechini methods, respectively (Taguchi, Matsu-ura, & Nagao, 1997) (Wang, Tao, Shao, & Wang, 2009). In the conventional sol gel method, lanthanum and manganese nitrate salt hydrates were mixed in stoichiometric ratios with citric acid and a small amount of distilled water to make a gel. The gel was produced by allowing the solution to set at 100°C for 12 hours. The gel was then fired at 300-900°C for 6 hours. Powders were characterized by thermogravimetric analysis, differential thermal analysis, infrared absorption spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and BET surface analysis. The primary focus of this particular study was the optimal citric acid concentration to be used in the synthesis. It was concluded that an equimolar amount of citric acid with the metal salts (e.g. 1[citric acid]:1[La]+1[Sr]) produced a hexagonal type perovskite lanthanum manganate with improved catalytic activity in CO oxidation over
that of other syntheses which did not use citric acid and the solid state method (Taguchi, Matsu-ura, & Nagao, 1997).

Nano-powders of LSM have been reported using the Pechini method. This study found a small and pure product under highly acidic conditions (pH=1) in the presence of citric acid (Wang, Tao, Shao, & Wang, 2009). X-ray diffraction indicated small, homogeneous powders and electron microscopy indicated a particle size of 50-80 nm (Wang, Tao, Shao, & Wang, 2009).

Citric acid has been employed as a complexing reagent in sol gel and hydrothermal perovskite syntheses. Taguchi, et al., outlined a mechanism for citric acid coordination in the synthesis of $\text{LaMnO}_3^{+\delta}$ (1997). Upon gelation of manganese and lanthanum nitrate salts with citric acid, it was proposed that the two starting salts existed along with $\text{LaMn(C}_6\text{H}_5\text{O}_7\text{NO}_3)_3$ (Taguchi, Matsu-ura, & Nagao, 1997). The observed weight loss after firing the gel was near the theoretical 57% for the reaction

\[
\text{LaMn(C}_6\text{H}_5\text{O}_7\text{NO}_3)_3 \rightarrow \text{LaMnO}_3^{+\delta} \quad (7)
\]

This data suggests that citric acid acts as a complexing agent, holding the metal ions in place to facilitate the reaction. It is burned off in the firing or calcinations steps of the reaction, leaving the lanthanum manganate perovskite structure.

D.1.3. Hydrothermal Method of Lanthanum Manganese Oxide Synthesis

Conventional hydrothermal synthesis has been used for the synthesis of many small, inorganic structures in the past, including zeolites and nanowires. This type of synthesis is carried out in a Teflon vessel contained in a metal cavity designed to prevent explosions due to high pressures. The assembly is then heated in air for an extended
period of time at a relatively low temperature, usually around 200°C. Hydrothermal syntheses are known to require very specific pH ranges and may require processing after the hydrothermal reaction step.

Lanthanum strontium manganites have been synthesized by the hydrothermal method. Bernard, et al., have published several studies characterizing and optimizing the process (Bernard, Laberty, Ansart, & Durand, 2003) (Bernabe, Gaudon, Bernard, Laberty, & Durand, 2004) (Bernard, Durand, Verelst, & Lecante, 2004). To design a successful synthesis procedure, the reaction was attempted using citric acid and ethylenediamine as complexing agents as well as without an agent. Citric acid was found to be the most effective, producing a pure, cubic lanthanum manganite structure after calcination of the hydrothermal product.

E. Use of Microwave in Synthesis

The microwave region of the electromagnetic spectrum is defined between 0.3 and 300 GHz. This broad frequency range lends microwave radiation to a wide variety of applications. The term ‘microwave’ is commonly used to refer to the microwave oven, but microwave radiation is ubiquitous in modern technology. Wireless LAN, such as Bluetooth, global navigation satellite systems (GPS), radar, and communications satellites all operate on microwave frequencies.

Over the past thirty years, microwave radiation has entered synthetic chemistry. Initially, microwave plasmas were used to activate chemical reactions rapidly and homogeneously. Microwave-assisted synthesis debuted in 1985 and has quickly become
a major area of study (Nüchter, Ondruschka, Bonrath, & Gum, 2004). In microwave-assisted syntheses, the sample is placed inside a microwave reactor, frequently a common kitchen microwave oven, although scientific models are now available, and irradiated. This method is appealing due to its rapid, homogeneous heating, relatively simple experimental design, and ability to produce high purity products (Man & Shahidan, 2007). Microwave-assisted synthesis is also of interest in green chemistry as organic reactions can be carried out in superheated water, which both displays interesting properties for organic synthesis and is more environmentally friendly than organic solvents.

Microwaves are relatively new to the laboratory. Figure 1.8 shows the exponential increase of microwave-assisted syntheses found in the literature from 1985-2000 (Nüchter, Ondruschka, Bonrath, & Gum, 2004). In 1974, they appeared in the literature as a heat source for moisture analysis (Hesek & Wilson, 1974). A year later, it was published for wet ashing procedures. The use of the microwave as a reactor appeared in two issues of Tetrahedron in 1986, first in an article by Gedye, et al., and a few months later in a submission by Giguere, et al. Gedye studied four different organic reactions using microwave heating (Gedye, et al., 1986) (Giguere, Bray, Duncan, & Majetich, 1986). Each reaction was performed by the conventional method and in a sealed Teflon vessel inside a standard kitchen microwave. A minimum of a five-fold increase in reaction time was found in the microwave-assisted synthesis over the classical method and an increased product recovery was observed in almost all samples presented in Table 1.3 (Gedye, et al., 1986). Even at this early stage, the advantages of microwave
heating in aqueous solution were noted, but could not be fully explored due to lack of pressure control in the system.

Safety and temperature control of microwave-assisted synthesis were addressed in more detail later (Giguere, Bray, Duncan, & Majetich, 1986). The study placed reaction vessels inside vermiculite-filled desiccators to absorb any materials released in the event of an explosion. Reactions which seemed especially prone to exploding were carried out in a fume hood. Temperature measurement technology appropriate for microwave reactions was not available at the time these studies were done. Instead, temperature was estimated using sealed capillaries of materials of known melting points. This innovative method of finding reaction temperature found that the temperature inside and outside the reaction vessel differed by only ±5°C, demonstrating that it was a reasonable method of temperature monitoring.

Microwave-assisted synthesis has taken its share of criticism in more recent years. Nüchter, among the more vocal critics, summarized the faults of microwave-assisted synthesis and the literature surrounding it in his 2004 review (Nüchter, Ondruschka, Bonrath, & Gum, 2004). He found that almost all reaction types and named reactions had been tested using microwaves and, unlike Man, believed that no reaction could be performed in the microwave region that could not be carried out under more traditional conditions (Man & Shahidan, 2007). He also claimed that the literature was severely lacking in clear descriptions of processes done by microwave-assisted synthesis and the reproducibility of yield and selectivity of such reactions. Another criticism was of the microwave technology itself. Microwave reactors designed for research purposes, at the
time the review was published, did not have the capability to control temperature or pressure; only power output and irradiation times were easily controlled. This issue has been resolved with more advanced equipment for microwave-assisted reactions. The CEM Mars-5, used in this study and built two years after Nüchter’s review was published, includes both temperature and pressure gauges and the ability to control both measurements.

E.1. Operational Principles of Microwave-Assisted Synthesis

Microwave-assisted heating is highly efficient for heating polar solvents, including water, which is especially appealing due to its interesting heating properties as well as it being environmentally friendly and readily available. Microwaves can heat a reaction with a significant increase in reaction rate, as shown in Figure 1.9 (Rao, Vaidhyanathan, Ganguli, & Ramakrishnan, 1999). This rate change can be traced to the Arrhenius equation:

$$k = A e^{-rac{E}{RT}}$$

(9)

The pre-factor A in the equation is in units per second, making it dependent on the frequency of the atomic vibrations at the reaction interface. The frequency of the microwaves directly alters A, which has a multiplicative effect on the reaction rate, k (Rao, Vaidhyanathan, Ganguli, & Ramakrishnan, 1999). E is the activation energy for the reaction, which is then divided by the constant R and temperature, T.

The microwave frequency sets the molecular dipoles out of phase. Figure 1.10 shows a schematic of particle behavior under microwave irradiation. The particles
rapidly adjust to align the dipoles, but movement is limited by intermolecular interactions. This friction produces heat. Microwave frequencies change phase on the same time scale as dipole polarization. Because of this, the polarization always lags slightly behind the phase changes. The phase lag can be measured by:

\[ \delta = \tan \delta = \frac{\varepsilon''}{\varepsilon'} \]  

(10)

where \( \delta \) is the phase lag and \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of the dielectric of the material, respectively, as shown in Figure 1.11. The dielectric quantity describes the concentration of electrostatic flux lines in a given material under a given set of conditions. The dielectric quantities are related to applied frequency, \( \omega \), by the Debye equations:

\[ \varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + i \omega \tau} \]

(11)

\[ \varepsilon'' = \frac{\varepsilon_s - \varepsilon_{\infty}}{(1 + i \omega \tau)^2} \]

(12)

\( \tau \) is the single relaxation time and \( \varepsilon_s \) and \( \varepsilon_{\infty} \) are the zero and infinite frequency dielectric constants. The imaginary part of the dielectric has a peak at \( \omega \tau = 1 \) which is reached at 2.45 GHz for water at 20°C, the standard frequency of a commercial microwave oven (Mingos & Baghurst, 1991). The ideal microwave frequency for heating a given substance can be found at the maximum \( \varepsilon'' \), for example, \( \varepsilon'' \) peaks at 20 GHz for distilled water at 25°C, shown graphically in Figure 1.12. However, commercial microwaves do not operate at 20 GHz. This is because at this temperature the heating is very fast, but not very deep. Microwave penetration depth can be calculated as a function of \( \varepsilon' \):

\[ D = \frac{2\lambda}{5.896 \arctan \left( \frac{2\varepsilon'}{\varepsilon''} \right)} \]

(13)
The microwave frequency is equal to \( \lambda_0 \). Mingos and Baghurst demonstrated the relationship between \( D \) and the dielectric quantity for a material with a small \( \epsilon'' \) as

\[
D \propto \lambda_0 \sqrt{\epsilon' / \epsilon''} \tag{14}
\]

Microwave power dissipation per unit volume can also be expressed in terms of \( \epsilon' \) or \( \epsilon'' \).

\[
P = (\omega_0 \epsilon' \tan \delta) |\mathbf{E}|^2 \tag{15}
\]

\[
P = \sigma |\mathbf{E}|^2 = (\omega_0 \epsilon' \tan \delta) |\mathbf{E}|^2 \tag{16}
\]

These equations can be combined with the Debye relations to define power dissipation per unit volume as

\[
P = \frac{\epsilon_0 \epsilon'_2 - \epsilon_0 \epsilon''}{1 + \omega_0 \epsilon'_2} |\mathbf{E}|^2 \tag{17}
\]

The heating rate has been further treated with Maxwell’s equations. In the case of a microwave applicator with single-mode resonant cavity, the calculation is simplified to express the heating rate \( \frac{dT}{dt} \) to

\[
\frac{dT}{dt} = \frac{4}{\tan \delta} \frac{1}{\rho C} \frac{1}{1/V_C} \frac{P_0}{S}\frac{\epsilon''}{\rho C \text{ (area/volume) sample \( \frac{(273 + T)^3}{T^3} \)}} \tag{18}
\]

where \( \rho \) is mass density of the sample, \( V_C \) is capacity volume, \( P_0 \) is the microwave power inside the cavity, \( S \) is the Stefan-Boltzmann constant, and \( \xi \) is the surface emissivity of the sample. This expression can be used to model the steady-state temperature of a material at various microwave powers.

E.2. Microwave Assisted-Synthesis of Lanthanum Metal Oxides
While much of the literature focuses on microwave-assisted organic reactions, the use of microwave-assisted technology in perovskite synthesis has been previously documented. One such study compared the conventional and microwave-assisted hydrothermal methods of synthesizing another lanthanum manganate-based perovskite, $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3^{+}\delta (x = 0, 0.2)$ (Ifrah, Kaddouri, Gelin, & Leonard, 2007). It was concluded that the microwave synthesis used a shorter reaction time of less than 120 minutes and yielded smaller particles of 20 nm, with a narrow size distribution and uniform morphology as well as improved catalytic properties. Many perovskite syntheses have been performed by the microwave-assisted sol gel method, in which a solution of reagents is evaporated to a gel, heated by microwave, and usually ignited to produce the final product. Solid-state reactions have been carried out by microwave as well (Parhi & Manivannan, 2008). This method has also successfully produced complex perovskite structures.

E.2.1. Microwave Solid State Synthesis of Perovskites

Microwave reactions have been carried out in the solid state. Under conventional conditions, this is one of the simplest reactions to prepare. The solid starting materials are ground together and homogenized, then heated, usually to a high temperature for an extended period of time. Using the microwave as a heating source for this type of a reaction is slightly more difficult due to the microwave susceptibility of the materials. If a material is not susceptible to microwave irradiation, the dipole friction which causes
internal heating will not occur. In these cases, the reaction is often carried out in a vessel that does heat under microwave conditions.

The microwave susceptibility of a material is determined by both physical and chemical properties (Rao, Vaidhyanathan, Ganguli, & Ramakrishnan, 1999). Imperfect materials tend to have high dielectric and loss constants, leading to improved microwave susceptibility. These imperfections include impurities, aliovalent substitutions and surface charges or defects. Certain crystal structures and highly ionic materials are easily polarized over longer time periods, making them good choices for microwave heating. The chemical nature of the material also affects microwave susceptibility (Rao, Vaidhyanathan, Ganguli, & Ramakrishnan, 1999). For example, the weak bonds in chalcogenides have rotational energies corresponding to microwave frequencies, making them heat very quickly under microwave irradiation. Bulk transition metals, on the other hand, do not heat well at all. Skin depth relates to $\frac{1}{\sqrt{\sigma}}$, or conductivity. The high electronic conductivity of transition metals makes them very poor microwave susceptors.

To make up for poor microwave susceptibility, solid state reactions are often carried out in specially made vessels, most commonly quartz (Rao, Vaidhyanathan, Ganguli, & Ramakrishnan, 1999). The quartz vessel heats rapidly under microwave irradiation so that the powders inside are exposed to direct heat rather than having to produce heat from the phase lag.

The microwave-assisted solid state method has been published for the synthesis of KMF$_3$ perovskites where M is Zn, Mn, Mg, or Co (Parhi & Manivannan, 2008). Potassium metal fluorides had been synthesized by the conventional hydrothermal
method in the past, but the reaction takes several days at 200˚C and involves complex preparation and work up. Parhi and Manivannan were able to synthesize pure KMF$_3$ compounds in a microwave reactor after only ten minutes with ethanol washing and overnight drying. No external susceptor was necessary in this case.

E.2.2. Microwave-Assisted Hydrothermal Method

Since the early microwave-assisted syntheses published by Gedye and Giguere, the use of microwave heating for aqueous reaction systems has been greatly improved upon. Gedye reported promising results from aqueous reactions, but was unable to optimize these reactions due to high pressure inside the reaction vessel (Gedye, et al., 1986). With the advent of technology to monitor temperature and pressure during the reaction, the microwave-assisted hydrothermal reaction has become a reality. Aqueous systems have been of great interest due to the ability to superheat water to 200-300˚C and the decrease in harmful wastes that can be achieved by using water as a solvent.

Ifrah, et al., compared conventional and microwave-assisted hydrothermal methods for the synthesis of lanthanum silver manganate perovskites (2007). It was found that the microwave synthesized material was pure and smaller than the conventionally synthesized product. The catalytic activity in methane combustion was greatly improved and the hydrothermal reaction time was decreased from 24 hours to less than 2 hours (Ifrah, Kaddouri, Gelin, & Leonard, 2007).

F. Current Work
This chapter has described the need for effective high temperature oxygen sensors and fuel cells. The literature has also been examined for studies of lanthanum manganate perovskite synthesis and applications. The current work takes advantage of the benefits of microwave-assisted hydrothermal method to synthesize small, pure LSAM for use in grain boundary sliding applications.
Table 1.1. Effects of various fuel components on different types of fuel cells. Fuel cell types are abbreviated as PEM, polymer electrolyte membrane, PAFC, phosphoric acid fuel cell, AFC, alkaline fuel cell, and SOFC, solid oxide fuel cell. Fuel components are classified as fuel if the cell can produce energy from them, diluents if they are not used in energy production but do not harm the cell, and poison if the cell is harmed by exposure to the substance (Farooque & Maru, 2001)

<table>
<thead>
<tr>
<th>Fuel Constituents</th>
<th>PEM</th>
<th>AFC</th>
<th>PAFC</th>
<th>Carbonate</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
</tr>
<tr>
<td>CO</td>
<td>Poison</td>
<td>Poison</td>
<td>Poison</td>
<td>Fuel (&lt;0.5%)</td>
<td>Fuel</td>
</tr>
<tr>
<td>CH₄</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Fuel a</td>
<td>Fuel a</td>
</tr>
<tr>
<td>CO₂</td>
<td>Diluent</td>
<td>Poison</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
</tr>
<tr>
<td>N₂</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
</tr>
<tr>
<td>S as (H₂S &amp; COS)</td>
<td>Poison</td>
<td>Poison</td>
<td>Poison (≥50 ppm)</td>
<td>Poison</td>
<td>Poison</td>
</tr>
<tr>
<td>NH₃</td>
<td>Poison</td>
<td>Inert</td>
<td>Poison</td>
<td>Fuel</td>
<td>No Information</td>
</tr>
</tbody>
</table>

* A fuel in the internal reforming fuel cells and diluent in non-internal reforming cells.
Table 1.2. Properties of various fuel cell types (Song, 2002).

<table>
<thead>
<tr>
<th>Features</th>
<th>Fuel cell type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Polymer electrolyte</td>
</tr>
<tr>
<td>Charge carrier</td>
<td>H⁺</td>
</tr>
<tr>
<td>Electrolyte state</td>
<td>Solid</td>
</tr>
<tr>
<td>Cell hardware</td>
<td>Carbon- or metal-based</td>
</tr>
<tr>
<td>Catalyst, anode</td>
<td>Platinum (Pt)</td>
</tr>
<tr>
<td>Fuels for cell</td>
<td>H₂</td>
</tr>
<tr>
<td>Reforming</td>
<td>External or direct MeOH</td>
</tr>
<tr>
<td>Feed for fuel processor</td>
<td>MeOH, natural gas, LPG, gasoline,</td>
</tr>
<tr>
<td>Oxidant for cell</td>
<td>O₂/air</td>
</tr>
<tr>
<td>Co-generation heat</td>
<td>None</td>
</tr>
<tr>
<td>Cell efficiency (% LHV)</td>
<td>40-50</td>
</tr>
</tbody>
</table>

| Name                          | Ion exchange membrane              |
| Charge carrier                | H⁺                                  |
| Electrolyte state             | Immobilized liquid                 |
| Cell hardware                 | Graphite-based                      |
| Catalyst, anode               | Platinum (Pt)                      |
| Fuels for cell                | H₂                                  |
| Reforming                     | External                            |
| Feed for fuel processor       | Natural gas, MeOH, gasoline, diesel, jet fuel |
| Oxidant for cell              | O₂/air                              |
| Co-generation heat            | Low quality                         |
| Cell efficiency (% LHV)       | 40-50                               |

| Name                          | Phosphoric acid                    |
| Charge carrier                | H⁺                                  |
| Electrolyte state             | Immobilized liquid                 |
| Cell hardware                 | Stainless steel                     |
| Catalyst, anode               | Nickel (Ni)                         |
| Fuels for cell                | Reformate or CO/H₂ or CH₄          |
| Reforming                     | External or internal, or direct CH₄ |
| Feed for fuel processor       | Gas from coal or biomass, natural gas, gasoline, diesel, jet fuel |
| Oxidant for cell              | O₂/air                              |
| Co-generation heat            | High                                |
| Cell efficiency (% LHV)       | 50-80                               |

| Name                          | Molten carbonate                   |
| Charge carrier                | CO₃²⁻                               |
| Electrolyte state             | Immobilized liquid                 |
| Cell hardware                 | Ceramic                             |
| Catalyst, anode               | Nickel (Ni)                         |
| Fuels for cell                | Reformate or CO/H₂ or CH₄          |
| Reforming                     | External or internal, or direct CH₄ |
| Feed for fuel processor       | Gas from coal or biomass, natural gas, gasoline, diesel, jet fuel |
| Oxidant for cell              | O₂/air                              |
| Co-generation heat            | High                                |
| Cell efficiency (% LHV)       | 50-80                               |

<p>| Name                          | Solid oxide                         |
| Charge carrier                | O₂⁻                                 |
| Electrolyte state             | Solid                               |
| Cell hardware                 | Ceramic                             |
| Catalyst, anode               | Nickel (Ni)                         |
| Fuels for cell                | Reformate or CO/H₂ or CH₄          |
| Reforming                     | External or internal, or direct CH₄ |
| Feed for fuel processor       | Gas from coal or biomass, natural gas, gasoline, diesel, jet fuel |
| Oxidant for cell              | O₂/air                              |
| Co-generation heat            | High                                |
| Cell efficiency (% LHV)       | 50-80                               |</p>
<table>
<thead>
<tr>
<th>Compound</th>
<th>Procedure</th>
<th>Reaction</th>
<th>Recovery&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Rate (microwave)</th>
<th>Rate (classical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis of benzoic acid</td>
<td>Classical</td>
<td>1 hr.</td>
<td>90%</td>
<td>5%</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;COOH</td>
<td>Microwave</td>
<td>10 min.</td>
<td>95%</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Oxidation of toluene to benzoic acid</td>
<td>Classical</td>
<td>25 min.</td>
<td>60%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;COOH&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Microwave</td>
<td>5 min.</td>
<td>80%</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Reduction of benzoic acid with methanol</td>
<td>Classical</td>
<td>3 hr.</td>
<td>74%</td>
<td>19%</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;COONa&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Microwave</td>
<td>5 min.</td>
<td>76%</td>
<td>11%</td>
<td>5</td>
</tr>
<tr>
<td>Reduction of benzoic acid with propionic acid</td>
<td>Classical</td>
<td>7.5 hr.</td>
<td>89%</td>
<td>7%</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;COOH&lt;sub&gt;3&lt;/sub&gt;H</td>
<td>Microwave</td>
<td>10 min.</td>
<td>88%</td>
<td>11%</td>
<td>25</td>
</tr>
<tr>
<td>Reduction of benzoic acid with n-butanol</td>
<td>Classical</td>
<td>1 hr.</td>
<td>82%</td>
<td>12%</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;COOH&lt;sub&gt;4&lt;/sub&gt;H</td>
<td>Microwave</td>
<td>7.5 min.</td>
<td>79%</td>
<td>17%</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Classical</td>
<td>12 hr.</td>
<td>72%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CONH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Microwave</td>
<td>3 min.</td>
<td>74%</td>
<td></td>
<td>240</td>
</tr>
<tr>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CONH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Classical</td>
<td>16 hr.</td>
<td>69%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CONH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Microwave</td>
<td>4 min.</td>
<td>92%</td>
<td></td>
<td>240</td>
</tr>
</tbody>
</table>

<sup>a</sup> Very high pressure was developed, and the study of this reaction was halted.

<sup>b</sup> The recovery values are based on isolated yields and represent the average of at least two experiments. The C<sub>9</sub>H<sub>5</sub>C<sub>2</sub>N<sub>2</sub>H<sub>3</sub> reaction was followed by titrating the chloride ion.

<sup>c</sup> Value for one run only.

Table 1.3. Table comparing reactions under classical and microwave conditions. These are the results of the first published microwave-assisted syntheses (Gedye, et al., 1986).
Figure 1.1. Optimal coal boiler operation based on air to fuel ratio.
Figure 1.2. Schematic of potentiometric oxygen sensor. The inset indicates $O^2-$ diffusion from $pO_2(\text{reference}) > pO_2(\text{sample})$. Oxygen concentration is measured based on this potential difference (Ramamoorthy, Dutta, & Akbar, 2003).
Figure 1.3. Schematic diagram of grain boundary sliding (Langdon, 2006). Possible sliding offsets are defined as $u$, $v$, and $w$ with sliding vector $S$ under applied stress $\sigma$. Angles $\theta$ and $\psi$ define angles between boundary surfaces and the tensile stress.
Figure 1.4. Plotted strain rate vs. stress for samples deformed at (a) varying temperatures and (b) with varying grain size (Dominguez-Rodriguez, Gutierrez-Mora, Jimenez-Melendo, Routbort, & Chaim, 2001).
Figure 1.5. Photographs of the hole in the seal of a high temperature oxygen sensor a) after deformation and b) with frit glass used to fill in the space and c) data showing sensor failure at 800°C (Spirig, Ramamoorthy, Akbar, Routbort, Singh, & Dutta, 2007).
Figure 1.6. Schematic of a fuel cell power system (Farooque & Maru, 2001).
Figure 1.7. Generalized schematic of a perovskite structure where A and B are different metal cations and the b-site cation is octahedrally bound with oxygen (Woodward, P.M., private communication).
Figure 1.8. Histogram of the number of publications related to microwave synthesis from 1985 until 2003. (Nüchter, Ondruschka, Bonrath, & Gum, 2004)
Figure 1.9. Graph relating temperature to microwave power (Mingos & Baghurst, 1991).
Figure 1.10. Schematic drawing of dielectric heating of water (Nüchter, Ondruschka, Bonrath, & Gum, 2004). As the electric field passes between the molecules, the polarization changes rapidly, leading to internal friction and heat.
Figure 1.11. A schematic representation of the dielectric components as a function of frequency. The real part is labeled $\varepsilon'$ and the imaginary is $\varepsilon''$ (Mingos & Baghurst, 1991).
Figure 1.12. Graphical representation of the real and imaginary dielectric properties of water as a function of frequency (Mingos & Baghurst, 1991).
Chapter 2: Microwave Synthesis of La$_{0.77}$Sr$_{0.20}$Al$_{0.90}$Mn$_{0.10}$O$_{3-\delta}$

A. Introduction

LSAM was appealing because it meets the requirements for both the sensor application and superplastic joining with YTZP (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008). The cubic dependence on grain size in Coble creep is of note. Grains must be small and, in the case of joining dissimilar materials, similar in size. LSAM is a good electrical conductor and a weak ionic conductor of oxygen between 400°C and 1000°C, the working temperatures of the proposed sensor. The LSAM and YTZP have similar thermal expansion coefficients (TEC), meaning they will not shrink at significantly different rates when the sample is cooled nor will they swell unevenly when heated to working temperatures that may exceed 1000°C. Lanthanum zirconates have slightly different TECs, near 7x10$^{-6}$ K$^{-1}$, from YTZP, approximately 11.6x10$^{-6}$ K$^{-1}$, causing the joint to become fragile (Bobzin, Lugscheider, & Bagcivan, 2006), (Figueiredo, Marques, & Frade, 2001). It is also important that no impurities develop as a result of chemical reactions along the joining plane during the deformation process. For example, lanthanum zirconates are a common side reaction in the superplastic joining of lanthanum manganate perovskites and zirconia. Aluminum doping in the perovskite b-site can limit the side-reactions between LSAM and YTZP (Fu, Tietz, & Stover,

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Synthesis and electrical conductivity of Sr- and Mn-substituted LaAlO₃ as a possible SOFC anode material, 2006).

Successful joining of LSAM with YTZP by plastic deformation was published in 2008 (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008). In that study, 0.4 μm grain size commercial YTZP was joined with approximately 2 μm grain size LSAM synthesized by the solid state method. Two sensors were constructed using this material, as shown in Figures 2.1a and b, but the sensors were shown to leak during operation. This leak can be seen in Figure 2.1c as the drifting baseline of the signal.

The present work has shown the successful synthesis of LSAM in the cubic perovskite phase under microwave-assisted hydrothermal conditions. The particles are small, on the order of 25 nm, and of uniform morphology. Complete joining with YTZP has been demonstrated.

B. Experimental

B.1. Microwave Synthesis Procedure

A stoichiometry of La₀.₈Sr₀.₂₀Al₀.₉₀Mn₀.₁₀O₃ was made in aqueous solution by mixing the nitrate salts of lanthanum, strontium, aluminum and manganese (Alfa Aesar). A typical reaction consisted of 3.46 g lanthanum nitrate, 0.42 g strontium nitrate, 3.38 g aluminum nitrate, and 0.18 g manganese nitrate in 40 mL of water. Citric acid was added in concentrations equal to, double, and triple that of the lanthanum and strontium combined. A single equivalent of citric acid was 2.10 g. Ammonia was used to adjust the pH of the solution to 9.00.
All experiments were carried out in a CEM Mars 5 microwave reactor with HP500 Plus reaction chambers. The reactor was programmed to reach a temperature of 200°C and a pressure of 150 bar over 5 minutes and hold that temperature for a set period of time. Soak times of 1, 1.5, and 3 hours were used. Upon cooling, water was evaporated from samples. The remaining solid was heated to 650°C for 2 hours in air.

Samples are labeled as LSAM-microwave time-microwave use-citric acid concentration-calcination. For example, a sample that has been heated in the microwave (MW) for 3 hours with \([\text{CA}] = 2(\text{[La]}+\text{[Sr]}) \text{(2X)}\) and calcined in air at 650°C for 2 hours is labeled LSAM-3-MW-2X-C. This naming system is detailed in Table 2.1.

**B.2. Solid State Synthesis Procedure**

La\(_{0.8}\)Sr\(_{0.2}\)Al\(_{0.9}\)Mn\(_{0.1}\)O\(_3\) was synthesized by the solid state method using nitrate salts of lanthanum, strontium, and aluminum and the chloride salt of manganese (Alfa Aesar). Starting materials were homogenized in stoichiometric ratios by a combination of grinding with an agate mortar and pestle and Spex milling. Reactions were composed of 13.64 g lanthanum nitrate, 1.70 g strontium nitrate, 7.69 g aluminum nitrate, and 5.84 g manganese chloride. The powder was heated to 1000°C in air for 4 hours and then removed from heat for further grinding. The reaction was returned to the furnace and heated to 1200°C in air for 50 hours in 3 segments with grinding between segments. This sample has been labeled LSAM-SS.

**B.3. Joining**

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LSAM-6-MW-1X-C and LSAM-SS powders were prepared for joining by pressing into 1.1 cm² pellets at 3000 kg of pressure. Pressed pellets were then sintered in air at 1500°C for 50 hours in a platinum crucible. Three percent yttria-stabilized zirconia polycrystal (YTZP) was purchased in pre-densified rods from Custom Technical Ceramics, Inc. (Arvada, CO). Wafers were cut from these rods and planarized by wet polishing with 600 grit sandpaper. Superglue was used to construct a sandwich with the LSAM pellet between two YTZP wafers for joining.

The sandwich was then placed inside a high temperature furnace connected to an Instron Universal Testing Machine (Instron, model 1125) at Argonne National Laboratories. The furnace was set to a temperature of 1250°C. The sample was compressed with a crosshead speed of 0.01 mm/min for a strain rate of $4.5 \times 10^{-5}$ s⁻¹ (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008). A load of 5 N was placed on the sample for 30 minutes to allow thermal equilibrium to be reached.

**B.4. Characterization**

Powders were characterized by X-ray diffraction, transmission electron microscopy, infrared spectroscopy, and Raman spectroscopy. The joining plane between LSAM and YTZP was characterized by scanning electron microscopy.

X-ray diffraction was performed using a Rigaku Geigerflex X-ray Powder Diffractometer with 1.54 Å Cu Ka.

Transmission electron microscopy (TEM) was performed using a Tecnai F20 instrument in scanning transmission electron microscope (STEM) mode. Samples were
prepared on size 400 holey carbon film over mesh. Each sample was prepared by probe sonication of a small amount of powder in water. The solution was applied to the film in two 20 μL drops. Excess water was wicked away from each drop and the film was allowed to dry before the second drop was applied. Several additional methods of sample preparation were tested before this was chosen. Without wicking, samples were found to aggregate heavily making it impossible to clearly view individual grains. The use of ozone exposure to increase the “stickiness” of the grid was also attempted, but found to destroy the grid. It is possible that very brief exposure to ozone would improve the sample quality. Scanning electron microscopy (SEM) was performed using a Sirion scanning electron microscope in scattered electron mode. Ultra-high resolution mode was used for images of less than 1 μm in scale. LSAM/YTZP sandwiches were cut using a diamond saw blade to expose the cross-section, then mounted in conductive Bakelite and diamond polished to 1 μm. The mounted and polished samples were etched in 1 M HCl for 30 minutes and sputtered with gold.

Diffuse reflectance infrared spectroscopy was performed using a Perkin-Elmer instrument. Samples were not diluted before use. Potassium bromide was used as a background sample in all spectra. Spectra were collected 450-4000 cm⁻¹ using an MCT mid-IR detector. Single beam spectra were then converted to Kubelka-Munk using Spectra software (Perkin-Elmer). Transmission infrared spectroscopy was done using a Bruker Tensor 27 instrument. Samples were diluted to 5% by weight with potassium bromide and pressed into pellets in air using a bolt. The scan range was 450-4000 cm⁻¹. Data was collected and manipulated using Opus software.
Raman spectroscopy was carried out on a Renishaw-Smiths Detection Combined Raman-IR Microprobe. A 514 nm laser was used to illuminate pellets of pure powders, pressed as described above. Spectra were collected from 100 to 1100 cm\(^{-1}\).

C. Results

C.1. Synthesis

Successful solid state synthesis of La\(_{0.8}\)Sr\(_{0.2}\)Al\(_{0.9}\)Mn\(_{0.1}\)O\(_3\) was confirmed by XRD, shown in Figure 2.2. The spectrum showed peaks at \(2\theta = 23.4, 33.3, 41.1, 47.8, 53.9, 59.6, 70.0, 75.0\) and 79.9. The powder was uniformly black in color. These characteristics are in agreement with published data (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008).

Microwave-assisted synthesis conditions were optimized in two ways. In the first optimization step, aqueous solutions of nitrate salts of lanthanum, strontium, aluminum, and manganese were made with three different concentrations of citric acid and the pH was adjusted to 9 with ammonium hydroxide (Bernard, Laberty, Ansart, & Durand, 2003). Water was chosen as a solvent due to the low environmental impact compared to other solvents. The reaction was carried out in the microwave for 1.5 hours at 200°C and a maximum pressure of 200 bar. After recovery from the microwave reaction chamber, the water was evaporated, and the remaining solid was heated to 650°C for 2 hours in air. Junliang et al. found that increased citric acid concentrations could improve the reaction rate of hydrothermal nanoparticle syntheses (2009). This conclusion was based on the study of M-type barium hexaferrite nano-powders (Junliang, Wei, Cuijing, & Yanwei,
Like LSAM, the barium hexaferrite was traditionally synthesized using a time-consuming solid state method. The goal of the barium hexaferrite synthesis study was to develop an alternative sol gel procedure which would reduce reaction times. The group used three different concentrations of citric acid and tested the reaction completion using XRD and TEM before concluding that increased citric acid concentration led to a decreased reaction time (Junliang, Wei, Cuijing, & Yanwei, 2009).

After microwave-assisted hydrothermal reaction, the LSAM solid remained incompletely reacted in aqueous solution. Evaporation was chosen over centrifugation because strontium is soluble in water and is lost with the supernatant if the sample is centrifuged. The three samples were LSAM-1.5-MW-1X -C, with \([\text{CA}]=[\text{La}]+[\text{Sr}]\), LSAM-1.5-MW-2X-C and LSAM-1.5-MW-3X-C. This sample naming scheme is detailed in Table 2.1. Figure 2.3 shows XRD patterns for the three samples. LSAM-1.5-MW-1X-C showed several peaks associated with the cubic perovskite LSAM (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008). The peaks are \(2\theta= 23.4, 33.3, 41.1, 47.8, 53.9, 59.6, 70.0, 75.0 \) and 79.9°. Broad peaks at 28° and 44° indicate an amorphous phase. The crystalline LSAM peaks still appeared in LSAM-1.5-MW-2X-C, but the intensity was significantly decreased and the broad peaks increased in intensity. No crystalline LSAM was observed in LSAM-1.5-MW-3X-C. Based on this data, it was concluded that the optimal citric acid concentration was \([\text{CA} ]= [\text{La}]+[\text{Sr}]\).

Further optimization was performed to choose the correct amount of time for microwave irradiation because the reaction was incomplete in LSAM-1.5-MW-1X-C, indicated by the broad XRD peak from \(2\theta = 25^\circ \) to 35°. The above experiments were
performed again with constant citric acid concentration and microwave reaction times of 1.5, 3, 5, and 6 hours followed by calcination for 2 hours at 650°C. All of the samples showed the expected LSAM peaks in the XRD spectra at $2\theta = 23.4$, 33.3, 41.1, 47.8, 53.9, 59.6, 70.0, 75.0 and 79.9° (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008). Two of the samples, shown in Figures 2.4a and b, included significant impurities: the spectrum for LSAM-1.5-MW-1X-C indicated a very broad peak at $2\theta = 28°$ and LSAM-3-MW-1X -C had some crystalline impurities at $2\theta = 25$, 26, 27, 28, 29, 31, 34, 43, 45, and 50°. Longer heating times yielded cleaner samples. LSAM-5-MW-1X-C can be seen in Figure 2.4c and had small impurities at 29° and 31° and, with further heating, LSAM-6-MW-1X-C had no unexpected XRD peaks, as can be seen in Figure 2.4d. All calcined samples were light grey in appearance.

Thus, the characterization and joining studies primarily focused on LSAM-6-MW-1X-C.

C.2. Characterization

The X-ray diffraction data was used to predict particle size through the Debye-Scherrer equation:

$$\tau = \frac{K \lambda}{\beta \cos \theta}$$

Where $\tau$ is the average crystallite size, $K$ is the shape factor (set to be 1 for this work), $\lambda$ is the X-ray wavelength (1.54 Å for this instrument), $\beta$ is the full width at half maximum, and $\theta$ is the Bragg angle. Based on the peak at $2\theta = 33.3°$, the crystal size of LSAM-6-MW-1X -C is approximately 30 nm.
Particle size was further studied by transmission electron microscopy (TEM) (Tecnai). Suspensions of LSAM-6-MW-1X-C were applied to holey carbon grids. Samples were studied in STEM mode. These images, shown in Figure 2.5, indicate an average particle size of 25 nm.

LSAM-6-MW-1X-C was analyzed in the previous section of this work using X-ray diffraction (fig. 2.4). Previous literature has matched this pattern to the cubic perovskite phase of LSAM (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008).

C.3. Spectroscopic Studies

Diffuse reflectance infrared spectroscopy was also used to analyze the reaction mechanism. Once again, the data indicated a change between LSAM-3-MW-1X and LSAM-5-MW-1X. LSAM-1.5-MW-1X and LSAM-3-MW-1X, shown in Figures 2.6a and b, had very similar spectra with peaks at 1069, 1052, and 837 cm\(^{-1}\) and at 1067, 1053, and 836 cm\(^{-1}\), respectively. LSAM-5-MW-1X also had peaks at 1068, 1050, and 836 cm\(^{-1}\) and an additional peak at 668 cm\(^{-1}\), which is labeled in Figure 2.6c. Similar peaks were observed in LSAM-6-MW-1X, shown in Figure 2.6c, at 1068, 1052, 835, and 666 cm\(^{-1}\). The carboxyl group of citric acid absorbs at 670 cm\(^{-1}\) and the N-O stretching of NO\(_3\) is at 820 cm\(^{-1}\) (Li, Yao, & Xue, 2009). A peak near 670 cm\(^{-1}\) appears after 5 hours of hydrothermal reaction.

Raman spectroscopy was performed on all calcined samples. Data was collected using a 514 nm laser beam to scan from 100-1100 cm\(^{-1}\). Literature lists LSAM peaks are at 567 and 745 cm\(^{-1}\) (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008). The
spectrum for LSAM-1.5-MW-1X-C had 2 peaks at 633 and 739 cm\(^{-1}\), shown in Figure 2.7a. A band near 640 cm\(^{-1}\) has been observed for LaMnO\(_3\) perovskites and could be attributed to incomplete reaction (Abrashev, et al., 1999) Figure 2.7b showed that peaks appeared in the LSAM-3-MW-1X-C spectrum at 594 and 734 cm\(^{-1}\). A new peak first appeared in LSAM-5-MW-1X-C at 401 cm\(^{-1}\) in addition to the original two peaks at 588 and 744 cm\(^{-1}\), which can be seen in Figure 2.7c. The new peak was more pronounced in LSAM-6-MW-1X-C, shown in Figure 2.7d, which had peaks at 398, 589, and 741 cm\(^{-1}\). Significant features appear to be the decrease in frequency of the far right peak from 739 cm\(^{-1}\) to 741 cm\(^{-1}\) and the appearance and shift of the peak near 400 cm\(^{-1}\) with increased hydrothermal reaction time.

Infrared spectra were collected for the diluted calcined samples LSAM-1.5-MW-1X-C, LSAM-3-MW-1X-C, LSAM-5-MW-1X-C, and LSAM-6-MW-1X-C, shown in Figure 2.8. A prominent peak near 450 cm\(^{-1}\) in all samples can be attributed to the Al-O bond in the octahedral configuration (Lavat & Baran, 2003). Another large band near 650 cm\(^{-1}\) can be attributed to the MnO\(_6\) octahedra (Staneva, Gattef, Dimitriev, Mikhov, & Geshev, 2004) (Milenov, Rafailov, Abrashev, Nikolova, Titorenkova, & Gospodinov, 2009). These groups can be identified in all samples, confirming a perovskite phase.

C.4. Characterization of Joining

The joinings of LSAM-6-MW-1X-C and LSAM-SS with YTZP were characterized using a Sirion scanning electron microscope. At the 2 \(\mu\)m scale, LSAM-SS was found to be indistinguishable from YTZP along the joining plane, shown in Figure
2.9. Some large crystals were observed along this boundary and can be attributed to known lanthanum zirconate-producing reactions between LSAM and YTZP at the high temperatures and pressures used in the joining process (Spirig, Routbort, Singh, King, Woodward, & Dutta, 2008), (Bobzin, Lugscheider, & Bagcivan, 2006), (Figueiredo, Marques, & Frade, 2001). The joining of LSAM-6-MW-1X-C with YTZP was shown to form a dense, uniform joining at the 200 nm scale in Figure 2.10. Though some sample appears to have been removed in the sample preparation process, no gaps or side products appear along the joint. Some difficulty was experienced in preparing these samples due to the aggressive vibration of the saw and repeated polishing using sandpaper. It was found that some of this abuse to the sample could be eliminated by mounting the cross-sectioned sample in Bakelite before polishing, but the cutting step cannot be replaced.

D. Discussion

The goal of this research was to develop a method of producing LSAM that resulted in smaller grain sizes than current methods. A variety of methods for lanthanum-based perovskite synthesis have been published, but many were not suitable for this project. The sol gel synthesis ends in the ignition of the gel; this is undesirable due to the fire hazard associated with burning the gel inside the microwave reactor. Solid state microwave-assisted synthesis involves significantly higher temperature as well as a specialized microwave reactor system. Hydrothermal synthesis was selected because it is relatively easy to do, safe, and environmentally friendly.
Based on previous studies of perovskite synthesis, it was concluded that the concentration of citric acid relative to the a-site and b-site ion total concentrations could be important. To find the optimal citric acid concentration, this work included a series of reactions which were heated with microwave radiation for 1.5 hours each, calcined for 2 hours at 650°C and characterized by XRD, shown in Figure 2.3. It was found that the 1:1 ratio of citric acid to a-site (lanthanum and strontium) produced the most crystalline LSAM product. This was determined by considering the presence of clearly defined peaks which matched the established pattern. Crystallinity appeared to decrease with double and triple the concentration of citric acid. The LSAM-1.5-MW-1X-C was chosen as the optimal sample from that set of experiments.

While LSAM-1.5-MW-1X-C was partially crystalline, it was apparent that the reaction was incomplete. Several peaks were visible which are not included in the documented XRD spectrum for LSAM and a broad band was visible below 50° (2θ). The next step in optimizing the synthesis was to establish the hydrothermal reaction time necessary to complete the synthesis. Hydrothermal reaction times of 1.5, 3, 5, and 6 hours were used. Each hydrothermal reaction was followed by evaporation of the liquid phase and calcination at 650°C for 2 hours, as established by Bernard, et al. (2004). After calcination, XRD (Figure 2.4) indicated increased crystallinity with increased reaction time. A broad peak at 2θ = 28° dominates the spectrum for LSAM-1.5-MW-1X-C, indicating a non-crystalline phase. That peak separated into several smaller, but still fairly broad, peaks in LSAM-3-MW-1X-C. Few differences were visible in the spectra of LSAM-5-MW-1X-C and LSAM-6-MW-1X-C, but the 6 hour reaction did show
increased peak intensity, suggesting a more crystalline product. This sample was further characterized by TEM. The images in Figure 2.5 indicated an average grain size near 25 nm, which is significantly smaller than the 2 μm grains produced by the solid state synthesis. The grains also appeared to be cubic in shape. This part of the study indicated that LSAM-6-MW-1X-C was small and pure. Previous work has indicated the synthesis of small lanthanum strontium manganate crystals using a 20-hour, 200°C hydrothermal treatment. Other methods have required significantly higher temperatures and produced micron-sized particles. The method described in this work has been shown to be faster, at lower temperature, and produces smaller grains than these methods.

The synthesis mechanism was explored by infrared diffuse reflectance infrared spectroscopy and Raman spectroscopy. The diffuse reflectance spectra indicated the presence of nitrate in all of the uncalcined samples (Figure 2.6). This was to be expected since all of the starting materials were nitrate salts. A carbonate band was also apparent, which is a common lanthanum compound. While the bands which appeared in LSAM-1.5-MW-1X-C were constant throughout the samples, an additional peak was visible for the samples which had been heated for 5 and 6 hours in the microwave. Raman spectroscopy was also less informative than had been hoped due to the high background intensity of the uncalcined samples. After calcination, Figure 2.7 showed that only perovskite crystalline bands were detected by Raman. An additional Raman band appeared in LSAM-5-MW-1X-C and LSAM-6-MW-1X-C. Fourier-transform IR spectroscopy, shown in Figure 2.8, indicated some change in relative intensity of octahedral complexes and lanthanum-oxygen bonding, but no notable change in structure.
While the exact event is still unclear, these mechanistic experiments suggest that a significant change in composition occurs between 3 and 5 hours of microwave irradiation.

Superplastic joining created dense joints between YTZP and LSAM synthesized by both methods. The solid state synthesized LSAM showed some larger crystals along the joining plane, pictured in Figure 2.9. The sample using LSAM-6-MW-1X-C was less prone to cracking within the LSAM layer, as is seen in Figure 2.10. The image shows a dense and complete joint between the LSAM-6-MW-1X-C and YTZP. This can be compared to the large crystals which formed along the joining plane of LSAM-SS and YTZP. Previous studies suggest that these crystals are lanthanum zirconates, which are side products formed under the high pressures and temperatures of the deformation process and can be limited by doping and grain size control. These large crystals have a different thermal expansion coefficient from LSAM and YTZP, preventing proper joining (Bobzin, Lugscheider, & Bagcivan, 2006).

E. Conclusions

This work has demonstrated the ability to synthesize $\text{La}_{0.8}\text{Sr}_{0.2}\text{Al}_{0.9}\text{Mn}_{0.1}\text{O}_3$ by the microwave-assisted method. The optimal conditions are 6 hours of microwave-assisted reaction at 200ºC using citric acid as a complexing agent with a concentration equal to that of lanthanum and strontium and 2 hours calcination at 650ºC. Shorter reaction times were shown to be ineffective in completing the reaction and varied citric acid concentrations resulted in non-crystalline products. Characterization of these
samples was done using X-ray diffraction, Raman spectroscopy, and infrared spectroscopy. Transmission electron microscopy was used to show that the perovskite grains produced were small, on the order of 25 nm. After the material was synthesized, it was shown to create a uniform, dense joint with yttria-stabilized tetragonal zirconia polycrystal. This sample was compared to joined samples of YTZP with 
$\text{La}_{0.8}\text{Sr}_{0.20}\text{Al}_{0.90}\text{Mn}_{0.10}\text{O}_3$ which had been synthesized by the solid state method. Scanning electron microscopy indicated an indistinguishable boundary between the LSAM-6-MW-1X-C and the YTZP. We have shown that LSAM-6-MW-1X-C is appropriate for these conditions and does not exhibit any side reactions.

F. Future Work

The next step for this project is to construct a sensor using LSAM as the internal reference electrode. This sensor was designed with the goal of creating a high temperature internal reference oxygen sensor with a dense seal and should be able to be sealed under the same deformation conditions used in the test joint described in this work. This construction should tolerate temperatures above 1000°C and maintain a stable response. Sensors of this nature would have applications in a wide variety of combustion-based processes and eliminate the issues of bulky plumbing and locating a reference sample.
<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Microwave Reaction Time (hr)</th>
<th>Microwave (MW) or Solid State (SS)</th>
<th>Citric Acid Concentration (equivalents [La]+[Sr])</th>
<th>Calcination (650°C for 2 hrs in air)</th>
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</thead>
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<tr>
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<td>MW</td>
<td>1X</td>
<td>No</td>
</tr>
<tr>
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<td>MW</td>
<td>1X</td>
<td>Yes</td>
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<td>MW</td>
<td>2X</td>
<td>No</td>
</tr>
<tr>
<td>LSAM-SS</td>
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<td>SS</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 2.1: Sample naming scheme. LSAM identifies the sample as La$_{0.8}$Sr$_{0.20}$Al$_{0.90}$Mn$_{0.10}$O$_3$. 

Figure 2.1. Schematic of oxygen sensor using LSAM sandwiched between two layers of YTZP (a), photograph of sensor made with LSAM internal reference electrode (b), and sensing data using LSAM-SS exposed to 3, 5, 7, 10, 14, and 21% oxygen (c).
Figure 2.2. X-ray powder diffraction data for LSAM synthesized by the solid state method.
Figure 2.3. X-ray powder diffraction data for LSAM after 90 minutes of microwave hydrothermal reaction calcined at 650°C for 2 hours with different citric acid concentrations. a. LSAM-1.5-MW-1X-C, b. LSAM-1.5-MW-2X-C, c. LSAM-1.5-MW-3X-C
Figure 2.4. X-ray powder diffraction data for LSAM after various microwave-assisted hydrothermal reaction times followed by calcination at 650°C for 2 hours. 

a. LSAM-1.5-MW-1X-C, b. LSAM-3-MW-1X-C, c. LSAM-5-1X-C, d. LSAM-6-MW-1X-C
Figure 2.5. Transmission electron micrographs of LSAM-6-MW-1X-C powders.
Fig 2.6. Spectra collected by diffuse reflectance infrared spectroscopy for LSAM-1.5-MW-1X-C (a), LSAM-3-MW-1X-C (b), LSAM-5-MW-1X-C (c) and LSAM-6-MW-1X-C (d).
Figure 2.7. Raman spectra of calcined powders (a) LSAM-1.5-MW-1X-C, (b) LSAM-3-MW-1X-C, (c) LSAM-5-MW-1X-C and (d) LSAM-6-MW-1X-C.
Figure 2.9. SEM of joining plane between LSAM-SS and YTZP after plastic deformation at 1250°C.
Figure 2.10. SEM image of joining between LSAM-6-MW-1X-C and YTZP after plastic deformation at 1250°C.
Bibliography


