Mixed Conduction and Defect Chemistry of Manganese and Molybdenum Substituted Gadolinium Titanate Pyrochlore

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Abstract

The Solid Oxide Fuel Cell (SOFC) is an electrochemical device that converts chemical energy directly to electrical energy. This device bypasses the pollution problems and relatively low efficiencies of conventional fossil fuels generators. The main drawback to SOFC utilization has been the need for high operating temperatures (1000 °C) to provide adequate efficiencies. The primary goal of SOFC research has been the reduction in this temperature. As operating temperatures around 700 – 800 °C have been achieved, it has become clear that the primary efficiency loss comes from the slow kinetics of the electrode reactions. This thesis will pursue mixed ionic and electronic conducting oxide ceramics that could be used to enhance the slow kinetics.

Electrical conductivity measurements were made on the pyrochlore Gd$_2$((Mo$_{1-x}$Mn$_x$)$_y$Ti$_{1-y}$)$_2$O$_7$ (GMMT) as a function of oxygen partial pressure (P$_{O_2}$) ($10^{-25}$ < P$_{O_2}$ < 1 atm), temperature (600 °C ≤ T ≤ 1000 °C), and composition (x,y). Particular emphasis was placed on the materials value as a mixed ionic and electronic conductor (MIEC). Previous work on the Gd$_2$(Ti$_{1-x}$Mo$_x$)$_2$O$_7$ system has shown it to have high electronic conductivity (10$^2$ S/cm) with a high minority ionic conductivity (up to 10$^{-1}$ S/cm) for high Mo values under anodic conditions. However, the material decomposes at higher P$_{O_2}$, due to a sharp increase in oxygen interstitial concentration accompanying the oxidation of Mo$^{4+}$ to Mo$^{6+}$. In this study, we investigated the ability of variable valent Mn to compensate the oxidation of Mo and thereby stabilizing the material to much higher P$_{O_2}$ while retaining the high conductivity.

The conductivity of GMMT was found to increase by over 4 orders of magnitude by increasing x from 0.01 to 0.3 with y = 0.66. The peak value in air of 0.2 S/cm was obtained at 1000 °C for the x = 0.33, y = 0.66 material. The conductivity was weakly dependent on y, increasing by about ½ order of magnitude under oxidizing conditions when increasing y from 0.33 to 0.66 (x = 0.1). The activation energy for the conduction in the characteristic P$_{O_2}$ independent plateau decreased systematically with x from nearly 1.5 eV at x = 0.01, y = 0.66 to 0.64 eV at x = 0.3, y = 0.66. All of the compositions were found to be stable pyrochlore up to 1000 °C, the highest temperature used in this study.
A detailed defect model was developed to model and explain the electrical conductivity of GMMT. Our analysis indicates that the material is primarily electronic at all \( x, y \), with some potential ionic conduction under reducing conditions. The conductivity conforms well to a dilute defect model for \( x \leq 0.05 \), while at \( x \geq 0.1 \), the material is suspected to experience defect band hopping conduction within the Mo and Mn levels. The incorporation of defect bands into the defect model is necessary to explain the large jump in conductivity and decrease in activation energy with increasing \( x \). Modeling of the conductivity data for \( x = 0.01 \) and \( 0.05 \) \( (y = 0.66) \) materials yields an estimate for the Mn ionization energy of \( \sim 2.6 \) eV as well as expressions for the reduction constant, \( K_r = 10^{77} \text{ (atm}^{1/2}\text{cm}^{-9})\exp(-6.4\text{eV/kT}) \), and Frenkel constant, 

\[ K_f = 10^{51}\text{(cm}^{-6})\exp(-2.9\text{eV/kT}) \] . Similar modeling for the \( x = 0.3, y = 0.66 \) material yields defect band hopping energies in the Mn and Mo defect bands of 0.19 eV and 0.22 eV respectively.

Independent measurements utilizing an electronic blocking cell to separate the ionic and electronic contributions to the conductivity were made for the \( x = 0.1, y = 0.66 \) composition. The measurements confirm that the material is electronic with a transference number of \( 0.9 - 0.95 \) under oxidizing environments. The level of the ionic conductivity is on the order of \( 10^{-2} - 10^{-3} \) S/cm at 900 °C.

The electrode impedance of Pt electrodes on Ca doped GT was monitored as a function of \( P_{O_2} \) and temperature for both 2% and 10% Ca levels in order to provide a reference for later studies with mixed conducting electrodes. The magnitude of the electrode conductance \( (1/R_{\text{electrode}}) \) is maximized under oxidizing regimes \( \text{(} P_{O_2} = 0.21 \) atm) and high temperatures \( (1000 \) °C) with a value of 0.1 S/cm. The conductance decreases in oxidizing environments as \( P_{O_2} \) decreases, reaching a minimum of approximately \( 10^{-4} \) S/cm at intermediate \( P_{O_2} \) \( (\sim 10^{-10} \) atm), which coincides with a switch from \( O_2/\text{Ar} \) gas mixtures to \( \text{CO/CO}_2 \) gas mixtures. Under reducing conditions, the conductance increases as \( P_{O_2} \) decreases (CO concentration increases).

The slopes of log-log plots of the electrode conductance vs. \( P_{O_2} \) were compared to those predicted by theoretical models of the electrode reaction for the purpose of identifying a likely microscopic rate limiting mechanism. In oxidizing environments, both materials are modeled as being largely limited by surface diffusion of adsorbed oxygen on the Pt surface, with a shift to control by dissociative adsorption of \( O_2 \) on the Pt at lower temperatures for the 10% Ca material (not exhibited by the 2% Ca material). The mechanism under reducing environments is unclear, but seems likely to involve the reaction of CO on the Pt surface with oxygen to form \( \text{CO}_2 \).

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1 INTRODUCTION

Present day energy consumption is well above the equivalent of six megatons of TNT per year \(^1\). The burning of fossil fuels represents nearly all of this amount. This combustion process not only yields a relatively low electrical efficiency, but also generates a myriad of pollution problems. These include, but are not limited to, potential global warming due to increased CO\(_2\) levels in the atmosphere, increased levels of noxious particles, and high levels of harmful chemicals such as nitrous oxides. Alternative electrical energy sources are being pursued that minimize or eliminate these pollution problems. The ideal solution would also provide a higher electrical efficiency.

The fuel cell could provide this solution. Fuel cells provide energy through the direct conversion of chemical to electrical energy, rather than through an intermediate combustion step to provide heat. This chemical conversion allows fuel cells to achieve higher efficiencies than conventional steam generators\(^1\) while reducing the level of emitted harmful pollutants to near zero. Fuel cells can also be used continuously in any area of the globe (avoiding limitations imposed on other alternative energy sources such as solar, wind, hydro, etc.).

The energy generated by a fuel cell is based on the electrochemical reaction between a fuel and an oxidant. The composition of the fuel and oxidant vary depending
on the exact type of fuel cell, but in all cases they are separated by a multilayer cell. This cell is composed of an electrolyte sandwiched between two electrodes. The electrolyte is a material that transports chemical species (ionic conductivity) but hinders electronic species. The electrodes facilitate the interaction of the fuel and oxidant with the electrolyte and generally allow the transport of both electronic and ionic species. The materials of each region of the cell should not only fulfill these requirements, but also be chemically stable with respect to each other and the chemical species in the fuels.

Many types of fuel cells exist. They range over cells with phosphoric acid, molten carbonate, polymeric, or solid oxide electrolytes. This thesis will focus on materials development relevant to the solid oxide fuel cell (SOFC), where each regime of the cell is composed of a solid ceramic oxide. The fuel and oxidant are gaseous (CH\textsubscript{4} or H\textsubscript{2} is often used as the fuel and air as the oxidant). This type of cell has several distinct advantages. All the materials are in the solid state, leading to increased flexibility and easier handling. Exhaust fuels are generally very hot and facilitate the use of cogeneration applications. Cell life is increased due to higher tolerance for impurities (such as sulfur) in the materials. Finally, emissions are reduced, especially of CO\textsubscript{2}. [3]. Along with these advantages come disadvantages, however. The need to provide facile movement of chemical species through a solid means that these cells must be operated at extremely high temperatures (as high as 1000 °C). This promotes detrimental chemical interactions between the various regimes of the cell that form poorly conducting phases at the interfaces. The high temperature is also responsible for failure due to cracking and

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1 Fuel cells have been operated at a net electric efficiency of around 60% at a capacity of 1 MW. A diesel generator plant operating at
warping on repeated on/off cycling due to mismatched thermal expansion properties in the various materials.

Past research in this area has focused on reducing the operating temperatures of the cells. This has largely been achieved by increasing the ionic conductivity of the electrolyte material or engineering cells with thinner electrolytes. This has led to some amount of success, allowing cells to operate at 700-800 °C. Some of the state of the art materials this research has produced include stabilized ZrO$_2$ (see [4] for a review), La based perovskites (e.g. $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ [5]), and Ca doped gadolinium titanate pyrochlore ($La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ [5]). However, as the operating temperature has decreased, a new problem has arisen. The kinetics of the chemical reactions at the electrodes are very sensitive to temperature. As the temperature has dropped, the slower electrode kinetics have become more important to the operation of the cell. It is now realized that to achieve even lower operating temperatures, research must be directed at increasing the kinetics of the electrode reactions.

The materials requirements of the electrodes include the ability to conduct both electronic and ionic species (mixed ionic and electronic conductivity (MIEC)) and remain chemically and structurally stable in contact with the electrolyte and the fuels.
Classically, electrodes were prepared via a thin layer of porous metal. The pores allowed the gaseous chemical species to penetrate to the electrolyte, and the metallic nature of the material provided the electronic conductivity. However, this restricts the reactions to the
"three phase triple points". That is, the electrode reaction occurs only where the gaseous chemical species, the electronically conducting metallic electrode, and the ionic conducting electrolyte come into mutual contact. This occurs only over a limited area of the electrode, thereby limiting the kinetics of the reaction.

Research into MIEC electrodes has only recently developed and has focused on a new class of MIEC ceramic oxide materials. Since these materials conduct both ionic and electronic species, the reaction can occur across the entire surface, leading to more rapid electrode kinetics. Research has focused on optimizing the conductivities of both ionic and electronic species while improving or maintaining the required stability of the electrode.

It should be noted that MIEC materials have a wide range of applications beyond fuel cell electrodes. The operation of gas permeation membranes, certain gas sensors, and electrochromic devices all rest on the level of MIEC in the constituent materials. New and improved MIEC materials will benefit all of these fields.

This thesis will focus on developing MIEC in the pyrochlore system (general formula $A_2B_2O_7$). This system has a distinct advantage over other material systems in that it provides a great degree of flexibility in adding new elements to the host material. This allows one to greatly vary the conductivity of the material by adding different chemical species. Tuller and co-workers [7] have recently patented a cell structure based on this system where each different region is the same host material doped appropriately to provide the required conduction values. This type of cell has distinct stability
advantages with respect to the electrolyte/electrode interaction. Since each region is the same phase, just slightly chemically different, detrimental chemical reactions are eliminated. Additionally, thermal expansion mismatch between the various layers is minimized. Past work in the Tuller group has yielded materials based on Gd$_2$Ti$_2$O$_7$ (GT) for the electrolyte (Ca doped GT [6]) and for an electrode which is stable in contact with the reducing fuel (Mo doped GT [8]). What remains to be found is an electrode MIEC material that is stable in the oxidizing environment (air).

In this work, the base pyrochlore system of GT will be systematically chemically modified to improve its level of MIEC and stability under oxidizing conditions. Experiments will be performed to investigate the magnitude of conductivity of the material and its stability with respect to the reactants used (oxygen and CO/CO$_2$ mixtures). The final goal will be the development of a pyrochlore material with high MIEC that is stable in air.
This chapter will review the area of mixed ionic and electronic conductors and their applications. In particular, concepts used to predict and control the mixed ionic and electronic conduction in the materials used in this work will be of interest. Particular emphasis will be placed on oxygen-based conductors and on reviewing research on the conductivity of pyrochlore materials. The solid oxide fuel cell will also be reviewed in depth, with particular focus on the need for mixed conducting materials as electrodes. It is hoped that the reader gains an appreciation of the technological importance of mixed conducting oxides and the role in which pyrochlore materials fulfill this need.

2.1 Applications utilizing Mixed Conductors

Mixed conductors are growing in importance for devices in many industries. The most important and widely recognized use is as Solid Oxide Fuel Cell electrodes. However, the list also includes sensor devices, electrochemical oxygen pumps or separators, electrochromic electrodes, and insertion electrodes.

Figure 2.1 shows an application map of conducting ceramic oxides. The vertical axis represents increasing ionic conductivity; applications lying on this axis involve pure ionic conductor (solid electrolytes). The horizontal axis represents electronic
conductivity, and applications lying on it involve semiconductors or metallic conductors.

In the middle regime, where $\sigma_{\text{ionic}} \approx \sigma_{\text{electronic}}$, lie applications that utilize mixed conductors.

A key potential application for mixed conductors is as fuel cell electrodes, the focus of attention in this work. Their use as oxygen separation membranes will also be covered briefly. Other applications are only mentioned in passing and will not be covered in any detail.

2.1.1 Solid Oxide Fuel Cell

The Solid Oxide Fuel Cell (SOFC) is a particular type of fuel cell; an ingenious device that directly converts electrical energy from chemical energy. The fuel cell is only one specific device of this class of electrochemically based energy conversion devices, which also includes batteries. This section will explain the basic principles of this device as well as some of the basic material requirements for its operations (including the role of mixed conductors). The special role that pyrochlores could fulfill in the SOFC is discussed in a separate section at the end.
Figure 2.1 Typical applications for ionic and electronic conductors as a function of increasing magnitude of conductivity. Included are applications which require mixed conduction and therefore fall within the quadrant bounded by the two axes. From [9].
2.1.1.1 Basic Principles

A schematic of the SOFC is shown in Figure 2.2. The basic driving force is the gradient in oxygen activity across the cell. Oxygen is incorporated at the cathode via interaction of the cathode material with the oxidizing environment above it. In this process, electrons are consumed and an oxygen ion is injected into the lattice of the electrolyte. The electrolyte conducts the oxygen ions to the anode where they are liberated by interaction with a very reducing environment (such as H\textsubscript{2}, CO\textsubscript{2}, or CH\textsubscript{4}) and the generation of electrons to the anode. In the ideal SOFC, the electrolyte is a very good conductor of oxygen but a very poor conductor of electrons. This forces the electrons liberated at the anode to travel through the external circuit and provide electrical energy to some load. The electrons are then consumed at the cathode, thereby completing the circuit. Very often, a series of these basic cells are connected via metallic interconnects to provide a higher external voltage. Interconnect materials will not be discussed in the following. The focus will be on the anode, cathode, and electrolyte.

The fuel cell is an electrochemical system where the equilibrium (zero current) cell potential can be described by the Nernst equation for the particular fuels involved. For a H\textsubscript{2}/O\textsubscript{2} cell, the equilibrium voltage will be on the order of 1.0 – 1.2 V depending on the exact temperature and fuel mixture [3]. This value assumes a pure ionic conductor as an electrolyte. Any electronic current in this region will correspondingly decrease the equilibrium potential.
Figure 2.2 Schematic of a fuel cell. The cell shown is a H₂/O₂ SOFC. The cathode half reaction is \( \frac{1}{2}O_2(g) + 2e^- (\text{cathode}) \Rightarrow O^{2-} (\text{electrolyte}) \). The anode half reaction is \( H_2(gas) + O^{2-} (\text{electrolyte}) \Rightarrow 2e^- (\text{anode}) + H_2O(gas) \). The net cell reaction is \( \frac{1}{2}O_2 + H_2 \Rightarrow H_2O(gas) \).
Ideally, when current is drawn from a fuel cell, the entire equilibrium potential drops across the load, providing maximum electrical efficiency. Unfortunately, this is not the case. In reality, the cell itself develops parasitic potential “sinks” as current is drawn that lower the actual potential, and current, that the load receives. Figure 2.3 shows how the typical voltage of the cell changes as the current increases. As shown, the actual voltage deviates substantially from the ideal case. This difference is called the overpotential, $\eta$. The sources of overpotential comes from all regions of the cell: the anode, cathode, and electrolyte.

At low current densities, the overpotential arises mainly from polarization (potential loss) at the electrodes due to a slow electrocatalytic step when oxygen is incorporated into the electrolyte (or vice versa). At intermediate current densities, the ionic resistance of the electrolyte starts to dominate the overpotential. This is just a linear resistance that is directly related to the generally low ionic conductivity in solids. Finally, at very high current densities, mass transfer effects may be seen. These occur when the higher currents have driven the concentration of reactants at the reaction zone of the electrode to near zero. The current is then limited by the diffusion of those species to the electrode from the surroundings.
Figure 2.3  Voltage vs. Current for a typical hypothetical fuel cell.
Figure 2.4 shows a schematic of a SOFC cathode at a microscopic level. The overall reaction incorporates oxygen from the gas into the electrolyte. An electrode of porous metal (Pt) is shown. The electrode must be porous so that oxygen from the gas can diffuse to reaction sites. As the reaction requires gaseous oxygen, electrons from the cathode and oxygen vacancies in the electrolyte, it can only proceed at so-called “triple points”; places where all three phases come in contact. Of all the kinetic steps involved in the process shown in Figure 2.4, the ones considered as possible rate limiting steps are: (1) diffusion of the oxygen through the pores to the triple points, either in the gas phase or as surface diffusion on the metal or electrolyte, (2) the actual transfer of charge at the triple point, or (3) adsorption and/or dissociation of the oxygen on the metallic surface [10], [11], [12], [13], [14], [15], [16], [17], [18]. Though a fair amount of work has been done on isolating the reaction mechanism, a substantial controversy still remains as to what is actually happening. It is clear, however, that the electrode polarization is very sensitive to both the environment and the electrode microstructure [18], [19]. The same arguments hold for the anode, though the mechanisms there usually involve the transfer of several types of gas (H₂ and H₂O or CO and CO₂) instead of just oxygen.
Cathode Reaction: \[ \frac{1}{2} \text{O}_2 \text{(gas)} + 2e^-(\text{electrode}) + V^*_o(\text{electrolyte}) \Rightarrow O_2^*(\text{electrolyte}) \]

Figure 2.4 Schematic of cathode reaction of a SOFC with porous metallic Pt electrodes and with MIEC electrodes. The need for a three phase "triple point" is emphasized in the metallic electrode. The entire surface can become active in the MIEC electrode.
2.1.1.2 Materials Requirements and Choices

Electrolyte

The primary materials requirements for SOFC electrolytes are high ionic and low electronic conductivities. State of the art values would be: $\sigma_1 > 0.1$ S/cm at 1000 °C and $t_e < 10^{-3}$ [3]. In addition, the material must remain an ionic conductor in the reducing atmosphere above the anode and the oxidizing one above the cathode. Secondary requirements include chemical stability with the electrodes, oxygen, and reducing gas, thermal stability with the electrodes and interconnects, and mechanical stability. The material must also be cost effective.

Most of the research on oxygen conductors and SOFCs in general have focused on providing a material with very high ionic conductivity [4], [6], [5], [20] so that the operating temperature of the SOFC could be lowered to values < 1000 °C. Lower operating temperatures offer numerous advantages such as increased overall efficiency, decreased operating costs, and fewer materials compatibility problems.

This research has largely been successful. The present day, state of the art, electrolyte is doped ZrO$_2$ (generally (ZrO$_2$)$_{0.92}$(Y$_2$O$_3$)$_{0.08}$) which has an ionic conductivity of up to $10^{-1}$ S/cm at 1000 °C [3]. This material meets all of the above requirements and has the advantage of being fairly widely available commercially. It does have some drawbacks, however. The activation energy is fairly steep, $\sim 0.8 - 0.9$ eV. As the
operating temperature is decreased, a large activation energy is unfavorable as the conductivity will decrease faster. In addition, the ionic conductivity, while high, can still be improved to even higher values. Finally, it is not fully chemically compatible with state of the art electrode materials. All of these factors guarantee that the search for new and better solid electrolytes will continue (the recent development of perovskites based ionic conductors is a notable example [5], [21]).

**Cathode**

The primary requirement for cathode materials is the ability to transport electronic and ionic species to reaction points. It must also be stable with respect to the electrolyte and oxidant, and must be catalytic with respect to oxygen adsorption and dissociation. As discussed above, classically, porous metallic electrodes (e.g. LaSrMnO\(_3\) or Pt) were often used. This worked fairly well at high temperature (1000 °C) where electrode polarization was negligible. However, as better electrolytes allowed the operating temperature to be reduced, the electrode polarization created more and more of a problem. It has become clear that metallic electrodes will not provide the solution, no matter how well engineered. The need for three phase triple points severally limits the useable area of the electrode, thereby decreasing efficiency and raising overpotential.

The proposed solution is to use mixed conducting ceramic electrodes. In this case, the electrode can transport both the electrons and ions through its bulk. The reaction area can therefore be increased many-fold over the case of a pure metal (see
Figure 2.4). In addition, if the right materials are chosen, a very close match in chemical and thermal properties can be achieved with the electrolyte.

The requirements for the state of the art MIEC cathode include: high electronic conductivity (> 10 S/cm), non-negligible ionic conductivity (about $10^{-1}$ S/cm), high catalytic activity of oxygen dissociation and adsorption, chemical stability with the electrolyte and interconnect, and the ability to control microstructure and achieve good adherence to the electrolyte [3]. Cost effectiveness must also be considered.

The most widely used material at the present time is the La$_{1-x}$Sr$_x$MnO$_3$ (LSM) perovskite. The electrical conductivity can reach nearly 400 S/cm at 800 °C for $x = 0.5$. The main advantage of the material over Pt is its dramatically lower cost. While possessing some ionic conduction, the material is not a very good mixed conductor [22], [23]. It still relies on gas phase diffusion through pores to triple points for the cathode reaction to proceed. Also, it has a tendency to react with ZrO$_2$ (especially at higher Mn content) and form non-conductive products at the interface.

Because of these drawbacks, the LSM material is probably not going to be the cathode material choice for long. Many groups are searching for a good MIEC in oxidizing environments to replace it (including the current work). If the goal is to use the cathode with the ZrO$_2$ electrolyte, any new MIEC materials must also be chemically compatible with it. Recent work has been done on Co and Fe doped perovskites La$_{1-x}$Sr$_x$(Co,Fe)O$_3$ towards this end [24], [25], [3]. It has exhibited excellent MIEC properties at reduced temperatures ($\sigma_i$ about $10^{-1}$ S/cm, $\sigma_e$ between 100 and 1000 S/cm at
800 °C). However, it reacts even faster than LSM with the ZrO$_2$ electrolyte. Though the potential for vast improvement exists, LSM remains the cathode of choice for SOFC development based on zirconia.

**Anode**

As with the cathode, the anode must transport electronic and ionic species very efficiently. In addition, the anode must be stable with respect to the electrolyte and in the very reducing atmosphere above it. It must also have a high catalytic rate with respect to oxidation of the fuel (H$_2$ for example). Finally, as in all the cases above, the cost of the material must be minimized.

Presently, the anode material of choice for SOFCs is a porous Ni – yttria stabilized ZrO$_2$ (YSZ) cermet [3]. This is used because it (a) is stable with respect to the electrolyte of choice, ZrO$_2$, (b) is stable in very reducing atmospheres, and (c) contains Ni, a very good catalyst with respect to H$_2$. In addition, the cost of the electrode is not large.

The Mo doped Gd$_2$Ti$_2$O$_7$ (GT) discussed in Section 2.3.3.3 exhibits very good mixed conduction in very reducing atmospheres. It could be a possible candidate for the MIEC anode material. However, it has not been tested with ZrO$_2$ (in terms of thermal or mechanical stability), and its catalytic properties with respect to H$_2$ oxidation are not known. Although, as discussed in the next section, it makes a very attractive anode in the proposed “monolithic” pyrochlore SOFC.
Summary

From the above discussion and reviewing the current literature, it is clear that the materials used in the state of the art SOFCs are not optimized. There is ample room for improvement in all three regimes, electrolyte, anode, and cathode. The successful development of mixed conduction electrode materials that are stable in oxidizing and/or reducing atmospheres is a clear goal for the industry. It is hoped that this thesis can provide a meaningful contribution to this search.

2.1.1.3 The Monolithic Pyrochlore SOFC

From the discussion in Section 2.1.1.2, it is clear that compatibility between the various materials in the SOFC is a concern. Problems include both chemical compatibility, such as the formation of non-conductive phases by reaction between the cathode ((La,Sr)MnO₃ or (La,Sr)CoO₃) and the electrolyte (ZrO₂), and thermal stability problems such as adherence between metallic anodes and the ZrO₂ electrolyte.

Tuller and co-workers have recently proposed and patented [7], [26] a monolithic pyrochlore SOFC. In this device, each different regime of the cell is a pyrochlore based material. However, each one is doped to provide the appropriate stability and conductive properties. Figure 2.5 shows a schematic of the cell side by side with the present day SOFC. The present day SOFC has three distinctly different types of materials for each different regime, leading to the host of stability problems described above. On the other
hand, the monolithic cell is composed of the same phase throughout, leading to a much more stable device.

As noted in Figure 2.5, an appropriate cathode material has still not been found for the monolithic device. Ca doped GT (see Section 2.3.3.2) would serve as a good electrolyte due to its high ionic conductivity and low electronic conductivity. The anode could be Mo doped GT with its very good MIEC in reducing atmospheres. As noted later, the Mo doped GT decomposes in oxidizing atmospheres. It cannot be used as a cathode. Some thought has been given to using Ru doped GT (see Section 2.3.3.3) as the cathode. However, this material is unstable and expensive. It is not an outstanding mixed conductor either.

The process of studying MIEC in this thesis is primarily geared towards finding a material to serve as a cathode in a monolithic pyrochlore SOFC. By modifying the Mo doped GT to increase its stability with respect to oxidizing environments (see Section 2.1.1.3), it is hoped that a cathode material will be created. With this final component in place, the device shown in Figure 2.5 could be fabricated and studied.
Figure 2.5 A schematic of the pyrochlore based monolithic SOFC shown side by side with present day state of the art fuel cell. Materials used for the cathode, electrolyte, and anode are emphasized. Note the uniform phase of the monolithic cell and lack of an adequate pyrochlore cathode material.
2.1.2 Oxygen Separation Membranes

In recent years, the use of MIEC ceramic membranes as oxygen separation devices has gained in importance [27]. A thin dense layer of mixed conducting material is inserted between two chambers with different \( P_{O_2} \). The differential \( P_{O_2} \) applied across the membrane provides the driving force for oxygen transport. Since the direct molecular movement of \( O_2 \) is blocked, the oxygen is incorporated as ions in the material and transported across the membrane. The flux of oxygen ions (with a two negative charge) is compensated by the simultaneous flow of electrons in the opposite direction.

Presently, solid electrolytes are used to accomplish this effect. However, since they do not conduct electronic carriers, the compensating electron flow needs to be driven by an external power source. MIEC offers the possibility to achieve oxygen separation without external circuits or power sources.

Present research is focusing on isolating very good MIEC materials such as the Co based La, Sr based perovskites discussed earlier. The material not only has to provide good conductive properties, but also needs to be stable in both \( P_{O_2} \) environments and very stable mechanically. Industrial applications for oxygen separators are numerous. They range from small scale uses such as medical units in hospitals to larger scale applications such as coal gasification [27]. It could also be important in the field of chemical processing, where a controlled fixed amount of oxygen is needed to control a certain
reaction such as the partial oxidation of light hydrocarbons (natural gas) to provide ethane or syngas [27].

2.2 Conduction in Oxides

The total electrical conduction in oxides is given by the sum of the partial conductivities of each mobile charged species in the material:

\[
\sigma_{\text{total}} = \sum_j \sigma_j
\]

where \( \sigma_j \) is the partial conductivity of species \( j \). Each partial conductivity is defined by

\[
\sigma_j = c_j Z_j q \mu_j
\]

where \( c_j \) is the concentration, \( Z_j q \) is the effective charge, and \( \mu_j \) is the mobility of species \( j \). The ratio of the partial conductivity of \( j \) to the total conductivity is termed the transference number,

\[
t_j = \frac{\sigma_j}{\sigma_{\text{total}}}
\]

The sum of all transference numbers in the material must equal one.
Conduction in oxides is often split into two subcategories [28]. Ionic conduction is given by the sum of the anionic and cationic motion, and electronic conduction represents the sum of conduction by electrons and holes. These can be represented formally by $t_i$ and $t_e$ ($= t_n + t_p$), respectively. Optimizing the conduction of any species requires optimizing two separate parameters, the concentration and the mobility.

2.2.1 Ionic Conduction

A flow chart of parameters for ionic conductivity is shown in Figure 2.6. Ionic motion in oxides is a thermally activated process involving the activated jumps of an ion from one crystal site in a material to an equivalent neighboring site. This can occur either by ions hopping via vacant sites or interstitial sites in the structure. This motion is described by [28]

\[
\sigma_{\text{ion}} = \gamma \frac{N q^2}{kT} c(1-c) a^2 r_0 \exp(\Delta S/k) \exp(-E_m/kT) \\
= \sigma_0 \exp(-E_m/kT)
\]

where $a$ is the jump distance, $r_0$ is the attempt frequency, $\gamma$ represents geometrical effects, $N$ is the atomic density of ions in the appropriate sublattice, and $E_m$ is the migration energy. The term $c$ represents the number of sites in the appropriate sublattice that are occupied. The conductivity is dependent on the product of the number of occupied and non-occupied sites. It is optimized when the value of $c = \frac{1}{2}$. 

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While ionic motion in oxides can be either cationic or anionic, it is of interest to focus on the motion of anions, namely oxygen, in this thesis. The mobility of oxygen ions in oxides is determined by the crystal structure of the material. The anions must have a sufficiently “wide” path to move through the crystal lattice. The main parameter governing ionic mobility is the migration energy, $E_m$. The effect is manifested through many factors. Perhaps the most obvious condition is the amount of free volume in the material. A crystal structure with a large distance between adjacent atoms will have a wider path for conduction and a lower migration energy [29], [30]. Mobility is also linked to the size of the mobile ion, with smaller ones having a higher mobility. Finally, more polarizable ions generally have a lower migration energy [31].

The other parameter controlling ionic motion, the concentration of mobile ions, is related to the concentration of defects on the appropriate crystal sublattice (manifested in the $c(1-c)$ term in equation (2.4). While a theoretical analysis of defect formation in oxides will be postponed until Chapter 3, the major mechanisms will be introduced here. The defect concentration can be modified directly through extrinsic means and is the most useful manner in which to tailor the ionic conduction of oxides.
Figure 2.6  Major parameters controlling ionic conductivity in oxides. The broken lines indicate that large number of carriers generated extrinsically or via deviations from stoichiometry may effect the carrier mobility. From [28].
Any crystal structure at a finite temperature will contain intrinsic defects. These form naturally as the result of entropic considerations. The Frenkel mechanism occurs when an ion in a normal lattice site jumps to an interstitial site in the structure, leaving behind a vacant lattice site. While costing energy, this disordering increases the entropy of the system. At any given temperature, a concentration of these defects will exist as these two forces balance. Increasing the temperature of the system gives greater weight to the entropic effect of disordering and, therefore, a greater concentration of defects. The Schottky mechanism involves the simultaneous removal of a stoichiometrically equivalent amount of ions on the sublattices (these ions can be considered to move to the surface of the material) to form vacant lattice sites. Usually, one of these mechanisms will dominate within a material at a given temperature. The formation energies of the two determine which one dominates. For example, in the pyrochlore structure, the formation energies heavily favor the oxygen Frenkel mechanism \([30]\).

The typical defect concentrations formed by the Frenkel and Schottky mechanisms is too low to provide an adequate level of ionic conductivity at typical temperatures (1000 °C) \([28]\). Occasionally, however, an intrinsically disordered crystal structure will provide defect concentrations high enough to provide a basis for high ionic conduction (often termed fast ion conduction). This disorder is the result of an incomplete occupancy of a certain sublattice in the crystal structure. Examples of materials with this property include sodium β-alumina and the pyrochlore \(\text{Gd}_2(\text{Ti}_x\text{Zr}_{1-x})_2\text{O}_7\) \([32]\).
Doping with negatively or positively charged ions (relative to the lattice elements) provides one means of extrinsically controlling the defect population of a material. These dopants skew the electrical charge balance of the material, requiring defect formation to provide charge compensation. Performed in an appropriate manner, this technique can alter conduction values by many orders of magnitude. Typical concentrations can run from the parts per million to 10% or more in the case of broad solid solutions [28].

A final method that provides control over mobile charge concentrations is controlled deviations from stoichiometry. Many oxides can be reduced or oxidized by varying the surrounding atmosphere (the partial pressure of oxygen, $P_{O_2}$) via the evolution or incorporation of oxygen respectively. This process affects the carrier concentration in the lattice, leaving elevated interstitial concentrations when oxidized and elevated vacancy concentrations when reduced. This subject is covered in more detail in Chapter 3.

2.2.2 Electronic Conduction

Electronic conduction refers to the movement of electrons and holes under an applied electric field. It is also governed by the carrier mobility and concentration. Figure 2.7 shows the parallel to Figure 2.6 for electronic conduction.

The mobility of electronic carriers in ionic compounds is largely determined by the interaction of the carriers with the polar vibrational modes of the crystal. Electrons tend to deform the surrounding lattice, becoming trapped in a potential well of radius $r_p$. 
Trapped electrons and their associated polarization are referred to as polarons. [28].

There are two types of common polarons: large and small.

A large polaron is formed by weak coupling between an electron and optical phonons. This weak coupling results in $r_p$ much larger that the interatomic spacing. The electron can therefore move throughout the material in an electronic band, but with a somewhat enhanced effective mass. Large polaron mobility can be described by [28]

\begin{equation}
\mu = \mu_0 T^{-1/2}
\end{equation}

Typical values of this mobility at elevated temperatures will be on the order of $1 - 100$ cm$^2$V$^{-1}$s$^{-1}$. [28].

Small polarons, on the other hand, occur in oxides with relatively narrow bands and very strong coupling between electrons and optical phonons. The electron becomes trapped at a specific lattice site and can only move through the lattice with a series of activated hopping steps (similar to the method for ionic diffusion). Small polaron mobility is thermally activated and can be described by [28].

\begin{equation}
\mu = \left[ \frac{(1-c)e^2 \nu_p}{kT} \right] \exp\left(- \frac{E_H}{kT} \right)
\end{equation}

where $E_H$ is the hopping energy and $(1-c)$ is the fraction of sites without trapped electrons. Materials exhibiting this type of electronic mobility exhibit greatly reduced
Figure 2.7 Major parameters controlling electronic conductivity in oxides. The broken lines indicate that large number of carriers generated extrinsically or via deviations from stoichiometry may effect the carrier mobility. From [28].
mobility compared to ones with large polarons. Typical values might be on the order of $10^4$ to $10^2$ cm$^2$/V sec at elevated temperatures [28].

The intrinsic electronic carrier concentration is governed by thermal generation of electrons and holes and is strongly dependent on the energy band gap between the valence and conduction band of the material (see Figure 2.8) [33],

$$n_i = p_i = \sqrt{N_C N_V} \exp(-E_g/2kT)$$

where $E_g$ is the band gap, $n_i$ is the intrinsic electron concentration, $p_i$ is the intrinsic hole concentration, and $N_C$ and $N_V$ are the effective density of states in the conduction and valence band respectively (which are dependent on the effective masses of electrons and holes respectively). The band gap in common oxides can range from 2 to 10 eV [28].

The concentration of electrons and holes can be extrinsically controlled by the addition of dopants. Impurity atoms in the structure can lead to defect electrical energy states being populated by carriers within the band gap (Figure 2.8). By choosing the appropriate dopant, these states can either lie near the conduction band to form a donor state, or near the valence band leading to an acceptor state. Carriers in these states are much easier to thermally excite to either of the respective bands, leading to elevated carrier concentration. For situations where donor ionization controls the electron concentration [34],

$$n = \left( \frac{N_C N_D}{2} \right)^{1/2} \exp\left(-\frac{E_D}{2kT}\right)$$
where \( N_D \) is the donor density and \( E_D \) is the energy donor ionization energy. A similar relation exists for acceptor ionization and hole concentration.

Nonstoichiometry within oxides can also be used to control the concentration of electron concentrations (see Figure 2.8). Oxygen vacancies created by reducing the material can act as donors and be doubly ionized, releasing two electrons. Similarly, oxygen interstitials formed by oxidizing a material act as acceptors and create two holes in the valence band.

2.2.3 Mixed Ionic and Electronic Conduction

All ionic materials are mixed ionic and electronic conductors (MIEC) to some degree. In most cases, however, this term is used for materials that contain significant levels of both types of conduction. Given the form of the conductivity relation in Equation (2.2), this implies [28],

\[
\text{(2.9)} \quad c_i \mu_i \approx c_e \mu_e
\]

Since electron mobilities are typically \( 10^4 - 10^8 \) times greater than ionic mobilities, a corollary of Equation (2.9) becomes that the ionic carrier concentration needs to be \( 10^4 - 10^8 \) times that of the electronic carrier concentration [28].
Figure 2.8 Various mechanisms of carrier generation in a semiconducting material. Arrows represent paths of excited electrons (leaving behind a hole when originating in valence band). Intrinsic generation is thermal ionization of an electron over the band gap (represented by $E_g$). Extrinsic carrier generation can be achieved either by doping with donors (increasing electron concentration) or acceptors (increasing hole concentration). Nonstoichiometric generation occurs via the interaction of material with the surroundings (written here for oxides). Reduction of the material (loss of oxygen) leads to vacancy generation, which act like donors. Oxidation of the material (incorporation of oxygen) leads to interstitials, which act like acceptors.
This corollary can be satisfied through careful materials engineering and selection. High band gap oxides have a better chance of satisfying Equation (2.9) due to the low intrinsic electron concentration. Selection of appropriate dopants can elevate ionic carriers relative to the electronic concentration, as can controlled deviations from stoichiometry. Naturally disordered crystals also have elevated ionic carrier concentrations. The use of materials with "loose", open crystal structures promotes the chances of finding MIEC by raising the ionic mobility. The use of crystals that form small polarons with mobile electrons also promotes MIEC due to the lowered electron mobility.

The techniques and ideas developed above will be used extensively in this thesis in seeking to provide not only high levels of MIEC, but also to develop a method to systematically control and predict its magnitude. The pyrochlore system was chosen as a likely candidate to exhibit MIEC for many of the reasons discussed above. It is discussed in some detail in the next section.

2.3 *The Pyrochlore System*

The general chemical composition of stoichiometric pyrochlore oxides is $A_2B_2O_7$, where $A$ and $B$ are cations. In the majority of cases, the $A$ site is +3 valent and the $B$ site +4 valent, although pyrochlores with a +2, +5 combination are possible. One of the most
useful aspects of this system is the fact that it can accommodate a very wide range of elements on the A and B sites. This will become apparent in the discussion on conductivity below. A review of the crystal structure is presented first.

2.3.1 Crystal Structure

The ideal pyrochlore structure is cubic with space group Fd3m. The unit cell has a lattice parameter of roughly 10 Å. The A and B sites have two different oxygen coordination polyhedra. A cations have 8-fold coordination and are located within distorted cubes (scalenohedra). The B cations (which are generally smaller than the A, about 0.6 Å as opposed to about 1 Å \[^{[35]}\]) have 6 fold coordination and lie within trigonal antiprisms.

There are many different ways to describe the overall pyrochlore structure, but perhaps the easiest to picture is its derivation from the defect fluorite structure. Figure 2.9 shows the fluorite structure of CaF\(_2\). The fluoride anions arrange themselves in a simple cubic arrangement. If this arrangement of fluoride ions is viewed as a series of cubes, the Ca cations occupy the center of every other cube. Viewed another way (Figure 2.10), the Ca atoms have a face centered cubic arrangement with the F atoms located in the tetrahedral interstices.
The pyrochlore structure based on $\text{A}_2\text{B}_2\text{O}_7$ can be viewed as an ordered superstructure with a cell edge double that of “defect” fluorite\(^2\) [36]. A projection of the structure is shown in Figure 2.11. 48 oxygen atoms on f positions (48f) form one sublattice. These account for 6 of the seven oxygen units. Each 48f site has 6 other 48f neighbors as well as an 8a and 8b site on next nearest neighbor sites. The seventh oxygen occupies the 8a sites. The 8b sites contain the oxygen vacancy that arises from the defect fluorite structure, which are arranged in a diamond like array. In an ideal pyrochlore structure, all A cations are on the 16c site, all B cations are on the 16d site, and the 48f and 8a oxygen sites are fully populated. The 8b site is fully unoccupied.

\(^2\) The defect fluorite structure can be developed from B\(^4\text{O}_2\), by replacing \(\frac{1}{2}\) of the B atoms with lower valent A\(^{+3}\) atoms. The result is a fluorite structure with 7 oxygen atoms randomly distributed over 8 equivalent oxygen sites.
Figure 2.9 The fluorite structure based on CaF$_2$. This view shows the F atoms in a simple cubic ordering with Ca atoms in the center of every other cube. From [37].

Figure 2.10 The fluorite structure of CaF$_2$ based on the view of the Ca atoms in a FCC arrangement with F atoms in tetrahedral interstices. From [37].
Pyrochlores are often intrinsically disordered. Anion disorder may arise as oxygen vacancies on the 48f or 8a sublattices. Oxygen atoms occupying 8b sites are referred to as oxygen interstitials. The cation sublattices may also disorder via anti-site defects (A cations on B sites and vice versa). As shown by [38], for the gadolinium titanate based system, the anion sublattice disorders more readily than the cation sublattice. Examples of intrinsically disordered pyrochlores include Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ and Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ [38], [39]. The degree of anion disorder appears to depend strongly on the ratio of cation radii, $r_A/r_B$ [38], [40] as discussed in the next sections (see Section 2.3.3.1 for example).

2.3.2 Phase Stability

The pyrochlore structure will accept a wide range of elements on both the A and B cation sites. Most pyrochlores end up A$^{3+}$B$^{4+}$O$_7$ because a large number of cations of suitable ionic radius for pyrochlore formation have +3 or +4 valance. The A$^{+3}$ site can be a rare earth such as Gd, Sc, Y, Bi, Tl, or In. The B$^{+4}$ site can be a transition metal or any element from group IV a [35]. The phase stability of these materials is strongly dependent on the ionic radii of the cations, as well as parameters such as temperature, pressure, and nonstoichiometry.
Figure 2.11 One quarter of the pyrochlore unit cell shown in projection. The various crystallographic positions and their occupancy are shown. From [39].
Figure 2.12 shows the existence range of the pyrochlore structure as a function of A and B cation radii for selected elements. The pyrochlore phase will form when the radius ratio, RR \((= r_A/r_B)\) is between 1.46 and 1.80 at one atmosphere \([35]\). Below RR = 1.46, the defect fluorite phase will form, and above RR = 1.8, a monoclinic phase will form. For the materials in this thesis, it is useful to note that the RR of Gd\(_2\)Ti\(_2\)O\(_7\) is 1.74 and that of Gd\(_2\)Mo\(_2\)O\(_7\) is 1.62. The RR of Gd\(_2\)Mn\(_2\)O\(_7\) is 1.99, out of the pyrochlore existence range at 1 atmosphere. However, as reviewed by \([35]\), the use of high pressure synthesis can extend the upper RR limit up to 2.3. As will become clear later, the pure end member Gd\(_2\)Mn\(_2\)O\(_7\) will not be made in this work. Solid solutions containing all of the above B site elements, Mo, Mn, and Ti, with Gd on the A site will be synthesized. The averaged RR ratio will always be within the pyrochlore existence range at one atmosphere.

A pyrochlore can experience phase decompositions if the system temperature extends out of its phase stability range as well. Figure 2.13 shows the phase diagram for Gd\(_2\)Zr\(_2\)O\(_7\) depicted as a solid solution of Gd\(_2\)O\(_3\) and ZrO\(_2\). It shows that the maximum temperature that the pyrochlore can exist is about 2000 °C. It also shows that, depending on the temperature, there is some latitude in the exact stoichiometry of the material (in terms of A and B). The pyrochlore phase can still exist in slightly A or B rich material. Oxygen nonstoichiometry can also drive the system out of the pyrochlore range.
Figure 2.12 Existence range of $\text{A}^{3+}\text{B}^{4+}\text{O}_7$ pyrochlores as a function of the A and B cation radii. A sampling of elements is shown. Bolded lines indicate compositions of particular interest to this thesis. The Mn based pyrochlores were made at high pressure. Data compiled by [35]. Ionic radii are taken from [41].
Figure 2.13  Phase diagram of the Gd₂O₃ – ZrO₂ system. The A region indicates pyrochlore structure with sharp superstructure peaks; B is pyrochlore with broad peaks; F, P, and C indicate fluorite, pyrochlore, and cubic C-type phases respectively. From [42] based on [43]
phase regime. Extreme oxidation or reduction can cause separate phases to form to compensate for the excess or deficiency of oxygen.

2.3.3 *Conductive Properties*

Due to the wide range of elements that the pyrochlore system can accommodate, it is impossible to speak of one set of general conduction properties for pyrochlores. This flexibility is, in fact, what makes the pyrochlore system so valuable for use as a conductive material. Many different compositions can be created, each with potentially significantly different conduction properties. This allows for the possibility of tailoring the conductive properties of the material to the exact needs of the researcher by modifying the types of elements in the material.

Oxygen conduction is known to occur via diffusive jumps of oxygen vacancies along the 48f sites in the structure [30], [38]. Oxygen interstitials are generally much less mobile in comparison. The level of oxygen conduction will be directly related to the concentration of vacancies on the 48f site network, which can be modified extrinsically. Intrinsic electronic conduction is low due to the relatively high band gap of most pyrochlores, around 3 – 4 eV, It is very possible to shift the electronic carrier concentrations extrinsically, however [36], [42], [44] as discussed in several sections below.
Subramanian [35] compiled an extensive catalog of pyrochlores and their properties prior to 1983. Conductive properties for many types of pyrochlores were included. These results will not be reviewed extensively here. Rather, the more relevant (to this thesis) work performed by Tuller and co-workers on the conductive properties of the gadolinium titanate system, Gd$_2$Ti$_2$O$_7$, will be reviewed in some detail. The reader is encouraged to explore [35] for earlier conduction results.

2.3.3.1 The Gd$_2$Ti$_2$O$_7$ – Gd$_2$Zr$_2$O$_7$ System

Moon and Tuller [32], [38], [45] studied the conductive properties of the solid solution Gd$_2$(Ti$_{1-x}$Zr$_x$)$_2$O$_7$ (GZT). Figure 2.14 shows the key result. The ionic conductivity of the system was found to increase systematically as the percentage of Zr in the material was increased. In addition, the electronic component of the conductivity was found to be negligible for high Zr percentage, making the GZT system a very attractive fast ion conductor. The higher end of the ionic conductivity in Zr rich compositions (over $10^{-2}$ S/cm at 1000 °C) approaches that of the commercial standard, stabilized ZrO$_2$ (about $10^{-1}$ S/cm at 1000 °C).

These results were explained using the RR of each end member. Gd$_2$Ti$_2$O$_7$ (GT) has a RR = 1.74, while that of Gd$_2$Zr$_2$O$_7$ (GZ) is 1.46. As noted in Section 2.2.2, the lowest RR for which the pyrochlore phase exists is 1.46; the GZ system is on the border
Figure 2.14 Ionic conductivity in $\text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7$. From [32].
of pyrochlore and defect fluorite. Numerous researchers [40], [46], [47], [48] have observed that the amount of ionic disorder in pyrochlore structures increases as the RR decreases towards the disordered defect fluorite. The increase in ionic conductivity with increasing Zr content was attributed to this internal disordering. Further data taken by Moon indicate a linear increase in the pre-exponential of the ionic conductivity (see Equation (2.4)) with increasing Zr content. Moon took this fact as further evidence for vacancy creation by disordering on the anion sublattice.

2.3.3.2 Acceptor Doped Gadolinium Titanate ((Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$))

The mixed conduction properties of calcium doped GT, (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$, was studied by Kramer [36]. Ca acts as an acceptor impurity and substitutes on the A site for Gd. The ionic conductivity of the material increased several orders of magnitude for small concentrations of Ca as shown in Figure 2.15. This composition (10% Ca doped GT) has yielded the highest value of ionic conductivity in GT based pyrochlores to date ($\sim 10^{-1}$ S/cm at 1000 °C).
Figure 2.15 The ionic conductivity of Gd$_2$Ti$_2$O$_7$ at 1000 °C as a function of acceptor doping on the "A" cation sublattice. From [6].
2.3.3.3 Electrically Conductive Gadolinium Titanate: Variably Valent Substituted GT (Ru, Mn, Mo)

The earlier works on the GT system discussed above proved that the system could be made a very good ionic conductor by appropriate choices of substitution elements. However, the materials exhibited a very low electronic conductivity. To find MIEC GT based systems, the above results needed to be extended to find compositions that exhibited high electronic conductivity while maintaining the high ionic conductivity. The focus of this work was doping with variably valent elements. The fact that these elements can shift valence can disturb the electrical balance of the material and lead to compensating defects (electrical and ionic) that alter the conductive properties of the material. In addition, variably valent transition metals can lead to the formation of defect bands in the band gap of GT due to 3d orbital interactions at higher dopant concentrations. This phenomenon can lead to very high electronic conductivities with low activation energies [8], [49], [50].

Spears and Tuller [42], [50] explored the effects of variably valent Ru on the B site of GT, Gd$_2$(Ru$_x$Ti$_{1-x}$)$_2$O$_7$. Ru was expected to enhance the electronic conductivity of GT because the Ru end member is a very good semiconductor ($\sigma_e$ up to 90 S/cm) [51]. In addition, Ru is known to have good catalytic properties [52] with respect to O$_2$, which would make it very desirable in certain applications such as solid oxide fuel cell cathodes. The results indicated that Ru acted as an acceptor and contributed to enhanced
vacancy concentration and elevated ionic conductivity. For low values of Ru (< 5%), the conductivity was primarily ionic with conduction values on the order of $10^{-2}$ S/cm with activation energies around 1 eV. At higher Ru values however, the activation energy decreases to 0.3 eV with an accompanying increase of total conductivity (up to $10^{-1.5}$ S/cm). This change was attributed to the onset of electronic conduction due to the formation of a conductive Ru defect band in the band gap of GT.

While Ru doped GT was found to be a MIEC and was stable under oxidizing conditions, the material decomposed under reducing conditions, and the volatile Ru made the material difficult to handle and fabricate. Therefore, other variable valent transition metals were explored. Kosacki, Porat, Long, and Tuller [49], [53], [54] explored the conduction and nonstoichiometry of Mn doped GT, Gd$_2$(Ti$_{1-x}$Mn$_x$)$_2$O$_7$. The material was mixed conducting with conduction values of up to $10^{-3}$ S/cm in oxidizing environments and $10^{-2}$ S/cm under reducing conditions. Figure 2.16 shows the total conductivity of Mn doped GT (for [Mn] = 10%) as a function of $P_{O_2}$ and T. By modeling this data [49], Porat, et al., were able to determine that a significant portion of this conductivity was ionic at intermediate and high $P_{O_2}$. This result was corroborated by nonstoichiometry measurements [53] in the same regimes which indicated elevated oxygen vacancy concentrations. The ionic component was directly isolated by Long, et al., [54] in an experiment utilizing an electron blocking cell composed of a Mn doped GT layer (a suspected mixed conductor) sandwiched between two layers of Ca doped GT (an ionic
Figure 2.16 The conductivity of Mn doped GT as a function of $P_{O_2}$ and $T$ for $[\text{Mn}] = 10\%$. From [54].
conductor). He found values of $t_1$ of up to 0.9 at high $P_{O_2}$, confirming that Mn doped GT does indeed have a significant MIEC value under oxidizing regimes. (Note: A similar experimental setup is used in this thesis and is covered in some detail in Chapter 4).

While the Mn doped GT was indeed a MIEC, this condition applied only under oxidizing regimes, and the overall conductivity values were still low compared to competing materials such as the perovskites. The search for MIEC pyrochlores was therefore extended to Mo doped GT, $Gd_2(Ti_{1-x}Mo_x)O_7$, by Porat and Tuller [8], [44]. The choice of Mo as a dopant originated from older data obtained by Subramanian and co-workers [55], [56] which showed that the end member $Gd_2Mo_2O_7$ was a metallic conductor with an electronic conductivity of $10^2$ S/cm at room temperature. Mo was also attractive because the radius of Mo$^{4+}$ in 6 fold coordination ($r = 0.65$ Å) is larger than that of Ti$^{4+}$ in the same coordination ($r = 0.605$ Å). Thus the average RR will decrease as the concentration of Mo is increased, leading to a higher intrinsic disorder and higher ionic conductivity. The variable valence of the Mo (as in the previous cases of Mn and Ru) was expected to aid in increasing the concentration of ionic and electronic defects.

Figure 2.17 shows the total conductivity for Mo doped GT as a function of $P_{O_2}$ and $T$ for $Gd_2(Ti_{1-x}Mo_x)O_7$ with $x = 0.1$. As expected, at high Mo concentrations, the conductivity was primarily electronic and extremely high, almost $10^2$
Figure 2.17 Total conductivity of 10% Mo doped GT as a function of $P_{O_2}$ and T.

From [8].
S/cm for the 70% Mo under reducing conditions. In fact, the 70% Mo material was a metallic conductor, reducing its conduction level as the temperature was increased. Compositions with smaller concentrations of Mo were semiconducting with activation energies up to 0.68 eV for the 10%. The ionic portion of the conductivity under reducing conditions was again separated by a blocking cell whose configuration was given as,

\[ \text{Pt, } \text{O}_2 | 50\% \text{ Mo doped GT} | 8\% \text{ Ca doped GT} | \text{Pt, } \text{O}_2 \]

This cell is similar to the one used by Long above, but shows that only the half cell is needed to perform the blocking experiments (that is, the second layer of ionic conductor is not needed). The results showed that \( t_i \) was on the order of 0.1 at high temperature (1000 °C) and somewhat lower at lower temperatures (resulting from the fact that the activation energy of the overall conductivity was very low, while that of the ionic portion rather high, about 2eV). While this transference number appears low for a MIEC, the level of ionic conduction must be considered. The total conductivity was on the order of \( 10^1 \) S/cm, which means that the ionic conductivity was on the order of \( 10^{-1} \) S/cm at 1000 °C. This is a very high level of ionic conduction, even though the ionic transference number is low.

The drawback of the Mo doped GT material is that it decomposed under intermediate or high P\(_{O_2}\) for high Mo concentrations (above 10%). Even for the 10% Mo material, the conduction in this regime was low. Porat, Heremans, and Tuller [44] made a detailed study of the stability of the Mo doped GT. The stability field (P\(_{O_2}\) and T) for the 70% Mo material was calculated as a function of P\(_{O_2}\) and T. It was evident that the
material has a very narrow existence range in the pyrochlore phase in terms of \( P_{O_2} \) and \( T \), which increased as the Mo content was decreased. The conductivity dropped drastically when the atmosphere passed out of this range. Obviously, this limits the usefulness of the material to a narrow range of reducing \( P_{O_2} \)’s.

The reason for the narrow existence range of the Mo doped GT was the very fact that allowed it to achieve such high conductivities in the first place, the variable valence of Mo. As the \( P_{O_2} \) is increased, Mo shifts valence from \( Mo^{4+} \) to \( Mo^{6+} \). In more oxidizing environments, this change is compensated by the formation of oxygen interstitials. At high Mo concentrations, so many interstitials were believed to be formed that the material was driven enough off stoichiometry to initiate a phase breakdown. The \( P_{O_2} \) boundary where this occurs is obviously dependent on the amount of Mo in the material. Even in the 10% Mo case, where the material remained pyrochlore at all \( P_{O_2} \), this shift in Mo valence decreased the electron concentration (while raising the interstitial concentration) and thereby lowered the conductivity down to the order of \( 10^{-3} \) S/cm under oxidizing conditions.

2.3.4 Mn/Mo Substituted Gadolinium Titanate: Preview of this Work

In the present work, an attempt is made to extend the existence range of the Mo doped GT to oxidizing regimes (important for many applications) while maintaining the
conductivity at or near the high values achieved with high Mo content. To accomplish this, the increase in oxygen interstitials accompanying the Mo valence shift must be reduced. In this work, this is attempted by adding Mn to the material to give the general composition $\text{Gd}_2((\text{Mo}_{y}\text{Mn}_{1-y})\text{Ti}_{1-x})_2\text{O}_{7.5}$ or GMMT for short.

Figure 2.18 shows a schematic band diagram of GT doped with Mo and GMMT under oxidizing conditions. For Mo doped GT, when the Mo shifts from $+4$ to $+6$, the two released electrons are compensated by the incorporation of charged oxygen interstitials in oxidizing environments. As discussed above, this leads to the eventual phase breakdown of the material because of the large shift in stoichiometry. The addition of Mn should minimize this effect. Mn is variably valent and lies lower in the gap than Mo [8], [49] (Case B). It’s valence can shift from $+4$ to $+3$ to compensate the Mo charge shift by trapping electrons at the Mn level. This not only suppresses the oxygen interstitial concentration, but keeps the electrons closer to the conduction band so that they can be ionized more easily and contribute to electronic conduction. The predicted net effect is to not only keep the material in the pyrochlore phase in oxidizing
Figure 2.18 A schematic of the band structure of GT under oxidizing conditions for the case of Mo doped GMMT with $y = 1/3$ (defect level energies below the conduction band for Mo and Mn come from [8] and [49] respectively). Two compensation mechanisms for the valence shift of Mo$^{4+}$ to Mo$^{6+}$ are shown. Case A represents the case of Mo doped GT (no Mn). The electrons are released and compensated by the creation of oxygen interstitials (and large deviation from stoichiometry). Case B represents the case of GMMT where Mn is present. The electrons are trapped by the shifting valence of the Mn$^{4+}$ to Mn$^{3+}$. 

$E_{Mo} \approx 1$ eV

$E_{Mn} \approx 2$ eV

$E_g \sim 3.5$ to 4 eV

$O_{2p}$ Valence Band

$O(g)$

Case A: Mo doped GT

Case B: GMMT

O$^i$ levels
environments, but also to maintain the conductivity at higher values under these conditions.

2.4 Summary of the Present Work

The present work will focus on investigating mixed ionic and electronic conduction in Mn and Mo substituted gadolinium titanate (GT) pyrochlore material, Gd$_2$(Mo$_{1\gamma}$Mn$_\gamma$)$_2$Ti$_{1-x}$O$_{7.8}$ (GMMT). Gadolinium titanate pyrochlores are used because of the large body of previous work that exists in support of its promising conductive properties. In addition, the material accommodates a large amount of compositional flexibility. This gives it unique advantages in terms of application possibilities, such as the monolithic Solid Oxide Fuel Cell (SOFC). Mo is chosen as a constituent because of previous work on Mo substituted GT which indicates it is a very good mixed conductor under reducing conditions. The material decomposed under oxidizing atmospheres, however, limiting its utility in potential applications. Mn is added in an attempt to stabilize the Mo based GT in oxidizing environments. The goal is to fabricate a pyrochlore material that is a good mixed conductor, especially under oxidizing conditions. Defect chemistry modeling (discussed in some detail in the next chapter) will be used extensively to analyze and understand the underlying microscopic mechanisms of the conduction process.

Because of the importance of mixed conducting materials as electrodes for SOFCs, experiments were also performed in characterizing the electrode polarization of electrodes on Ca doped GT. The present work is limited to metallic Pt electrodes only.
Ideally, this work will serve as a basis for comparison of electrode polarization improvements when a monolithic pyrochlore SOFC is created (see Section 2.1.1.3).

Powders of GMMT are made in-house with an organic citric acid based liquid mixing technique. Conduction experiments are largely 2 probe AC impedance scans as a function of T and P_{O_2}. AC impedance experiments are conducted on a 3 electrode electronic blocking cell to isolate the ionic conductivity in predominately electronic conductors. The electrode polarization studies are also based on 2 probe AC impedance scans. Powder x-ray diffraction is used to assess the stability of the various compositions. Defect modeling is performed on the conductivity results and is based on a model described in the next chapter.
3 THEORY

This chapter will cover the fundamentals of defect chemistry in solids needed to understand the modeling techniques used to analyze the results in this thesis. The defects within oxide conductors that give rise to anionic and electronic conduction are the focus of the chapter, with particular examples drawn from the pyrochlore $A_2B_2O_7$ system. Kroger-Vink [57] defect notation will be used throughout.

3.1 Intrinsic and Atmospheric Nonstoichiometric Defect Relations

The two major internal ionic defect formation mechanisms are the Frenkel and Schottky reactions. The Frenkel reaction involves taking an oxygen (or other ion) from a lattice site and placing it on an interstitial site, leaving behind a vacancy,

\[(3.1) \quad n i l \rightleftharpoons O_i^{\prime\prime} + V_o^{\prime\prime} \]

where $O_i^{\prime\prime}$ indicates an oxygen interstitial and $V_o^{\prime\prime}$ indicates a vacant oxygen lattice site where both defects are doubly ionized. The Frenkel reaction mass action law is given by,

\[(3.2) \quad K_F = [O_i^{\prime\prime}][V_o^{\prime\prime}] \]
where \( K_F \) is the thermally activated Frenkel equilibrium constant given by,

\[
K_F = K_F^0 \exp\left(-\frac{E_F}{kT}\right)
\]

(3.3)

where \( K_F^0 \) is a pre-exponential constant containing all the temperature independent terms, \( E_F \) is the Frenkel pair formation enthalpy, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. In Equation (3.2), the activity of the species has been replaced by the concentration consistent with the assumption of a dilute solution. This assumption will be used throughout this thesis.

For the most part, the vacancies and interstitials are assumed to be fully ionized at all times [38]. However, under extremely reducing (vacancies) or oxidizing (interstitials) conditions, the defects tend towards lower ionization states, i.e.,

\[
V^* \rightleftharpoons V^{*+} + e^-
\]

(3.4)

\[
O^{\prime+} \rightleftharpoons O^{+} + e^-
\]

(3.5)

for which the respective equilibrium conditions are,

\[
K_{v2} = K_{v2}^0 \exp\left(-\frac{E_{v2}}{kT}\right) = \left[\frac{[V^{*+}]}{[V^*]}\right]
\]

(3.6)

\[
K_{i2} = K_{i2}^0 \exp\left(-\frac{E_{i2}}{kT}\right) = \left[\frac{[O^{+}]}{[O^{\prime+}]}\right]
\]

(3.7)
where $E_{V2}$ is the energy between the singly ionized vacancy energy level and the conduction band and $E_{I2}$ is the equivalent for interstitial energy levels.

The Schottky mechanism involves taking a stoichiometrically equivalent number of ions from each separate site on the lattice (A, B, and O in $A_2B_2O_7$) and removing them from the material to form corresponding vacancies. In the pyrochlore (and fluorite) phases, however, the Schottky mechanism is reportedly energetically unfavorable [58]. Defects arising from it are therefore not considered here.

The intrinsic electronic generation across the band gap can be described by,

\[
\text{nil} \Leftrightarrow e^\prime + h^*
\]

where $e^\prime$ is a conduction band electron and $h^*$ is a valence band hole. The intrinsic electronic equilibrium can be described by,

\[
K_e = N_CN_V \exp \left( \frac{-E_g}{kT} \right) = np
\]

where $N_C$ and $N_V$ are the effective densities of states in the conduction and valence band respectively, $E_g$ is the band gap, $n$ is the electron concentration, and $p$ is the hole concentration. The relatively weak temperature dependence of $N_C$, $N_V$, and $E_g$ are ignored throughout.

The oxygen stoichiometry of intrinsic $A_2B_2O_7$ is determined by the activity of oxygen in the surrounding environment, which is determined by the partial pressure of
oxygen, \( P_{O_2} \). The equilibrium that exists can be written as (written here for reducing environments),

\[
(3.10) \quad \frac{1}{2} O_2(g) + V_{O}^{**} + 2e' \rightarrow O^X
\]

The mass action relation for this equation is written as,

\[
(3.11) \quad K = K_0^e \exp\left(\frac{-E_R}{RT}\right) = n^2[V'O^*]^2 P_{O_2}^{1/2}
\]

where \( E_R \) is the reduction energy. The link between the atmospheric \( P_{O_2} \) and the ionic and electronic defects is clear in this equation.

For the above set of defects, the concentrations must maintain the electrostatic equilibrium within the material. This can be expressed as,

\[
(3.12) \quad [O'] + 2[O''] + n = p + 2[V'O^*] + [V'O^*]
\]

This system of equations (Equation (3.1) through Equation (3.12)) can be solved simultaneously to give the concentration of any given defect at any \( P_{O_2} \) or \( T \). This would in turn give some indication of the relative magnitudes of the ionic and electronic partial conductivities in the material and how they would shift with \( P_{O_2} \) and \( T \). To calculate the actual conductivities, however, the mobility of each species must be known.
3.2 Extrinsic Impurity Substitution

The Frenkel enthalpy and band gap of gadolinium Titanate (GT) are such that the intrinsic defect concentrations are so low that they are often swamped by those arising from impurities (whether intentional or not). Impurities in GT can act as either acceptors or donors in the semiconducting sense (they either accept or donate electrons). The defect relations involving each will be covered in this section.

3.2.1 Donor Impurities

Donor impurities create defect states in the band gap of the material that lie near the conduction band. These impurities must have a positive charge relative to the ion for which they are substituted. For example, in $A^{3+}B^{4+}O_7^-$, the substitution of a $+5$ valent (or higher) ion on the B site or $+4$ valent on the A site would create a donor, $D^*$. A donor ion can be charge compensated by an electron in the conduction band. An illustrative example is Mo$^{+6}$, which may substitute on the Ti site of GT,

$$ Gd_2O_3 + 2MoO_3 \xrightarrow{Gd_2TiO_7} 2Gd^X_{Gd} + 2Mo^{**}_{Ti} + 4e^- + 7O_2^- + O_2(g) $$

The formation of excess electrons is very evident. This increase in electrons also leads to an increase in $O_{i''}$ concentration. This is evident by noting that as electron concentration
goes up, \(V_{O}^{\cdot\cdot}\) concentration must go down (Equation (3.11)), which in turn must be compensated by an increase in \(O_{i}^{\cdot}\) concentration (Equation (3.2)).

The donor ionization (or deionization) can be written as,

\[
D_{M}^{X} \Leftrightarrow D_{M}^{\cdot} + e^{\cdot} \tag{3.14}
\]

where the M site is any cation site within the material. The mass action relation is

\[
K_{D1} = K_{D1}^{0} \exp\left(-\frac{E_{D1}}{kT}\right) = \frac{[D_{M}^{\cdot}]n}{[D_{M}^{X}]}
\tag{3.15}
\]

where \(E_{D1}\) represents the energy of the donor level beneath the conduction band. The D1 designation represents this reaction as the first ionization of the donor. Successive ionizations (D2, D3, etc.) may occur in a similar fashion if the donor supports the various valence states, such as,

\[
D_{M}^{\cdot} \Leftrightarrow D_{M}^{\cdot\cdot} + e^{\cdot} \tag{3.16}
\]

which will have an equilibrium reaction similar to Equation (3.15),

\[
K_{D2} = K_{D2}^{0} \exp\left(-\frac{E_{D2}}{kT}\right) = \frac{[D_{M}^{\cdot\cdot}]n}{[D_{M}^{\cdot}]}
\tag{3.17}
\]

where \(E_{D2}\) is the energy of the second ionization level below the conduction band.
Though $E_{D1}$ is generally within a few tenths of an eV to the conduction band, it is possible to have so called “deep” donors that lie near the middle of the band gap. While these deep donor may not ionize to the extent of a shallower donor, they can still have interesting effects on the conduction properties of the material and may need to be considered. It is important to note that the concentration of the donor ion in the material will remain constant, no matter how the valence is distributed. That is,

\[
\sum_{j=0}^{n} [D_{ij}] = \text{const} = D
\]

where the notation $j^\bullet$ represents the jth valence on the donor and $D$ is defined as the total donor concentration.

3.2.2 Acceptor Impurities

Acceptors impurities create states in the band gap that lie near the valence band of the material and generally increase the electronic hole concentration of a material. Impurity ions that act as acceptors have a lower valence than the ion they are replacing. An example in GT is that of Ca being introduced on the Gd site via the following [36], [42],

\[
2\text{CaO} + 2\text{TiO}_2 \rightarrow 2\text{Ca}^{2+}_{\text{Gd}} + 2\text{Ti}^{4+} + 6\text{O}^{2-} + V^{5+}_{\text{O}}
\]
This reaction is written to emphasize the fact that impurities can also effect the oxygen stoichiometry of a binary or ternary material (such as GT). Equation (3.19) could also be written in terms of the more traditional view of acceptors increasing the hole concentration via Equations (3.9) and (3.11) (at a given \( P_{O_2} \) and \( T \), as the vacancy concentration rises, \( n \) must decrease to keep \( K_r \) constant; in turn, the hole concentration must increase to keep \( K_e \) constant). The generic acceptor is defined by \( A_M \).

Acceptors ionize or deionize via the following reaction,

\[
A_M^x \rightleftharpoons A_M^{y} + h^* \tag{3.20}
\]

for which the equilibrium condition is,

\[
K_{A1} = K_{A1}^0 \exp \left( \frac{-E_{A1}}{kT} \right) = \left[ A_M \right] \left[ A_M^x \right] \left[ h^* \right] \tag{3.21}
\]

where \( E_{A1} \) is the acceptor defect energy above the valence band. Acceptors can have multiple valence states. The doubly ionized state, for example, may be achieved by the ionization reaction,

\[
A_M^{y} \rightleftharpoons A^{2+} + h^* \tag{3.22}
\]
for which the equilibrium condition is,

\[
K_{A_2} = K_{A_2}^* \exp\left(\frac{-E_{A_2}}{kT}\right) = \left[\frac{A_M^n}{A_M}\right]
\]

where \(E_{A_2}\) is the second acceptor ionization energy. As in the case of donors, the total sum of acceptors in the material must be constant independent of the actual valence,

\[
\sum_{j=0}^{n'} A_M^n = \text{const} = A
\]

where the notation \(n'\) represents the \(n\)th valence on the acceptor and \(A\) is the total amount of acceptor in the material.

### 3.3 Solving the Defect Equations

The goal of using defect chemistry is ultimately to solve for the various defect concentrations as a function of \(T, P_{O_2}\), and dopant concentrations. These can then be related to observed (experimental) materials properties such as electrical conductivity, diffusion, optical adsorption, etc. Techniques can then be developed to enhance or depress the concentration of species of interest, thereby tailoring the properties of the material.
The most general case of an oxide doped with a donor and acceptor will be examined. In addition, to make it consistent with this thesis the donor ion (Mo) will be assumed to have a neutral state, single and double positive valences, relative to the lattice. The acceptor (Mn) will have a single and double negative valence states along with the neutral state. The example host material will be GT.

One first attempts to solve for every defect concentration as a function of one of the others. Though any defect could potentially be used as the independent variable, the convention is to select \( n \), the electron concentration. From the defect equations above, the concentration of each defect is determined as a function of \( n \),

\[
(3.25) \quad [V^+_{O^2}] = \frac{K_R}{n^2} P_{O_1}^{1/2}
\]

\[
(3.26) \quad [O^{+2}] = \frac{K_F n^2}{K_R} P_{O_2}^{1/2}
\]

\[
(3.27) \quad [O^-] = \frac{K_R}{K_{V^{-}_2}} P_{O_1}^{1/2}
\]

\[
(3.28) \quad [O^{-}] = \frac{K_{D_1} n}{K_R} P_{O_2}^{1/2}
\]

\[
(3.29) \quad [D^*_M] = \frac{K_{D_1} Dn}{n^2 + nK_{D_1} + K_{D_1} K_{D_2}}
\]

\[
(3.30) \quad [D^*_M^*] = \frac{K_{D_1} K_{D_2} D}{n^2 + nK_{D_1} + K_{D_1} K_{D_2}}
\]

\[
(3.31) \quad [D^*_M] = \frac{Dn^2}{n^2 + nK_{D_1} + K_{D_1} K_{D_2}}
\]
\[ A'_M = \frac{K_e K_{A1} A_n}{K_e^2 + K_e K_{A1} n + n^2 K_{A1} K_{A2}} \]

\[ A''_M = \frac{K_{A1} K_{A2} A_n^2}{K_e^2 + K_e K_{A1} n + n^2 K_{A1} K_{A2}} \]

\[ A^X_M = \frac{AK_z^2}{K_e^2 + K_e u n + n^2 K_{A1} K_{A2}} \]

The defects listed above are also subject to charge neutrality within the material, i.e.,


Equations (3.25) - (3.35) represent a system of 10 equations with 10 unknowns (the defect concentrations) and one independent variable, \( n \). The typical goal is to solve for \( n \) in terms of \( P_{O_2} \). Finding this will yield all of the other concentrations as a function of \( P_{O_2} \), which is the goal of the modeling. For meaningful numerical predictions, the values of the various equilibrium constants must be known (or at least a good approximation) beforehand. This includes both the pre-exponential constants and the activation energies. Fortunately, there exists a large body of former work on the pyrochlore GT, and good estimations exist for these values. The specifics of the GT system will be covered shortly.
3.3.1.1 Brouwer Approximation

The simplest approach to solving for defect equilibrium is to make simplified estimations to Equation (3.35) based on the environmental conditions (usually $P_{O_2}, T$). In most regimes, two defects of opposite charge will dominate, and hence determine Equation (3.35). With this simplified equation, the defect concentrations can be solved analytically in terms of $n$. This technique is generally referred to as the “Brouwer” approximation [59].

As a case example, consider intrinsic GT. In this case, there are six unknown concentrations ($V_{O}^{--}, V_{O}^{--}, O_{i}^{--}, O_{i}^{+}, p, n$) and a system of six equations with $n$ as the independent variable. Solving for $n$ in terms of $P_{O_2}$ yields a 5th order equation in $n$. Such an equation cannot, in general, be solved analytically. However, consider an extremely reducing atmosphere. In this case, Equation (3.10) will be driven to the right. The products, $V_{O}^{--}$ and $e^+$ will then become the dominant charge carriers in the material. In this case, the charge neutrality equation simplifies to $n = 2[V_{O}^{--}]$. Using this, one can solve for all the defect concentrations as a function of $P_{O_2}$ in the regime where this neutrality holds. For example,

\begin{align*}
(3.36) & \quad n = (2K_R)^{1/3} P_{O_2}^{-1/6} \\
(3.37) & \quad \left[V_{O}^{--}\right] = \left(\frac{K_R}{4}\right)^{1/3} P_{O_2}^{-1/6}
\end{align*}
and so on for each defect in the material. Figure 3.1 shows a hypothetical Brouwer approximation for GT. Note the three regimes with their respective dominant charge neutrality simplifications. In this case, the intermediate regime where the material becomes stoichiometric is shown as \( n=p \). It could also be \([V_{O^{\bullet\bullet}}] = [O_{i\bullet\bullet}]\). Determining which one to use involves inspecting the relative magnitudes of \( K_F \) and \( K_e \) at that given temperature. Also note the symmetry of the hole and electron concentrations as well as the interstitial and vacancy concentrations. This symmetry must always exists in GT (or other Frenkel dominated materials) via Equations (3.2) and (3.9) no matter how complicated the defect chemistry may become.

The advantages of the Brouwer approximation are very evident. It very quickly provides a rough estimation of the relative magnitudes of the defect concentrations in a material over well defined regions of \( P_{O_2} \). In addition, it provides a prediction of the slope of these concentrations with \( P_{O_2} \). This can be most useful when looking at a plot of conductivity vs. \( P_{O_2} \). Comparing the slope of the conductivity in the various regimes with the Brouwer approximation can yield the probable identity of the majority charge carrier.
Figure 3.1 Hypothetical Brouwer approximation diagram for intrinsic GT. The concentration of the dominant charge defects is shown as a function of $P_{O_2}$. Exact values for the concentrations and $P_{O_2}$ could be inserted via the use of approximations to the equilibrium constants.
However, the weaknesses of the approximation are also very evident. It is of most use in relatively simple cases such as intrinsic material or materials doped with fixed valent acceptors or donors. In more complex materials, such as ones doped with variably valent donors or acceptors (or both), the approximation is less useful because it becomes difficult to account for all of the different neutrality regimes. In addition, it provides inadequate information in the areas immediately adjacent to regime borders, where many carriers may influence charge neutrality. To overcome these problems, the full defect equilibrium must be solved.

3.3.1.2 Numerical Solution to the Full Defect Equilibrium

Solving the full defect equilibrium, in general, for the case of a material with multiple valent acceptors and donors results in an $k^{th}$ order equation in $n$, where $k$ can be 4 or higher depending on the number of defects in the material. This is impossible to solve analytically in general; numerical methods must be used to solve it. This is most often performed on a desktop computer with a root finding algorithm such as the Newton-Raphson method [42].

While this technique can be used successfully, it requires the use (and in most cases, creation) of a complex program. It also requires the use of an initial guess to the root, which is not always known. This may lead to convergence problems if the initial
guess is not obvious. In addition, the numerical processes have some inherent error as they are only providing estimations to the root within some error limit. The program can be time consuming depending on how often it needs to be run and the error one is prepared to accept. For these reasons, numerical solutions were not used in this thesis. Instead, an much simpler and quicker alternative approach that provides the same results was used.

3.3.1.3 Analytical Solution to the Full Defect Equilibrium

Given that solving for n in terms of $P_{O_2}$ for the most generalized defect case (multi-valent acceptors and donors) results in a higher order polynomial equation in n, it would appear that a technique which provides an analytical solution to the defect equilibrium may seem improbable. The technique rests on rewriting the governing equation (n in terms of $P_{O_2}$) in a slightly different form so that it becomes a quadratic equation. Porat and Tuller [60] developed this solution for donor doped materials. It is extended here to include acceptors.
The neutrality equation (Equation (3.35)) is first solved for \( n \). Then the expressions for each of the defects in terms of \( n \) and \( P_{O_2} \) (Equations (3.25) - (3.34)) are substituted into the equation,

\[
\begin{align*}
n & = \left[ V'_0 \right] + 2 \left[ V'^{*}_0 \right] + \left[ D'_M \right] + 2 \left[ D''_M \right] + p - \left[ O'_1 \right] - 2 \left[ O'^{*}_1 \right] - \left[ A'_M \right] - 2 \left[ A''_M \right] \\
& = \frac{K_R}{K_{V_2}} P_{O_2}^{-1/2} + 2 \frac{K_R}{n^2} P_{O_2}^{-1/2} + n^2 \frac{K_{D1} Dn}{n^2 + n K_{D1} + K_{D1} K_{D2}} + 2 \frac{K_{D1} K_{D2} D}{n^2 + n K_{D1} + K_{D1} K_{D2}} \\
& + \frac{K_e}{n} - \frac{K_{D1} K_{F_n}}{K_R} P_{O_2}^{1/2} - 2 \frac{K_{F_n} n^2}{K_R} P_{O_2}^{1/2} - \frac{K_{A1} K_{A2} n}{K_{F_n} + K_A K_{A1} n^2 K_{A1} K_{A2}} \\
& - 2 \frac{K_{A1} K_{A2} n^2}{K_{F_n} + K_A K_{A1} n^2 K_{A1} K_{A2}} \\
(3.38)
\end{align*}
\]

At this point, one could solve for \( n \) by solving the resulting 9th order equation numerically. However, the \( P_{O_2} \) dependence comes only from the reduction reaction (Equation (3.11)). Thus, one can solve for \( P_{O_2}^{1/2} \) instead of \( n \) and obtain a quadratic equation. Multiplying through by \( P_{O_2}^{1/2} \) in Equation (3.38), rearranging terms on the left, and factoring out the \( P_{O_2}^{1/2} \) terms yields,

\[
\begin{align*}
& \left( \frac{K_{I2} K_{F_n}}{K_R} + \frac{2 K_e n^2}{K_R} \right) (P_{O_2}^{1/2})^2 \\
& + \left( n + \frac{K_e K_{A1} A n + 2 K_{A1} K_{A2} n^2}{K_e^2 + K_A K_{A1} n + n^2 K_{A1} K_{A2}} - \frac{K_{D1} Dn + 2 K_{D1} K_{D2} D}{n^2 + n K_{D1} + K_{D1} K_{D2}} - \frac{K_e}{n} \right) P_{O_2}^{1/2} + \left( \frac{K_R}{K_{V_2} n} + \frac{2 K_R}{n^2} \right) = 0 \\
(3.39)
\end{align*}
\]

This has only one meaningful solution,

\[
P_{O_2}^{1/2}(n) = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \\
(3.40)
\]
where,

\[ a = \frac{K_{12}K_F n}{K_R} + \frac{2K_F n^2}{K_R} \]  

\[ b = n + \frac{K_eK_{A1}A_1n + 2K_{A1}K_{A2}n^2}{K_e^2 + K_eK_{A1}n + n^2K_{A1}K_{A2}} - \frac{K_{D1}Dn + 2K_{D1}K_{D2}D}{n^2 + nK_{D1} + K_{D1}K_{D2}} \frac{K_e}{n} \]  

\[ c = \frac{K_R}{K_{V2}n} + \frac{2K_R}{n^2} \]  

Test values of \( n \) can be substituted into Equation (3.40) to find the corresponding \( P_{O_2} \) range. This can be done in an iterative process until one finds the appropriate \( P_{O_2} \) range. Once values for \( n \) and \( P_{O_2} \) are found, they can then be substituted back into Equations (3.25) - (3.34) to obtain values for the other defects as a function of \( P_{O_2} \).

The inherent advantage in this approach is obvious. The solutions are exact. Apart from the intrinsic error in the numerical solutions, the solutions in this case are the same as the numerical solutions. It provides the full and continuous defect equilibrium. The above system of equations can easily be entered into any commercial spread sheet program without any formal programming knowledge. Once entered, the system is very easy to manipulate and run multiple times very quickly.
3.4 Application to Mn/Mo Doped Gadolinium Titanate

The modeling technique outlined in Section 3.3.1.3 will be used in this thesis. Table 3.1 shows the various equilibrium constants that will be used along with the respective references. The Mn dopant will be considered a deep acceptor, lying slightly below mid gap. The Mo is a shallower donor in GT.

To illustrate the approach, the case of intrinsic GT will be modeled here. Figure 3.2 presents the full solution of the defect equilibrium generated using the methods in Section 3.3.1.3. The defect concentrations vs. $P_{O_2}$ at 800 $^\circ$C are shown. The result is completely equivalent to previous attempts to model intrinsic GT with numerical methods. One can also note the correspondence between Figure 3.2 and Figure 3.1. In this case, the Frenkel equilibrium dominates in Regime II, so the neutrality simplification becomes $[V_{O^{\ddagger\ddagger}}] \approx [O_i^{\prime\prime\prime}]$ rather than $n \approx p$. However, as shown in Figure 3.3, the neutrality assumption in Regime II is not very accurate in this case. This illustrates the degree to which the Brouwer assumptions can be in error.
<table>
<thead>
<tr>
<th>Pre-exponential (cm$^b$)</th>
<th>Activation Energy (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_R$</td>
<td>$6 \times 10^{69}$</td>
<td>6.25</td>
</tr>
<tr>
<td>$K_F$</td>
<td>$10^{20}$</td>
<td>5.25</td>
</tr>
<tr>
<td>$K_e$</td>
<td>$2.53 \times 10^{45}$</td>
<td>3.48</td>
</tr>
<tr>
<td>$K_{V2}$</td>
<td>$1 \times 10^{30}$</td>
<td>1</td>
</tr>
<tr>
<td>$K_{12}$</td>
<td>$1 \times 10^{16}$</td>
<td>1</td>
</tr>
<tr>
<td>$K_{D1}$ ($Mo^{5+}$)</td>
<td>$7.5 \times 10^{92}$</td>
<td>0.1</td>
</tr>
<tr>
<td>$K_{D2}$ ($Mo^{6+}$)</td>
<td>$1 \times 10^{40}$</td>
<td>1</td>
</tr>
<tr>
<td>$K_{A1}$ ($Mn^{3+}$)</td>
<td>$1.5 \times 10^{22}$</td>
<td>2</td>
</tr>
<tr>
<td>$K_{A2}$ ($Mn^{2+}$)</td>
<td>$1 \times 10^{8}$</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 3.1 Equilibrium constants (Pre-exponential, and activation energies) for various defect reactions in Gd$_2$Ti$_2$O$_7$. References for data are included, ones indicated by a * are unpublished estimations based on a variety of sources. $K_{D1}$ and $K_{D2}$ are developed from [8] and include estimations based on a variety of sources.
Figure 3.2 Defect concentrations of intrinsic GT vs. $P_{O_2}$ at 800 °C generated using analytical solution to defect equilibrium. The correspondence to Figure 3.1 is readily evident.
Figure 3.3 Expansion of the defect regime II for intrinsic GT at 800 °C. Note that in this instance, the neutrality equation simplification used in the Brouwer diagrams, $[V_{0}^{*-}] \approx [O_{i}^{+}]$, is not very accurate.
Figure 3.4 shows the defect concentrations for Mo doped GT with [Mo] = 50% at 800 °C vs. P_{O_2}. This is considerably more complex than the previous cases. This situation would be very difficult to predict with any accuracy with the Brouwer approximation. Note the high interstitial concentration in Regime IV. This is the region where the Mo doped GT was found to decompose as Mo^{4+} shifted to Mo^{6+} [44]. It is clear that in the oxidizing environments of Regime IV, the shift in Mo oxidation state is compensated by an increase in oxygen interstitial concentration. This feature, and how it compares to the case of Gd_{2}((Mo_{1-y}Mn_y)_{x}Ti_{1-x})_{2}O_{7-d}, will be covered in detail in Chapter 6.

This defect modeling approach will be applied to Gd_{2}((Mo_{1-y}Mn_y)_{x}Ti_{1-x})_{2}O_{7-d} in this thesis. The defect concentrations will be compared to conductivity measurements made as a function of P_{O_2} and T. While the mobility is needed to model the actual conductivity, this approach will allow some determination of the microscopic conduction mechanisms in the material in both oxidizing and reducing atmospheres. Confirmation of the conclusions about the conduction mechanisms will be performed by isolating the separate electronic and ionic conductivities with blocking cell measurements.
Figure 3.4 Defect concentrations for Mo doped GT with [Mo] = 50% at 800 °C vs. $P_{O_2}$. Predominant electronic neutrality regimes are shown.
3.5 Modeling Limitations

While the analytical technique outlined above is very useful, there are several limitations to its application. The first is the omission of reactions involving defect complexes arising from interactions between oppositely charged species (such as acceptor-vacancy complexes). In addition, the presence of any unionized vacancies or interstitials is neglected. However, considering that the temperatures of interest will be very high (600 – 1000 °C), it is assumed that the concentration of complexes (which is more prevalent at lower temperatures) and the presence of unionized vacancies and interstitials can be ignored. In further support of this assumption, the actual conductivity plots obtained in this thesis show no evidence of effects due to these species (such as a drop in conductivity at higher dopant concentrations, as exhibited in YSZ). If such reactions were needed in the future, their inclusion would result in no basic change in the theory above. The number of terms (equilibrium constants) required to perform the modeling would simply increase.

On a more fundamental level, the above theory assumes a dilute solution model. In reality, the concentrations in the equilibrium mass action relations should be activities. The equations can only use the concentrations when the concentrations of the species are so low that they can be assumed not to interact with each other. While the concentrations of the various defects in this thesis will be found to be fairly high, the activity of the
species will not be known and cannot be used practically. The use of the dilute solution model has met with success in the past in predicting key trends [42], [60], [61]. Due to this fact and the lack of knowledge regarding defect activities, the dilute solution model will be used throughout.

Finally, the fact that the equilibrium constants were developed from different materials needs to be considered. This will probably be a source of errors in the model. $K_R$ determined from experiments on pure GT is unlikely to be accurate for GMMT where 30% of the Ti is replaced by Mo and Mn. Similar problems arise with all the constants in Table 3.1. However, the differences are probably reasonably small give the same parent phase. In addition, as in the case of the dilute solution approximation, the assumption of continuity of the equilibrium constant over a wide range of dopants has been used before with success [42], [60], [61] on GT based solutions. The equilibrium constants as they appear in Table 3.1 will be used throughout this thesis. Where the experimental data allows it, the validity of these energies will be confirmed by the data gathered in this work.
4 EXPERIMENTAL

4.1 Sample Fabrication and Characterization

4.1.1 Powder Preparation

Powders of Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7.5}$ (GMMT) were prepared using a liquid mix technique first developed by Pechini [62]. This method provides a greater degree of mixing uniformity and a finer control over sample chemistry than traditional dry powder mixing. Citric acid and ethylene glycol are used to form a solution in which the various cations can be dissolved. These stock solutions are then mixed in the appropriate amounts to form the exact composition (x and y in Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7.5}$). The organic can then be burned off to leave the desired powder. Numerous researchers have found that this technique provides a very fine control over the composition as well as an excellent mixing of the various cations in the material [36], [38], [40], [42]. When Ca doped GT was used, pre-prepared powders from previous studies [6] were used.

Isolating a compound of each cation that will dissolve in the base solution (citric acid/ethylene glycol) is critical. Appendix A presents the various recipes that were used to form the Gd, Mo, Mn, and Ti stock solutions for use in GMMT.
4.1.1.1 Stock Solution Assaying

The various cation stock solutions listed above each have some amount of cation dissolved in an organic mixture. It is necessary to perform an assay heating step on each solution to determine the amount of cation per gram of solution in each case. This amount can then be used in determining how much of the mixture to use when making a final powder of GMMT. Table 4.1 shows the results of the assaying procedure.

To perform as assay, an amount of solution was weighed out into three separate alumina crucibles. These were then capped and heated in various stages up to a maximum of 950 °C (lower for the more volatile ones such as Mo (700 °C)). The resulting powders were weighed and compared to the original solution weight. The average of the three crucibles was used as the final assay. The identity of each powder was identified using x-ray diffraction. As can be seen in Table 4.1, the stability of each solution was very constant over a period of over 1 year.
<table>
<thead>
<tr>
<th>Cation</th>
<th>First assay (1/96) (g cation/g solution)</th>
<th>Second assay (8/97) (g cation/g solution)</th>
<th>Resulting powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>0.0538</td>
<td>0.05336</td>
<td>Gd$_2$O$_3$</td>
</tr>
<tr>
<td>Ti</td>
<td>0.0266</td>
<td>0.0296</td>
<td>TiO$_2$</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0519</td>
<td>0.0555</td>
<td>Mn$_2$O$_3$</td>
</tr>
<tr>
<td>Mo</td>
<td>0.021612</td>
<td>0.232</td>
<td>MoO$_3$</td>
</tr>
</tbody>
</table>

Table 4.1 Assay values of Gd, Mo, Mn, and Ti stock solutions used in this thesis.
4.1.1.2 Mixing and Calcining

To form a particular composition of $\text{Gd}_2((\text{Mo}_{1-y}\text{Mn}_y)_x\text{Ti}_{1-x})_2\text{O}_{7-8}$, the appropriate amount of cation stock solutions were measured and mixed together over low heat while stirring vigorously. After a period of 8-12 hours, the solution was placed over very high heat for a period of 1-2 days. The result was a black polymerized mixture. This was then placed in a furnace under a hood and calcined at 600 °C for a period of 2 days to burn off the majority of the organics. The resulting powder char was ground with a mortar and pestle for 15 – 30 minutes and placed in an alumina tray. This was placed back into the furnace and heated to 700 – 800 °C for 12 hours to obtain the final powder.

It should be noted that these powders were not fully pyrochlore. The final phase was not formed until after the final sintering step as described below.

4.1.2 Forming, Sintering, and Electroding

To form a sample, 1-2 grams of the appropriate powder was weighed. This was placed in a ½ inch die and loaded uni-axially under 6000 PSI for 1-2 hours. The resulting pellet was then pressed in an isostatic press at 40,000 PSI for 10 minutes. The result was a pellet with a diameter of ½ inch (1.27 cm) and a thickness of between 0.25 and 0.5 cm.
This pellet was encased in a Pt sheet and placed on an alumina tray. This was loaded into a sintering furnace. Two different sintering conditions were used. The first was at 1500 °C for 15 hrs. in air. Two initial GMMT compositions (x=0.05, 0.1 with y = 0.66) and the Ca doped GT compositions were prepared under this condition. A significant blue discoloration was noted on the alumina with the GMMT samples, assumed to come from loss of either Mo or Mn. To correct for this observed material loss, all other samples (including repeats of the two compositions above) were sintered at 1250 °C under a reducing atmosphere containing a mixture 50% CO/50% CO₂ for 72 hours, then air quenched. With these conditions, there was no discoloration on the alumina tray. In addition, the sintered weight was >99% of the original weight in all cases. For the Ca doped GT samples, the pellets were sintered in air at 1500 °C for 15 hrs. As confirmed by later x-ray diffraction, the density of all sintered pellets was > 90%.

To form electrodes, a Pt black ink (Engelhard, NJ, Part 6926, Lot M24981) was slightly diluted with Ethyl Acetate and painted on each side of the pellet. The pellet was then fired at 1000 °C to burn off the organics in the ink. This was usually repeated 3 or more times until a continuous thin film of Pt was well adhered to the pellet.

Electronic Blocking cells were prepared by co-pressing a layer of GMMT with a layer of 8% Ca doped GT. The resulting structure was co-sintered in air at 1500 °C in air for 15 hrs. A schematic of the structure is shown in Figure 4.1. Electrodes on the ends of the sample were applied in the same manner as just described. The 3rd electrode was formed by cutting a small groove around the circumference of the pellet on the Ca GT side of the junction between GMMT and Ca GT with a diamond saw. A layer of Pt paste
was applied into the groove and fired in the same manner as the end electrodes. Pt wire was wrapped around the pellet in the groove to provide a contact.

4.1.3 Phase Characterization (X-ray diffraction)

The phases of sample pellets of each composition was evaluated by using x-ray diffraction. X-ray scans were obtained using a Rigaku RU-300 diffractometer with a rotating copper target at 50 kV and a current of 200 mA. Typically a 1° divergence and soller slit was used along with a 0.15° receiving slit. The range on most scans ranged from 2θ = 15° to 85° with a scan speed of 2°/min and a sampling interval of 0.05°.

The generated diffraction patterns were compared to JCPDF files via a software program. Since file patterns for compositions of GMMT did not exist, a peak match with the pyrochlore phase Gd2Ti2O7 was taken as an indication of a pyrochlore material. The peaks of each pyrochlore composition were entered into a standard x-ray analysis computer program to determine the lattice constant of the composition (see Chapter 5).
Figure 4.1 Schematic of electronic blocking cell of GMMT and Ca doped GT with electrodes labeled.
4.1.4 Microstructure/Compositional Analysis

The microstructure of the sintered samples was studied with a ISI SMS Super II tabletop SEM. The images were only used for qualitative assessment of pore and phase distribution. Quantitative measurements on the cation stoichiometry was performed using Wavelength Dispersive Spectroscopy. A JEOL Superprobe 733 was used to determine atomic percentages in the samples. Samples for which this was performed were sectioned with a diamond saw, polished to a 1 micron finish, and mounted in a clear epoxy sample holder. They were then coated with a thin carbon film and put into the microprobe. Concentrations of Gd, Ti, Mo, and Mn were monitored.

4.2 Test Apparatus

After a pellet of the appropriate GMMT composition in the pyrochlore phase was obtained, it was mounted in the conductivity testing apparatus used in most of the experiments performed for this thesis. Figure 4.2 shows a schematic of the testing apparatus. The same setup was used for both the GMMT experiments and Ca doped GT electrode studies.

The pellets were placed inside a ½” diameter quartz tube approximately ¾ of a meter long (2-3 feet). Two alumina rods of ¼” diameter were obtained with 2 or 4 bores.
Pt wire was strung through one of the bores, and a small section Pt wire mesh attached to the strung wire on one side of the rod. One rod was placed into the quartz tube on either side of the sample, which was positioned in the middle of the quartz tube. The attached Pt mesh on each alumina rod was positioned against the Pt electrodes one either side of the sample. The ends of the quartz tube and alumina rods were fitted with appropriate Cajun fittings to provide a gas tight seal. These fittings also had connections to provide a gas in and out connection from external gas tanks. The out gas feed was piped to an exhaust hood for removal. After applying the gas tight fittings, a length of the alumina rods extended outside the quartz tubes and fittings. The external ends of the Pt wires (outside of the quartz tube) threaded through the alumina rods were connected to BNC leads that ran to the measuring instruments. The exposed bores of the alumina rods were sealed with a silicone based sealant paste.

This entire setup was placed in a tube furnace such that the central part of the quartz (with the sample inside) was in the hot zone. The fittings and exposed wires extended beyond the hot zone. Temperatures were controlled with an external thermocouple (typically type S) connected to a Eurotherm programmable temperature controller. Temperatures at the sample ranged from 600 °C to 1000 °C.
Figure 4.2 Experimental sample holder for conductivity experiments. Details appear in the text.
Oxidizing gaseous atmospheres were provided with argon diluted with oxygen in 10%, 1%, 0.1%, 100 ppm increments (to provide $P_{O_2} = 0.1$, 0.01, 0.001, and 0.0001 atm respectively). Reducing atmospheres were achieved with mixtures of CO and CO$_2$ which provide a temperature dependent $P_{O_2}$ fixed by the equilibrium reaction,

$$\text{(4.1)} \quad CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$$

The $P_{O_2}$ can be described by [63],

$$\text{(4.2)} \quad \log(P_{O_2}) = 9.067 - \frac{29496}{T} + 2\log\left(\frac{P_{CO_2}}{P_{CO}}\right)$$

The CO/CO$_2$ mixtures used were 100 ppm, 0.1%, 1%, 10%, and 50%. More dilute mixtures did not achieve equilibrium and thus resulted in unpredictable $P_{O_2}$ values. At higher temperatures (1000 and 900 °C), a 90% CO/CO$_2$ mixtures was occasionally used. At lower temperatures this mixture led to solid carbon deposition. Occasionally, the $P_{O_2}$ was checked by flowing the outlet gas through a ZrO$_2$ oxygen sensor with an air reference. In all cases, the observed voltage corresponded with the $P_{O_2}$ calculated from Equation (4.2). Since $P_{O_2}$ for each CO/CO$_2$ mixture was temperature dependent, unavoidable $P_{O_2}$ gaps existed in the conductivity measurements (see Chapter 5) when one switched from the non-temperature dependent O$_2$/Ar mixtures to the temperature dependent CO/CO$_2$ mixtures. This effect became more pronounced at lower
temperatures. Other gas mixtures were used to try to obtain results in the gap regime. However, the $P_{O_2}$'s obtained with these mixtures tended to be unstable, and thus this approach resulted in little success.

4.3 Measurement Techniques

4.3.1 AC Impedance Spectroscopy

AC impedance spectroscopy was used extensively in this thesis, from the study of electrode polarization to electronic blocking. It is, therefore, given a fairly in depth review in this section.

A typical ceramic sample with metallic electrodes will have several contributions to its measured DC conductivity (conductivity measured with a conventional DC voltage and current) as shown in Figure 4.3. The bulk conductivity is the conductivity of the lattice that is typically sought. Space charge effects at grain boundaries can also lead to a large contribution to the measured conductivity. Finally, resistances at the metallic electrodes (which are typically non-ohmic) will typically contribute to the measured DC value.

The main advantage of AC impedance spectroscopy is that each of these contributions is separated from the other with a fairly simple experimental setup.
1. Bulk

2. Electrodes

2. Grain Boundary

\[ R_{\text{total, DC}} = R_{\text{bulk}} + R_{\text{grain boundary}} + R_{\text{electrodes}} \]

Figure 4.3 Schematic of typical contributions to the measured DC conductivity in a typical polycrystalline ceramic sample with metallic electrodes.
The next several section will explain the principles behind this technique.

### 4.3.1.1 Principles

AC Impedance spectroscopy consists of perturbing a system from equilibrium by applying a time dependent sinusoidal voltage signal of frequency, ω, and amplitude, Vₒ, over the sample and measuring the resultant time-dependent current to calculate the impedance, \( Z(\omega) = \frac{V(\omega)}{I(\omega)} \). The amplitude value must be low enough to avoid driving the material out of the near equilibrium regime (within the thermal energy, kT) and high enough to overcome background noise. Typical values range from 10 to 50 mV [64]. The impedance is complex in general and can be represented as \( Z = Z' - jZ'' \). Frequency is typically scanned over several orders of magnitude and the resulting impedance is plotted in the \( Z'' \), \( Z' \) plane. Figure 4.4 shows a simulated plot typical of that obtained on a ceramic pellet. While this 3D plot conveys all of the information (including the impedance and frequency), typically only the projection on the \( -Z'' \), \( Z' \) plane is used. Though this eliminates the frequency information, it makes fitting and analyzing the data somewhat easier.

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3 All simulations and analysis of impedance data is done with Zview v.2.1 for a PC running Windows 95. The program is © Scirbner Institutes, 1990-1998.
Figure 4.4 Simulated impedance scan of a ceramic pellet with the shown parameters. Frequency range is from $1 \times 10^6$ to 0.01 Hz. Typically, only the $Z''$, $Z'$ projection of the scan is used (back plane) in analysis. The equivalent circuit for the hypothetical material is also shown.
It will be instructful to analyze the impedance response in Figure 4.4 in some detail [64]. As shown in the figure, these responses can often be modeled by an equivalent circuit where each element represents some physical process in the material. Each semicircular arc in the impedance scan represents a separate RC parallel processes. This can be seen by noting that the impedance, $Z$, of a RC parallel element is given by,

\begin{equation}
Z = \frac{1}{\frac{1}{R} + j(2\pi f)C} 
\end{equation}

where $f$ is the frequency of the signal. Multiplying through by the complex conjugate of the denominator yields the real and imaginary parts of the impedance,

\begin{equation}
Z' = \frac{1}{\left(\frac{1}{R}\right)^2 + (2\pi fC)^2} 
\end{equation}

\begin{equation}
Z'' = \frac{2\pi fC}{\left(\frac{1}{R}\right)^2 + (2\pi fC)^2} 
\end{equation}

Eliminating $f$ from Equation (4.4) and (4.5) and rearranging yields the equation for a circle centered on the real axis at $(R/2, 0)$ with a radius of $R/2$,

\begin{equation}
(Z'')^2 + (Z' - \frac{R}{2})^2 = \frac{R^2}{4} 
\end{equation}

Thus, every RC element will give a semi-circular arc in the $-Z''$, $Z'$ quadrant.
The response and corresponding circuit shown in Figure 4.4 is very typical of polycrystalline ceramic pellets with porous metallic electrodes [65]. Each RC parallel unit in the equivalent circuit has a distinct time constant,

\[
\tau_j = R_jC_j = \frac{1}{\omega_{\text{peak}}} \quad \omega = 2\pi f
\]

where \( \omega_{\text{peak}} \) represents the angular frequency at which the corresponding semi-circle has its peak on the \(-Z''\) axis. \( R_j \) can be obtained from the diameter of the semi-circle response on the \(Z'\) axis as described above. With this value, \( C_j \) can be obtained from Equation (4.7) knowing \( \omega_{\text{peak}} \).

If the frequency is scanned from high to low, the varying time constants of each RC response in the material will appear as the frequency nears the time constant of the response and disappear as the frequency passes it. The only process with a time constant in the range of the highest frequencies (> \(10^6\) Hz) is the bulk conduction of charged carriers. All of the other RC elements occurring in series with this have time constants such that their capacitors act as short circuits at these frequencies; they do not contribute to the impedance. Thus, the RC response of the bulk, \( R_bC_b \), contributes the first response at the highest frequencies. At intermediate frequencies, a response is often observed related to the blocking effect of grain boundaries in the specimen. At these frequencies, the capacitance of the bulk response has charged and acts as a open circuit so that only the resistance contributes to the response. Thus, the second response (in terms of decreasing frequency), due to the grain boundaries (\( R_{gb}C_{gb} \)) is a semi-circle of radius \( R_{gb} \).
offset from the origin by a value $R_b$. Any RC elements with time constants at lower frequencies still appear as short circuits and do not contribute to the impedance. At even lower frequencies (on the order of 0.1 Hz), the low capacitance of the electrode process appears while the capacitance of bulk and grain boundary RC responses are charged and become open circuits. Thus, the final semi-circle seen is due to the electrode response, $R_e C_e$, with a radius $R_e$ offset from the origin by a value $R_b + R_{gb}$.

The advantage of the AC impedance spectroscopy technique is immediately obvious compared to traditional DC conductivity measurements. With a DC measurement, one aggregate measurement is obtained which includes the sum of each response in the material (bulk, grain boundary, electrodes). AC impedance spectroscopy offers the possibility of deconvoluting each separate contribution to the conductivity. This is a tremendous advantage because one can focus on the component of interest by using a relatively straightforward experimental technique. In addition, information on the capacitance values can be obtained, which is not possible with a traditional DC measurement.

While this technique can be extremely useful, there are some non-idealities that must be overcome. The scan shown in Figure 4.4 is a very ideal one. In many cases, the time constants of each response will not be separated so nicely. When time constants become close, the semi-circle responses start to overlap and merge. This is illustrated in Figure 4.5 A. When this happens, it is impossible to judge the various parameters by eye. A fitting computational program must be used to fit the data such as the one provided by
Figure 4.5 Non-idealities of AC impedance spectroscopy. (A) A simulated pattern with overlapping responses due to close time constants. (B) A fit of real data taken at 1000 °C in 50%CO/CO₂ on GMMT with x = 0.01. It illustrates the dominance of lead inductance in experimental setups, especially with more conductive samples.
Scribner Institutes, Zview. In rare cases, the data is so merged that separating any data becomes impossible. This can be a particular problem when doing experiments on systems with many interfaces, such as electronic blocking cells.

The problem of overlapping responses can be avoided by using one or more reference electrodes. A reference electrode serves as a fixed voltage reference; it does not draw current. Rather than measuring the impedance by taking the voltage drop across all the responses on the material, one can use the reference electrode(s) to take the impedance just between the successive pairs of electrodes. For example in Figure 4.1, the current is always drawn between the two end electrodes, 1 and 2. Since electrode 3 does not draw current, it does not become polarized and will be a measure of the potential at that position on the sample. Thus, if the voltage drop between electrodes 1 and 3 is used to calculate an impedance, the response in the $\mathbf{-Z''} , \mathbf{Z'}$ plane will arise solely from responses occurring spatially between electrodes 1 and 3. So, the responses from the majority of the bulk and grain boundary of the Ca doped GT and the polarization of the 2nd electrode will not appear. The only responses will be the bulk and grain boundary of the GMMT, polarization at the 1st electrode, the internal interface, and any Warburg response that develops at low frequency (see Section 4.3.2). Similar arguments can be made for any successive pair of electrodes. It is easy to see how this might help distinguish responses when compared with a impedance spectra where the voltage is taken between electrodes 1 and 3 (the whole cell). Various responses that had merged beforehand may appear alone or more clearly when using reference electrodes. As shown
in Figure 4.1, three electrodes will be used in the electronic blocking cells constructed for this thesis.

Another problem is an experimental one that has a particularly noticeable effect on scans made of samples with low bulk resistances (< 500 Ω). The actual lead wires running from the sample out of the sample chamber to the measuring apparatus develop a significant inductance, especially at high frequencies. Figure 4.5B shows the effect that this can have with an actual scan taken for this thesis (of x = 0.01 GMMT at 1000 °C in 50%CO/CO₂) which exhibited no grain boundary or electrode effects in the frequency range shown (10⁶ to 0.1 Hz). The scan appears as a straight vertical line extending beneath the Z' axis and intersecting the Z' axis at the bulk conductivity. While it is possible to fit this data as shown, the only value obtained from the fit with any accuracy is the bulk resistance. The bulk capacitance and lead inductance have very high errors associated with them and are not very meaningful other than for an order of magnitude estimate. The lead inductance is more of a problem at higher temperatures and in gas environments that provide high conductivities (typically high CO/CO₂ mixtures). Methods exist that can reduce or eliminate this problem [66], but they can be time consuming and experimentally cumbersome. As the bulk resistance was the main parameter of interest in this work, the corrective measures were not employed.

The semi-circle responses shown in the previous discussions had centers lying on the Z' axis. This is an ideality. In reality, each RC response is a “lump” parameter that represents a finite distribution of values within the material. This leads to a series of time constants for the response rather a single discreet one. In these cases, the center of the

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semi-circle will lie some distance beneath the $Z'$ axis, and the response will appear as an arc as shown in Figure 4.6. This depression is characterized by the angle, $\theta$, a radial line makes with the $Z'$ axis. The RC element is replaced by a Constant Phase Element (CPE) that can be used to model this depressed response [64].

It is also possible to have a response that is not a semi-circle at all. As discussed in the following section, a diffusional response call the "Warburg" response can develop at low frequencies in certain situations. This response has the distinguishing feature of forming a 45° line with the $Z'$ axis. This response can bend down towards the $Z'$ axis at lower frequency if the diffusion is over a finite length on the laboratory scale or continue to rise at a 45° angle if it occurs over a infinite length. Though this response is most often seen in artificially modulated structures such as the electron blocking cell (see next section), it can also appear due to gaseous diffusion on a two probe sample with porous electrodes. [18]

A final problem that will be briefly mentioned is the fact that one response can always be modeled with more than one equivalent circuit. This leads to some obvious ambiguity in the results obtained. The proper course of modeling the data involves developing a realistic hypothesis as to the responses in the material and developing a realistic circuit based on it. A more complex circuit that models the same data may not be of any use or importance if it cannot be correlated to any likely mechanisms in the material.
Figure 4.6 Simulation of a depressed RC response spectrum.

\[ R = 4000 \, \Omega \]
\[ C_{\text{approx}} = 2 \times 10^{-5} \, \text{F} \]
\[ \theta = 45^\circ \]
4.3.1.2 Experimental Details

AC impedance spectroscopy scans were performed with a Solartron 1260 Frequency Response Analyzer (FRA) in this work. Data was taken with the commercially available driver software, Zplot, from Scribner Institutes. For the electrode impedance study, scans were made from $1 \times 10^7$ to $1 \times 10^{-3}$ Hz with an voltage amplitude of 50 mV. The low frequency end was essential for the study of the electrode response. For conductivity studies, the scans were made from $1 \times 10^7$ to 0.1 Hz with an amplitude of 50 mV. In this case, the low frequency regime was cut off because the electrode impedance details were not important. Reducing the low end frequency from $1 \times 10^{-3}$ Hz to 0.1 Hz saved hours for each scan.

Data analysis was performed with the corresponding product from Scribner Institutes, Zview. Conductivity scans were often ideal enough to analyze by non-computational means, though the electrode data were often depressed and overlapped. Fitting was performed for all electrode scans.
4.3.2 Electronic Blocking Cell

Bulk conductivity measurements taken with AC impedance spectroscopy or any other method yield only the aggregate conductivity, the sum of the ionic and electronic components. Splitting the contributions of these two responses has been the focus of many novel experimental techniques. In most cases, either the ionic or electronic component dominates ($\sigma_{\text{total}} \approx \sigma_\text{e}$ or $\sigma_{\text{total}} \approx \sigma_\text{i}$), and the value of the minority conductivity is sought. Methods for determining the electronic conductivity of a predominately ionic conductor are now well established. The most common technique is transference number measurements [67]. In this method, the open circuit voltage of a ionic conductor is measured in a $P_{O_2}$ gradient (for an oxygen conductor) and compared to the theoretical voltage for an ideal ionic conductor as determined by the Nernst equation. The deviation in the actual measurement is directly related to the electronic component of the conductivity.

Measuring the ionic conductivity of a predominately electronic carrier is considerably more difficult. Unfortunately, this applies to most MIEC materials, which are often predominately electronic with a significant ionic component. Many techniques have been put forth in the past such as the electronic blocking cell, galvanostatic intermittent titration technique, short circuit method, and oxygen chemical diffusion measurements via $^{18}$O exchange. Riess [68] has presented an excellent review of these methods and their limitations. The electronic blocking cell [8], [54], [67], [69], [70], [71]
is used in this thesis. This method employs a solid electrolyte placed in intimate contact with the MIEC. Two (or more) probe AC impedance measurements can be employed to measure the properties of the cell (discussed in detail below). This method is used in this work because the gadolinium titanate system can be doped to create a solid electrolyte (Ca doped GT) as well as the MIEC being studied. Thus, each region of the blocking cell can be of the same phase, allowing for easier construction by co-sintering the different materials. This also reduces common problems of the technique such as gas leakage at the material interface (as discussed below).

Figure 4.7 shows a schematic of the electronic blocking cell used in this work. The MIEC material is pressed against the electronic blocking material (a solid electrolyte, SE). As emphasized in the figure, under an applied signal, the electrons can only flow in the MIEC, while the ions can travel through both materials. This blocking of the electrons leads to a diffusional movement of ions in the MIEC that can be related to the ionic conductivity in the MIEC as described below. This technique can be used with either DC signals or AC impedance spectroscopy. AC impedance will be used in this work because of the advantages listed previously in this chapter.

Figure 4.8 shows the simulated AC impedance response of the cell shown in Figure 4.7 assuming negligible grain boundary contributions (which results in no loss of generality). The standard semi-circular arcs are observed for both the bulk and electrode responses at high frequencies (> 10^2 Hz). However, an interesting phenomena is observed at very low frequencies (approaching 10^4 Hz). The response in the Z'-'Z’’
Figure 4.7 Schematic of the electronic blocking cell.
Figure 4.8 Simulated response of oxide system in an electronic blocking cell showing Warburg response. An equivalent circuit for the response is also shown.

\[ 10^{-4} \text{ Hz} < \omega < 10^7 \text{ Hz} \]

- \[ R_b = 3000 \, \Omega \]
- \[ C_b = 1 \times 10^{-8} \, \text{F} \]
- \[ R_e = 7000 \, \Omega \]
- \[ C_e = 1 \times 10^{-6} \]
- \[ Z_w(\, R) = 20000 \, \Omega \]
- \[ Z_w(\, S) = 100 \]
plane becomes a straight line at a 45° angle to the Z' axis. It then bends over and becomes a partial semi-circle as it intersects with the Z' axis at the very lowest frequency. This behavior is well known and is the result of a diffusional impedance response known as the finite length Warburg impedance* (also known as the “Short Circuit” Warburg, hence the S subscript on the circuit elements) given by,

\[
Z_W = R_W \frac{\tanh \sqrt{\frac{S}{\omega}}}{\sqrt{\frac{S}{\omega}}}
\]

where \( S = \frac{L^2}{D} \), \( L \) is the diffusion length (the thickness of the MIEC), \( D \) is the chemical diffusion constant, and \( R_W \) is the observable resistance of the Warburg impedance.

Figure 4.9 shows a physical picture of the blocking cell under low frequencies during an AC impedance measurement at frequencies in the Warburg range. The picture shows the distribution of the electrochemical potential of ions within the cell in the situation where the positive polarity is applied to the MIEC. Also shown are the response from Figure 4.8, as well as equivalent circuits emphasizing the spatial distribution of the circuit elements in the blocking cell. Recall that the electrochemical potential is given by,

\[
\mu_i = \mu_i + z_i F \phi
\]

where \( \mu_i \) is the chemical species of species i, \( z_i \) is the charge of species i, and \( \phi \) is the

* As opposed to the infinite Warburg impedance where the straight line never bends over but appears to extend forever. The distinction depends on the diffusion length and the frequency range of the measurements. All systems will appear finite if a low enough frequency can be achieved.
Figure 4.9 Physical representation of the Warburg impedance. A simulated response and equivalent circuits emphasizing the spatial positioning of the elements are shown in addition to a schematic of the electrochemical potential of ions in the cell. Details appear in the text.
electrical potential experienced by species \( i \). Thus, applying a potential across the cell will raise the electrochemical potential of the oxygen ions on one side and lower it on the other. The electronic carriers in the two materials also experience a shift due to the electric field, but they cannot flow throughout both materials (blocked by the solid electrolyte). The electrons can redistribute within the MIEC however. This can be shown by noting that the electronic flux (due to both drift and diffusion) must be zero,

\[
J_e = q\mu_n n E + qD_n \nabla n = 0
\]

where \( \mu_n \) is the mobility of electrons, \( n \) is the concentration of electrons, \( D_n \) is the diffusivity of electrons, and \( E \) is the electric field. Equation (4.10) is written for electrons since it will be found that the MIEC materials used in this thesis are primarily n-type. The same principles hold if hole conduction is included. Since the electronic current is zero, a gradient in the electron concentration develops over the MIEC that counteracts a large portion of the electric field. This means that the solid electrolyte is acting as a capacitor to electronic movement as the interface of the MIEC and solid electrolyte becomes charged with electronic carriers.

A schematic of the steady state profile of the ions (for the polarity shown) is shown in the figure. At low frequencies, the electrons in the MIEC redistribute as described above to mask most of the electric field. Thus, the movement of ions in the MIEC is largely governed by diffusion (instead of drift). Since the movement of ions in the solid electrolyte is much more facile than in the MIEC, the rate limiting step in
establishing equilibrium is the diffusion movement in the MIEC. At intermediate low frequencies, the ions in the MIEC do not have enough time to redistribute themselves to achieve the steady state profile before the AC signal is swept in the reverse position. The ions then have to redistribute to accommodate the new profile until the signal is swept once more. These frequencies constitute the regime of the straight line in the Warburg impedance, Regime I as shown in Figure 4.9. Eventually the frequency becomes low enough for the ions to have the time to diffuse and establish the steady state profile. At this point, the response begins to bend down again towards the $Z'$ axis. This frequency is related to the $S$ parameter in equation (4.8). $S$ is given by the expression $s = \frac{L^2}{D}$ which can be seen to be directly related to the diffusion length of the MIEC (e.g. $x = \sqrt{Dt}$ with $x = L$ and $t = S$).

The redistribution of the charged ions also has an effect on the electron profile in the MIEC. At higher frequencies, where ions have less time to move, the electrons charge the internal interface to some degree, creating a capacitance-like effect over the solid electrolyte. But at these frequencies, the amount of ions that move is frequency dependent. Thus, the charge on the internal interface, and, therefore, the capacitance behavior of the solid electrolyte, is also frequency dependent. This type of behavior will suppress the value of the capacitance compared to that which would be established if the ions were able to establish the steady state profile. This is the reason for the straight line behavior of the spectrum in regime I. In Figure 4.9, the dotted line in the spectrum in regime I indicates what the response would look like if the ions were able to establish the steady state profile. At the frequency related to $S$ parameter above, the ions establish the
steady state profile, and the behavior of the blocking solid electrolyte becomes that of a true capacitor. The spectra then becomes that of a typical RC element and bends over to the $Z'$ axis. This behavior shift is emphasized in the circuits shown, where the Warburg element becomes a capacitor in regime II.

The main experimental observable is the value $R_w$. This is the width of the Warburg response on the $Z'$ axis. As derived by [72] and [73],

$\begin{equation}
R_w = t_{el} R_{ion} = t_{el} \frac{l}{A} \frac{1}{\sigma_{ion}}
\end{equation}$

where $t_{el}$ is the electronic transference number in the MIEC, $R_{ion}$ is the ionic resistance in the mixed conductor, $l$ and $A$ are the length and area of the MIEC respectively, and $\sigma_{ion}$ is the ionic conductivity of the MIEC. This equation can be used with the measured $\sigma_{tot}$ to separate $\sigma_e$ and $\sigma_{ion}$.

There are two main conditions that must be satisfied for Equation (4.11) to hold and electronic blocking to occur,

$\begin{align}
(4.12) & \quad R_i(SE) & < & & R_e(SE) \\
(4.13) & \quad R_i(MIEC) & < & & R_e(SE)
\end{align}$

The first condition states that the SE must have a much lower resistance to ions than it does for electrons. This is just a statement of the fact that the material must block electrons and be a SE. The second condition is a statement of the fact the ionic current in
the MIEC should be much higher than the electronic current in the SE. This insures that at low frequencies the current is carried by ion diffusion in the MIEC, not electronic leakage through the SE. Otherwise, one would have an ionic blocking cell instead of an electronic one.

This method is not perfect, and the data is usually subject to a significant amount of scatter. One of the major problems is gas leakage at the internal interface. Often, the two materials are simply mechanically pressed into intimate contact which does not afford a high degree of sealing. Oxygen incorporated at this interface skews the internal concentration gradient providing the diffusional movement of oxygen ions in the MIEC. The measured response would not be an accurate reflection of the ionic conductivity of the MIEC. In this work, however, the two materials are co-pressed and co-sintered. This provides a uniform and dense interface. Gas leakage should be eliminated with this design. Another problem is the large number of responses occurring in the cell (grain and bulk conductivities, electrodes, the internal interface, the Warburg response, etc.). Often these responses in an AC impedance scan become hopelessly merged so that obtaining data is difficult or impossible, even with the aid of a computational modeling program. The use of reference electrodes should alleviate this problem, at least in part. Finally, the need for extremely low frequency to observe the Warburg response requires a very lengthy period of time. An AC scan down to $10^{-4}$ Hz (the limit used in this thesis) takes upwards of 12 hours. Lowering this to $10^{-5}$ Hz raises this time to the order of days. This seriously limits the amount of data that can be taken in a reasonable amount of time.
4.4 Summary of Experimental Methods

Samples of Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7-d}$ were fabricated for various $x$ and $y$ via the citric acid based powder preparation route. The actual compositions synthesized are shown in Table 4.2. Each sample was pressed and sintered as described above and noted in the table. Sample diameters were either $\frac{1}{4}''$ or $\frac{1}{2}''$ and the lengths were on the order of 2 cm. All of the compositions constructed were analyzed for phase purity using x-ray diffraction.

For the electrode impedance studies, 2% and 10% Ca doped GT samples were fabricated. AC impedance scans were generally made from $1 \times 10^7$ Hz to $1 \times 10^{-3}$ Hz. Porous Pt electrodes were prepared by applying 3 layers of Pt paint and firing for $\frac{1}{2}$ hour at 1000 °C. AC impedance scans were made at $P_{O_2}$ from 0.21 atm down to $< 10^{-20}$ atm and 600 °C < $T$ < 1000 °C. The responses were fitted using the Zview program.

Conductivity measurements were performed on the samples listed in Table 4.2. Pt electrodes were constructed in the same manner as the electrode experiments. AC impedance spectroscopy was used from $1 \times 10^7$ Hz to 0.1 Hz. Measurements were take at $P_{O_2}$ from 1 atm down to $< 10^{-20}$ atm and 600 °C < $T$ < 1000 °C. The bulk conductivities were determined by fitting using the Zview program.

The final set of measurements were made on electronic blocking cells. Two cells were made with the structure Pt/8 % Ca doped GT/ $x = 0.1$, $y = 0.66$ GMMT/ Pt. Three electrodes were used. The current carrying Pt electrodes were made in similar fashion to
<table>
<thead>
<tr>
<th>Material</th>
<th>X</th>
<th>Y</th>
<th>Pressing Conditions</th>
<th>Sintering Conditions</th>
<th>Experiment</th>
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<td>(Gd&lt;sub&gt;1&lt;/sub&gt;,Ca&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
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<td>1500 °C for 15 hrs. in air</td>
<td>Electrode</td>
</tr>
<tr>
<td>(Gd&lt;sub&gt;1&lt;/sub&gt;,Ca&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>0.1</td>
<td>----</td>
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<td>1500 °C for 15 hrs. in air</td>
<td>Electrode</td>
</tr>
<tr>
<td>Gd&lt;sub&gt;2&lt;/sub&gt;(Mo&lt;sub&gt;y&lt;/sub&gt;Mn&lt;sub&gt;x&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;1-x&lt;/sub&gt;O&lt;sub&gt;26&lt;/sub&gt;</td>
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<td>0.66</td>
<td>U: 6000 PSI</td>
<td>1250 °C for 4 days in 50% CO/CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Conductivity</td>
</tr>
<tr>
<td>Gd&lt;sub&gt;2&lt;/sub&gt;(Mo&lt;sub&gt;y&lt;/sub&gt;Mn&lt;sub&gt;x&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;1-x&lt;/sub&gt;O&lt;sub&gt;26&lt;/sub&gt;</td>
<td>0.05</td>
<td>0.66</td>
<td>U: 6000 PSI</td>
<td>1500 °C for 15 hrs. in air</td>
<td>Conductivity</td>
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<tr>
<td>Gd&lt;sub&gt;2&lt;/sub&gt;(Mo&lt;sub&gt;y&lt;/sub&gt;Mn&lt;sub&gt;x&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;1-x&lt;/sub&gt;O&lt;sub&gt;26&lt;/sub&gt;</td>
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<td>0.66</td>
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<td>1250 °C for 4 days in 50% CO/CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Conductivity</td>
</tr>
<tr>
<td>Gd&lt;sub&gt;2&lt;/sub&gt;(Mo&lt;sub&gt;y&lt;/sub&gt;Mn&lt;sub&gt;x&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;1-x&lt;/sub&gt;O&lt;sub&gt;26&lt;/sub&gt;</td>
<td>0.1</td>
<td>0.66</td>
<td>U: 6000 PSI</td>
<td>1500 °C for 15 hrs. in air</td>
<td>Conductivity</td>
</tr>
<tr>
<td>Gd&lt;sub&gt;2&lt;/sub&gt;(Mo&lt;sub&gt;y&lt;/sub&gt;Mn&lt;sub&gt;x&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;1-x&lt;/sub&gt;O&lt;sub&gt;26&lt;/sub&gt;</td>
<td>0.1</td>
<td>0.66</td>
<td>U: 6000 PSI</td>
<td>1250 °C for 4 days in 50% CO/CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Conductivity</td>
</tr>
<tr>
<td>Gd&lt;sub&gt;2&lt;/sub&gt;(Mo&lt;sub&gt;y&lt;/sub&gt;Mn&lt;sub&gt;x&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;1-x&lt;/sub&gt;O&lt;sub&gt;26&lt;/sub&gt;</td>
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<td>0.33</td>
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<td>Gd&lt;sub&gt;2&lt;/sub&gt;(Mo&lt;sub&gt;y&lt;/sub&gt;Mn&lt;sub&gt;x&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;1-x&lt;/sub&gt;O&lt;sub&gt;26&lt;/sub&gt;</td>
<td>0.2</td>
<td>0.66</td>
<td>U: 6000 PSI</td>
<td>1500 °C for 15 hrs. in air</td>
<td>Conductivity</td>
</tr>
<tr>
<td>Gd&lt;sub&gt;2&lt;/sub&gt;(Mo&lt;sub&gt;y&lt;/sub&gt;Mn&lt;sub&gt;x&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Ti&lt;sub&gt;1-x&lt;/sub&gt;O&lt;sub&gt;26&lt;/sub&gt;</td>
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<td>0.66</td>
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<td>1250 °C for 4 days in 50% CO/CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Conductivity</td>
</tr>
</tbody>
</table>

Table 4.2 Compositions studied. U=uni-axially, I=isostatic pressing.
the ones above. The reference electrode was constructed by cutting a groove around the circumference and firing Pt paste in it. The third electrode was on the Ca doped GT side of the interface. AC impedance scans were made from $1 \times 10^7$ Hz down to $10^{-4}$ Hz. Measurements were made as a function of $P_{O_2}$ from 1 atm down to $10^{-4}$ atm and $600 \, ^\circ C < T < 1000 \, ^\circ C$. Several scans were taken at each different condition, to monitor the impedance over the various combinations of reference electrodes. All data was fitted with the Zview program.
5 RESULTS

This chapter will present the results gathered for this thesis. These include (1) structural data taken on the synthesized compositions of Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7-\delta}$, (2) electrode impedance data taken with Pt electrodes on Ca doped GT, (3) conductivity measurements taken on the GMMT samples, and (4) the electronic blocking cells.

5.1 Structure and Composition of Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7-\delta}$

Figure 5.1 shows a typical x-ray scan of a sintered pellet taken on Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7-\delta}$ (GMMT). This scan was taken on a GMMT pellet with $x = 0.1$, $y = 0.66$ sintered at 1250 °C under a flow of 50% CO/CO$_2$. The peaks marked with the symbol “1” match with the JCDPF file of the cubic pyrochlore Gd$_2$Ti$_2$O$_7$ (GT). All samples up to $x = 0.2$, $y = 0.66$ had a similar pattern. Three minor peaks are observed that cannot be attributed to this phase. They are at roughly 32°, 76°, and 81.5°. The phase origin of these peaks could not be identified because of the relatively high background. The $x = 0.3$, $y = 0.66$ showed increased intensity at these peaks, as well as other smaller peaks.

Examination of the $x = 0.05$, 0.1 samples under SEM while doing the WDS measurements showed a second phase in the samples sintered at 1250 °C in CO/CO$_2$ that
Figure 5.1 X-ray diffraction pattern of $x = 0.1$, $y = 0.66$ GMMT sintered at 1250 °C under 50% CO/CO$_2$. 
was absent in the samples sintered in air at 1500 °C. This phase was Mn rich with the rough composition of Gd$_2$(Ti$_{1/2}$Mn$_{1/2}$)$_2$O$_7$. It contained no Mo. Though the structure was not confirmed during the SEM measurements, it is reasonable, based on the composition, to assume it is a Mo depleted pyrochlore phase. This may explain why the peaks were not observed in the x-ray if they matched with the major phase peaks. The x = 0.05 sample sintered in air showed a separate minor phase rich in Si, an unexpected impurity. It is not clear how the Si might have entered the sample. None of the other samples exhibited this impurity.

Table 5.1 shows the result of the WDS chemical analysis performed on the bulk region of various samples of GMMT. Good agreement is shown between the predicted composition and the experimentally verified value. The samples sintered in air at 1500 °C did not show the expected depletion of material (based on observed discoloration of the sintering trays and weight loss upon sintering) compared to the samples sintered at 1250 °C in CO/CO$_2$ (which showed no weight loss or tray discoloration). The material loss in the air sintered samples most likely originated from the surface region, which was not tested during the WDS analysis.

The peak pyrochlore positions in the various x-ray scans were used to calculate the cubic lattice constant of the compositions of GMMT. The calculations were performed with programs written for desktop personal computers. Table 5.2 shows the actual values calculated.
Table 5.1 Results of WDS chemical analysis of GMMT. Stoichiometric concentrations are shown in parentheses.
<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameter, $a_0$ (angstroms)</th>
</tr>
</thead>
<tbody>
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<td>$x=0.01, y=0.66$</td>
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</tr>
<tr>
<td>$x=0.05, y=0.66$</td>
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</tr>
<tr>
<td>$x=0.1, y=0.66$</td>
<td>10.2</td>
</tr>
<tr>
<td>$x=0.1, y=0.33$</td>
<td>10.217</td>
</tr>
<tr>
<td>$x=0.2, y=0.66$</td>
<td>10.198</td>
</tr>
<tr>
<td>$x=0.3, y=0.66$</td>
<td>10.212</td>
</tr>
</tbody>
</table>

**Table 5.2** Lattice constants of GMMT with varying composition.
Figure 5.2 shows the corresponding plot. Note that the plot uses the value of the lattice parameter of undoped GT, 10.186 Å [36]. All compositions shown in the Table and Figure were sintered in the CO/CO₂ conditions, except the x=0.2 which was sintered in the air conditions. As can be seen, the lattice parameter shows a weak, and roughly linear, increase with increasing x. There is a further increase when y is increased while holding x constant. No reference standard was used in the x-ray scans or in calculating the lattice constants.
Figure 5.2 Plot of lattice parameter vs. $x$ (expressed as a percentage) in GMMT.
5.2 Electrode Impedance of Pt Electrodes on Ca doped Gd$_2$Ti$_2$O$_7$

This section will present work performed on analyzing the electrode impedance developed with Pt electrodes on Ca doped Gd$_2$Ti$_2$O$_7$ via AC impedance spectroscopy. Figure 5.3 and Figure 5.4 show typical impedance scans obtained on the samples. The former illustrates the effect of oxidizing environments on the electrode impedance of the 10% Ca sample, while the latter shows the effect of reducing environments on the electrode impedance for the 2% Ca sample. Other scans under similar conditions (different temperature, pressure) showed the same features, namely a decreasing impedance with increasing P$_{O_2}$ in oxidizing environments and with decreasing P$_{O_2}$ in reducing environments.

The figures show proposed equivalent circuits for the response as well. Two relaxations plus the high frequency offset on the real axis are seen in Figure 5.3. This was typical of the 10% Ca material at temperatures greater than 700 °C. The high frequency offset was largely independent of P$_{O_2}$ and attributed to the bulk resistance of the sample. The bulk conductivity of the 10% and 2% Ca doped GT are shown in Figure 5.5 and Figure 5.6 respectively.
Figure 5.3 Impedance scans for Ca GT with 10% Ca at 750 °C in oxidizing environments (0.001 atm ≤ P_{O_2} ≤ 1 atm). The frequency ranges from 0.1 Hz to 100 kHz. Also shown is a proposed equivalent circuit for the spectra.
Figure 5.4 Impedance scans for Ca doped GT with 2% Ca at 750 °C in reducing environments (7.2 x 10^{-21} atm ≤ P_{O_2} ≤ 7.18 x 10^{-15} atm, imposed by CO/CO_2 mix). The frequency ranges from 0.001 Hz to 100 kHz. Also shown is a proposed equivalent circuit for the spectra.
Figure 5.5 Bulk conductivity of 10% Ca doped GT as a function of $P_{O_2}$ and T.
Figure 5.6 Bulk conductivity of 2% Ca doped GT as a function of $P_{O_2}$ and T.
The bulk impedance appeared in series with a lead inductance that masked the high frequency bulk arc. The low frequency arcs, with relaxation frequencies < 1 Hz, were attributed to the electrode impedance elements. The 10% Ca material exhibited two responses in this regime, presumably coming from each electrode (Figure 5.3). This was more noticeable at high temperatures. They tended to merge into one response at low temperatures. When analyzed separately, each response had the same P\textsubscript{O2} and T dependence. Therefore in the results that follow, R\textsubscript{electrode} used for the 10% Ca material is the sum of the individual values for each response. On the other hand, the 2% Ca material exhibited one electrode arc at all temperatures. At lower temperatures, the 2% Ca material exhibited a P\textsubscript{O2} independent response at intermediate frequencies (100,000 Hz > \omega_{\text{peak}} > 10,000 Hz) attributed to grain boundaries. The 10% Ca doped GT did not exhibit a similar arc at any temperature.

The electrode conductance (G\textsubscript{electrode} = 1/R\textsubscript{electrode}) is clearly very dependent on P\textsubscript{O2} (see Figure 5.3 and Figure 5.4). Figure 5.7 shows the electrode conductance for 10% Ca doped GT. Figure 5.8 shows the same for the 2% Ca material. The magnitude of G\textsubscript{electrode} is very similar in both materials. Also in both cases, G\textsubscript{electrode} decreases with decreasing P\textsubscript{O2} with a slope of +1/2 at high P\textsubscript{O2} and high T. As the temperature is lowered under oxidizing environments, the behavior becomes more complex. The plot eventually flattens out and even shows a maximum at 600 and 700 °C for the 2% Ca material.
Figure 5.7 Log-log plot of the electrode conductance, $G_{\text{electrode}}$, vs. $P_{O_2}$ for 10% Ca doped GT.
Figure 5.8 Log-log plot of the electrode conductance, $G_{\text{electrode}}$, vs. $P_{O_2}$ for 2% Ca doped GT.
Under reducing conditions, both the 2% and 10% Ca material show an increase in $G_{\text{electrode}}$ with decreasing $P_{O_2}$. The minimum in the plot corresponded with the switch from $O_2/Ar$ mixtures to $CO/CO_2$ mixtures used to control the $P_{O_2}$. So it can also be said that $G_{\text{electrode}}$ increased with increasing CO percentage in the gas mixture. In the 10% Ca material, the plot exhibits a slope of roughly $-1/6$ (vs. $P_{O_2}$) in this regime. The 2% Ca material, on the other hand, exhibits a steeper slope of $-1/4$ (vs. $P_{O_2}$).

The activation energies of $G_{\text{electrode}}$ for the 10% and 2% Ca materials under reducing conditions are shown in Figure 5.9 and Figure 5.10. The former shows the energies at a fixed $P_{O_2}$ of $10^{-15}$ atm, while the latter shows the energies at a fixed CO/CO$_2$ (= 0.01) ratio. As seen in both cases, there is a significant difference between the 2% and 10% Ca doped materials, with the 10% showing lower energies in both cases. The activation energies of the bulk conductivity (not shown) were calculated as 0.64 eV for the 10% Ca material and 0.4 eV for the 2% Ca material at a fixed $P_{O_2} = 0.01$ atm.
Figure 5.9 Activation energy of the electrode conductance of 10% and 2% Ca doped GT at a fixed $P_{O_2}$ of $10^{-15}$ atm.
Figure 5.10 Activation energy of the electrode conductance for 10% and 2% Ca doped GT at a fixed CO/CO$_2$ ratio = 0.01.
5.3 Conductivity of Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7-\delta}$

This section will review the results obtained using 2 probe AC impedance to measure the bulk conductivity of Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7-\delta}$ (GMMT) as a function of x and y. Figure 5.11 summarizes the overall effect of x on conductivity. In air at 900 °C, the conductivity of undoped Gd$_2$Ti$_2$O$_7$ is increased by over 4 orders of magnitude, reaching a maximum of over 10$^{-1}$ S/cm for the x = 0.3 sample with the dependence of conductivity on x becoming weaker at the higher concentrations. Also of note is the increased conductivity by almost ½ an order of magnitude due to decreasing y for the x = 0.1 sample. All compositions shown here were sintered at 1250 °C under 50% CO/CO$_2$ except for x = 0.2 sample, which was sintered in air at 1500 °C. The conductivities of two other samples sintered in air at 1500 °C (not shown) of x = 0.05 and 0.1 were somewhat higher than the equivalent composition sintered under CO/CO$_2$, with the x = 0.05 nearly an order of magnitude higher and the x = 0.1 being nearly equivalent.
Figure 5.11 Total conductivity of $\text{Gd}_2(\text{Mo}_{1+y}\text{Mn}_y\text{Ti}_{1-x})_2\text{O}_{7.8}$ vs. composition in air at 900 °C. The point marked by a "*" was sintered in air at 1500 °C. All others were sintered in 50% CO/CO$_2$ at 1250 °C. Data for $x = 0$ was taken from [36].
Figure 5.12 through Figure 5.19 shows the conductivity of GMMT as a function of $P_{O_2}$ and $T$ for the various $x$ and $y$ combinations used in this thesis. All of the compositions show a nearly $P_{O_2}$ independent regime of some magnitude at intermediate to high $P_{O_2}$. The $x = 0.01, y = 0.66$ sample (Figure 5.12) shows this regime to the most limited extent. At high $P_{O_2}$, the conductivity decreases with increasing $P_{O_2}$ with a slope of roughly $-1/4$ on a log-log scale (shallower at high $T$). At low $P_{O_2}$, the conductivity follows first a $-1/4$ slope and finally an approximately $-1/6$ slope at the lowest $P_{O_2}$.

The conductivity of the $x = 0.05, y = 0.66$ sample is shown in Figure 5.13 and Figure 5.14. The latter shows the sample sintered at 1250 °C in CO/CO$_2$ and the former at 1500 °C in air. Note the significant difference. The sample sintered in air at 1500 °C shows a sharp decrease at high $P_{O_2}$, followed by a nearly $P_{O_2}$ independent regime at intermediate $P_{O_2}$ and a slight increase at low $P_{O_2}$ and high temperature. The other sample shows a $P_{O_2}$ independent regime up to the highest $P_{O_2}$. At lower $P_{O_2}$, the conductivity increases with a slope of roughly $-1/4$ followed by a weaker slope at even lower $P_{O_2}$ of $-1/6$. Furthermore, the magnitude of the conductivity is found to be lower in the sample sintered in CO/CO$_2$. 
Figure 5.12 Conductivity as a function of $P_{O_2}$ and $T$ for $\text{Gd}_2(\text{Ti}_{0.99}(\text{Mo}_{1/3}\text{Mn}_{2/3})_{0.01})_2\text{O}_{7.8}$ with $x = 0.01$ and $y = 0.66$. 
Figure 5.13  Conductivity as a function of $P_{O_2}$ and $T$ for $\text{Gd}_2((\text{Mo}_{1-y}\text{Mn}_y)\text{Ti}_{1-x})_2\text{O}_{7.8}$ with $x = 0.05$ and $y = 0.66$. Sintered in air at 1500 °C.
Figure 5.14 Conductivity as a function of $P_{O_2}$ and T for $Gd_2((Mo_{1-y}Mn_y)_{1/3}Ti_{1-x})_2O_{7.5}$ with $x = 0.05$ and $y = 0.66$. Sample sintered at 1250 °C with 50% CO/CO$_2$. 
Figure 5.15 Conductivity as a function of $P_{O_2}$ and $T$ for $\text{Gd}_2(\text{Mo}_{1/3}\text{Mn}_{2/3})_2\text{O}_7$ with $x = 0.1$ and $y = 0.66$. Sintered at 1500 °C in air.
Figure 5.16 Conductivity as a function of $P_{O_2}$ and $T$ for $\text{Gd}_2(\text{Ti}_{0.9}(\text{Mo}_{1/3}\text{Mn}_{2/3})_{0.1})_2\text{O}_7$ with $x = 0.1$ and $y = 0.66$. Sintered at 1250 °C with 50% CO/CO$_2$. 

$\text{Gd}_2(\text{Ti}_{0.9}(\text{Mo}_{1/3}\text{Mn}_{2/3})_{0.1})_2\text{O}_7$
Figure 5.17 Conductivity as a function of $P_{O_2}$ and $T$ for $\text{Gd}_2(\text{Ti}_{0.8}\text{(Mo}_{1/3}\text{Mn}_{2/3})_{0.2})_2\text{O}_{7.6}$ with $x = 0.2$ and $y = 0.66$. 
Figure 5.18 Conductivity as a function of $P_{O_2}$ and $T$ for Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7-\delta}$ with $x = 0.3$, $y = 0.66$. 
Figure 5.19 Conductivity as a function of $P_{O_2}$ and $T$ for $\text{Gd}_2((\text{Mo}_{1-y}\text{Mn}_y)_{1/3})_{0.1}O_{7.5}$ with $x = 0.1$ and $y = 0.33$. 
Figure 5.15 and Figure 5.16 show the conductivity measured for the $x = 0.1$, $y = 0.66$ composition vs. $P_{O_2}$ and $T$ for two different sintering conditions. The former was sintered in air at 1500 °C and the latter in 50% CO/CO$_2$ at 1250 °C. While there are some difference, e.g. the sample sintered in air exhibits a somewhat stronger atmosphere dependence than the one sintered in CO/CO$_2$, these differences are not nearly as striking as those of the $x=0.05$ sample. Indeed, the magnitude of conductivity in the two cases remained nearly equal.

The conductivity of the $x = 0.2$, $y = 0.66$ sample is shown in Figure 5.17. This sample was sintered in air at 1500 °C. However, considering the fact that the $x = 0.1$, $y = 0.66$ sample showed little difference between the magnitude of conductivity when sintered under the two different conditions, the $x =0.2$, $y =0.66$ sample was not repeated with the CO/CO$_2$ sintering condition. The conductivity remains nearly $P_{O_2}$ independent at high $P_{O_2}$. However, the conductivity exhibits a dramatic drop at lower $P_{O_2}$ indicative of a phase change. Furthermore, the material did not recover its original conductivity upon re-oxidation in air.

The conductivity of the specimen with $x = 0.3$, $y = 0.66$ is shown in Figure 5.18. The conductivity remains independent of $P_{O_2}$ over the experimental range. This specimen exhibited the highest values of conductivity obtained in this work.

Figure 5.19 shows the conductivity of the $x = 0.1$, $y = 0.33$ composition. The conductivity of the $y = 0.33$ composition is higher by about $\frac{1}{2}$ an order of magnitude compared to the $x = 0.1$, $y = 0.66$ sample (Figure 5.16) under oxidizing environments.
While both are $P_{O_2}$ independent at high $P_{O_2}$, the conductivity for the $y = 0.33$ specimen begins to increase and forms a second plateau under reducing conditions.

The conductivity data taken from the plateau regimes show an Arrhenius dependence when plotted vs. reciprocal temperature as shown in Figure 5.20. The activation energies are collected in Table 5.3. The maximum energy is almost 1.5 eV for the $x = 0.01$, declining to nearly 0.4 eV in the $x = 0.2$ sample. The corresponding pre-exponential constants are also shown but show no clear trend.
Figure 5.20 Arrhenius plots of various compositions of GMMT ($y = 0.66$ in all cases) taken in the plateau regime. All samples shown here were sintered in CO/CO$_2$ at 1250 °C except $x = 0.2$ which was sintered in air at 1500 °C. Corresponding activation energies are shown in Table 5.3.
Table 5.3 Activation energies and pre-exponentials for various compositions of GMMT taken in the plateau regime. The air designation indicates that this composition was sintered in air at 1500°C (others were sintered at 1250°C under 50% CO/CO₂).

<table>
<thead>
<tr>
<th>Composition</th>
<th>$E_a$ (eV)</th>
<th>$\sigma_0$ (S K/cm)</th>
</tr>
</thead>
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<td>0.66</td>
<td>$8.99 \times 10^4$</td>
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<tr>
<td>$x = 0.2, y = 0.66$ (AIR)</td>
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<td>$5.6 \times 10^3$</td>
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<td>$6 \times 10^3$</td>
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<td>$x = 0.05, y = 0.66$</td>
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<tr>
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<tr>
<td>$x = 0.1, y = 0.66$ (AIR)</td>
<td>0.66</td>
<td>$4.77 \times 10^3$</td>
</tr>
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</table>
5.4 *Electronic Blocking Cell*

The results obtained on the electronic blocking cells are presented in this section. The cell employed had the following composition:

**Pt/GMMT (x = 0.1, y = 0.66)/8% Ca doped GT/Pt**

A third electrode acted as a reference electrode and was inserted on the Ca doped GT side of the sandwich.

Figure 5.21 shows a schematic of the cell. Note that the current always travels between electrodes 1 and 3. Electrode 2 draws no current and serves as a voltage probe (reference electrode). An equivalent circuit is shown, emphasizing the spatial distribution of the elements. As discussed in Chapter 4, each of these RC elements can lead to a semi-circular response in the \(-Z',Z'\) plane of an AC impedance spectroscopy scan. Data can be obtained from this spectrum if the time constant of each RC response is separated enough from the others to observe an adequate portion of their respective semi-circle. The chances that each of the RC responses in Figure 5.21 will be well separated from all of the others is relatively remote. The reference electrode is used to eliminate some of the responses from the observed spectrum, leading to a spectrum that is easier to analyze (as described in Section 4.3.1).
Figure 5.21 3 electrode electronic blocking cell used in this work. The spatial distribution of the proposed equivalent circuit is also shown.
Figure 5.22 shows typical responses of the electronic blocking cell. There are three responses shown, each representing a voltage drop across various regions of the cell, between electrodes 1 to 3 (referred to here after as $V_{13}$), 1 and 2 ($V_{12}$), and 2 and 3 ($V_{23}$).

Several interesting features are apparent. $V_{13}$ represents the response of the whole cell. At the highest frequency, part of a semi-circle is observed (response 2 in Figure 5.22) with the high frequency intercept ($\omega > 10^6$ Hz) offset from the origin. Based on the typical response of a polycrystalline ceramic material with metallic electrodes (see Section 4.3.1.1), this offset was attributed to the total bulk resistance of the cell. The origin of response 2 is not immediately evident and will be discussed in more detail shortly. At lower frequencies ($\omega_{peak} \approx 0.1$ Hz), a semi-circle (response 3) with a depressed center is evident. Again, based on a typical response of polycrystalline materials with metallic electrodes (which exhibit an electrode response at these frequencies), response 3 was attributed to electrodes 1 and 3 (which are the only electrodes to carry current and develop an impedance). Finally at very low frequency, a response (response 4) is observed that corresponds to the shape of a Warburg type element (see Section 4.3.2). This spectrum exhibits reasonably good separation of the various time constants. The semi-circles tended to merge at lower temperatures making it difficult to isolate the individual responses.
Figure 5.22 Typical impedance spectrum from the 3 probe electronic blocking cell at 900 °C at 0.1 atm. Three scans are shown with the voltage drop over varying regions of the cell as noted in the legend (numbers in legend refer to electrodes in Figure 5.21). The numbers with arrows are references to aid discussion of the various responses of the spectrum.
The $V_{12}$ response includes the GMMT material, its electrode, and the internal interface and is very similar to the $V_{13}$ response. The same high frequency arc (response 2) is seen, just offset to a lower intercept on the $Z'$ axis since the Ca doped GT material is no longer included in the voltage response. The electrode response (response 3) is very similar to the $V_{13}$ response, indicating that most of this response is coming from electrode 1 (since electrode 3 is not included in this response). Finally, at very low frequency, the same Warburg response is observed.

Finally, the $V_{23}$ spectrum is quite different. This response includes just the Ca doped GT material and its electrode. An offset is seen that is attributed to the bulk conductivity of Ca doped GT. This offset should equal the offset observed between the $V_{12}$ and $V_{13}$ response as this is the material that is left out when switching from $V_{13}$ to $V_{12}$. This can be seen by taking the low frequency intercept of the large high frequency arc (response 2) in the $V_{12}$ and $V_{13}$ responses, subtracting them and observing that this amount equals the offset of the $V_{23}$ response,

\[
V_{13,\text{intercept}} - V_{12,\text{intercept}} = 1150\Omega - 956\Omega = V_{23,\text{offset}} = 200\Omega
\]

This offset is followed by a small depressed response attributed to electrode 3 (response 1). No grain boundary arcs were observed in the Ca doped GT. Of note is the absence of responses 2 – 4 that are present in the $V_{12}$ and $V_{13}$ responses. It is obvious then that the Warburg response is indeed coming from the blocking of ions in the GMMT material.

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(remember the $V_{23}$ response is only over the Ca doped GT). Also, the unidentified high frequency arc (response 2) is originating from either the internal interface or the GMMT material.

To further investigate response 2, a DC voltage was superimposed on the AC signal during the AC impedance scan. A DC bias of +200 mV was applied to the sample for a fixed time (5000 seconds). At time intervals of 5 minutes, AC impedance scans were taken over the frequency range of $10^6$ Hz down to 100 Hz (which covered all of the arc in response 2). The DC bias was then removed while continuing to monitor the impedance every 5 minutes. After another 5000 seconds with no DC bias, a DC bias of -200 mV was applied, again continuing to take AC impedance scans every 5 minutes. After a further 5000 seconds, the DC bias was again removed, and the AC impedance monitored every 5 minutes for another 5000 seconds.

Figure 5.23 shows a plot of the low frequency intercept of response 2 on the $Z'$ axis (termed $R_{int}$) versus time under varying applied DC voltage. The AC amplitude was 10 mV. The polarity of the DC voltage has a distinct effect on $R_{int}$. The meaning of this effect and postulations on the origin of response 2 will be reserved for the next chapter.
Figure 5.23 Voltage dependence of the low frequency intercept of the high frequency semi-circle (response 2 in Figure 5.22) in the electronic blocking cell AC impedance spectra. The baseline represents the value under no DC voltage.
Figure 5.24 through Figure 5.27 shows plots of the data obtained with the 3 probe electronic blocking cell. Data collection was limited to the high P$_{O_2}$ regime (> 10$^4$ atm). This was due to the fact that the electrode impedance (response 3) increased sharply upon going to CO/CO$_2$ mixtures needed for lower P$_{O_2}$. This masked the Warburg response, making it impossible to obtain reliable data. Even under oxidizing regimes, the responses became very overlapped at low temperatures, where the electrode response became dominant. For this reason, the Warburg data at 600 °C is considered suspect and is not presented in the plots.

Figure 5.24 shows the bulk offset conductivity of the 8% Ca doped GT obtained on the V$_{23}$ scans. The conductivity was roughly independent of P$_{O_2}$ with an activation energy was about 0.9 eV as noted on the plot. Figure 5.25 shows the conductance of response 2 observed on the V$_{12}$ and V$_{13}$ responses, G$_2$. It shows a very slight increase with decreasing P$_{O_2}$ (with a slope of < -1/8) and has an activation energy of 1.2 eV. Figure 5.26 shows the Warburg conductance as determined from the width of the Warburg response (R$_w$, see Figure 4.8 for a graphical definition) on the Z' axis in a fit of the V$_{12}$ impedance scans. This was used rather than V$_{13}$ because V$_{12}$ was often clearer than V$_{13}$ because of the absence of the electrode 3 response. As expected, this data does show some scatter. This plot exhibits a positive slope that appears to be steeper at higher temperature (reaching roughly +1/4 at high T). Since the data is much more accurate at
Figure 5.24 Plot of the offset (bulk) conductivity of the V23 response over the Ca doped GT portion of the electronic blocking cell versus P02 and T.

E_a = 0.9 eV
Figure 5.25 Plot of $G_2$ (response 2 in Figure 5.22) versus $P_{O_2}$ and $T$. 

$E_a = 1.2$ eV
Figure 5.26 The Warburg conductance, $G_{\text{warburg}}$, versus $P_{O_2}$ and $T$ as determined by the $V_{13}$ response.
Figure 5.27 Electronic transference number, $t_e$, as a function of $P_{O_2}$ and $T$ for $x = 0.1, y = 0.66 \text{Gd}_2((\text{Mo}_{1-y}\text{Mn}_y)_x\text{Ti}_{1-x})_2\text{O}_{7-\delta}$ as determined by electronic blocking cell.
high T (because the response semi-circles were much more separated), it is difficult to
tell if the reduction in slope at reduced temperatures is significant or an artifact of the
error in the data.

The final plot, Figure 5.27, shows the electronic transference number of the
x=0.1, y=0.66 GMMT. This was determined by using the Warburg data (e.g. $R_w$) and
Equation (4.11) in combination with the total conductivity for the same material (Figure
5.16) and recalling that $\sigma_{tot} = \sigma_e + \sigma_i$ and $\sigma_e = t_e \sigma_{tot}$ to obtain the following,

\[
(5.2) \quad t_e = \frac{\sigma_{ne}}{\sigma_{tot} + \frac{L}{AR_w}}
\]

where $L$ is the length of the MIEC portion of the blocking cell, $A$ is the area of the
blocking cell, $\sigma_{tot}$ is the total conductivity measured experimentally, and $R_w$ is the data
obtained from the Warburg response by fitting the blocking cell spectrum (as shown in
Figure 5.22). The data indicate that this value is, on average, between 0.9 and 0.95.
6 DISCUSSION

6.1 Structure and Composition of Gd$_2$((Mo$_{1-y}$Mn$_y$)$_2$Ti$_{1-y}$)$_2$O$_{7-8}$

All of the compositions synthesized in this thesis were stable in air and showed a predominant pyrochlore phase. The lattice parameter shows a slight increase with the percentage of GMMT in the material (Figure 5.2). This can be explained by comparing the various radii of the cations in 6 fold coordination: $R_{Ti}^{4+} = 0.605$, $R_{Mo}^{6+} = 0.59$, $R_{Mn}^{3+}$ = 0.645 (high spin) [41] (all radii data is presented in Å). These oxidation values are the predicted values (via the defect model) under the sintering conditions of 1250 °C under 50% CO/CO$_2$. Replacing a Ti atom with a unit composed of 2/3 Mn and 1/3 Mo ($y = 0.66$) results in a 3.5% increase in average radius (from 0.605 to 0.627). This is confirmed by the upward slope in Figure 5.2. The $x = 0.1$, $y = 0.33$ composition showed an increase over the $x = 0.1$, $y = 0.66$ material. This cannot be explained via the above argument, which predicts a slight decrease in the average radius. The explanation rests on the fact that the dominant valence of Mo under the sintering conditions becomes 4+ instead of 6+ when shifting $y$ to 0.66 from 0.33. The radius of this, $R_{Mo}^{4+}$, is 0.65. The Mn valence state remains the same. The average radius of the replacement unit (Mo$_{2/3}$Mn$_{1/3}$ ($y = 0.33$) as opposed to Mo$_{1/3}$Mn$_{2/3}$ ($y = 0.66$)) increases from 0.627 to 0.648, hence the observed increase in the average cell parameter.
Two sintering conditions were used in this study, (1) in air at 1500 °C and (2) in 50% CO/CO₂ at 1250 °C. Several features can be noted about the samples sintered under each condition:

1. Material loss was observed while sintering samples under condition (1). This was observed both by discoloring of the alumina trays used during the sintering step and weight loss of the sample after sintering. WDS measurements did not show the expected depleted cation concentration in the bulk. Though the surface area was not monitored during WDS, the material loss is suspected to have originated there.

2. The material loss was corrected upon sintering under condition (2). No discoloration of the sintering trays was observed, and the materials weighed > 99% of the pre-sintering weight.

3. Samples sintered under both conditions showed a predominant pyrochlore phase after sintering upon x-ray diffraction analysis. However, upon analysis by WDS, several additional phase features were observed, as listed below.

4. Samples sintered under condition (2) showed a small percentage (approximately 5%) of a Mo deficient phase distributed through the bulk pyrochlore phase. This phase appeared as small islands isolated from one another. The amount of this phase did not appear to be dependent on x.

5. The samples sintered in condition (1) showed a predominant pyrochlore phase. However, the x = 0.05, y = 0.66 sample exhibited a unexpected Si rich impurity.
phase constituting about 10% of the material. The $x = 0.1$, $y = 0.66$ sample sintered under condition (1) showed only a pyrochlore phase with no Si rich phase or Mo deficient phase.

Based on these facts, sintering condition (2) appears to be the more desirable condition. While samples did exhibit a Mo deficient second phase, the material loss was corrected. It is not believed that this second phase was detrimental to the conductivity measurements of the samples. If the conductivity of the $x = 0.1$, $y = 0.66$ sample sintered under condition (1) (Figure 5.15) is compared to the conductivity of same composition under condition (2) (Figure 5.16), very little difference is observed. The sample sintered under condition (1) did not exhibit the Mo deficient phase, but the material sintered under condition (2) did. Since the conductivity changes very little when incorporating this phase, it is concluded that it does not have a significant effect on the conductivity characteristics. In the rest of this chapter, the conductivity obtained on the $x = 0.1$, 0.66 under condition (2) is used for discussion, because the majority of the other compositions discussed were sintered under condition (2) as well.

The large difference in the conductivity of the $x = 0.05$, $y = 0.66$ material sintered under condition (1) and (2) (Figure 5.13 Figure 5.14) is considered to have originated from the Si rich impurity phase present in the sample sintered under condition (1). This impurity is probably not realted to the sintering condition. Rather it was most likely picked up during one of the processing step, perhaps from the pyrex beaker used to burn off the organics in the original citrate mix. However, it is unclear why the impurity only
appeared in this particular sample. The source of the impurity was not investigated further. The measured conductivity on the \( x = 0.05, y = 0.66 \) material sintered under condition (1) is considered spurrious and is not considered in the rest of this chapter.

The origin of the Mo deficient phase in samples sintered under condition (2) was not explored further. It could be that the lower temperature (compared to condition (1)) did not allow the starting materials to react fully. The material could also have some sort of miscibility gap under the conditions of sintering condition (2) not present under condition (1).

### 6.2 Electrode Impedance of Pt Electrodes on Ca doped \( \text{Gd}_2\text{Ti}_2\text{O}_7 \)

The AC measurements performed in this section provided information on both the bulk conductivity and the interfacial processes with the main focus being on the interfacial process occurring at Pt electrodes on Ca doped GT as shown in Figure 5.7 and Figure 5.8. Bulk conductivity data of Ca doped GT as shown in Figure 5.5 and Figure 5.6 were compared with those obtained by Kramer [36]. The magnitude and trend of the conductivity with \( P_{O_2} \) agree very well for both 2\% and 10\% doped Ca doped GT. The activation energy of the 10\% Ca sample in this study (0.64 eV) corresponds almost exactly with that determined by Kramer. The 2\% Ca sample, however, showed an energy of 0.4 eV, somewhat lower than that observed by Kramer (around 0.6 eV). The origin of this differing activation energy was not explored here.
The interfacial impedance showed a very complex dependence on P\textsubscript{O\textsubscript{2}} as shown in Figure 5.7 and Figure 5.8. Certain well defined features can be noted, however. A +1/2 slope was obtained at high P\textsubscript{O\textsubscript{2}} and high temperature (T > 900 °C) for both compositions (2% and 10% Ca). On the other hand, a −1/6 slope is exhibited at low P\textsubscript{O\textsubscript{2}} for the 10% Ca sample, while the 2% Ca sample exhibits a −1/4 slope at low P\textsubscript{O\textsubscript{2}}.

The behavior of both samples at high P\textsubscript{O\textsubscript{2}} can be explained by a model developed by Mizusaki, et. al. [13]. In general, the P\textsubscript{O\textsubscript{2}} dependence of the electrode conductance (σ\textsubscript{e} = G\textsubscript{e} = 1/R\textsubscript{e}) is based on the adsorption of oxygen on the Pt surface. If a Langmuir-type isotherm for adsorption with dissociation is assumed then [74],

\begin{equation}
\frac{\theta}{1 - \theta} = \frac{(KP_{O_2})^{1/2}}{1 + (KP_{O_2})^{1/2}}
\end{equation}

where θ is the coverage of O\textsubscript{ad} (adsorbed oxygen) on the Pt surface and K is the ratio of the adsorption and desorption rate constants. If one defines P\textsubscript{O\textsubscript{2}}\textsuperscript{*} as the partial pressure of oxygen where \( \theta = \frac{1}{2} \), then K = 1/P\textsubscript{O\textsubscript{2}}\textsuperscript{*}. Substituting this back into Equation (6.1) and noting that each O\textsubscript{2} atom in the gas dissociates into two adsorbed oxygen atoms yields,

\begin{equation}
\frac{\theta}{1 - \theta} = \left( \frac{P_{O_2}}{P_{O_2}^*} \right)^{1/2} = \frac{a_O}{a_O}
\end{equation}
where \( a_0 \) is the oxygen activity on the surface and \( a_0^* \) is the oxygen activity on the surface at \( P_{O_2}^* \).

Mizusaki presented two different rate-limiting models: (i) dissociative adsorption of oxygen and (ii) surface diffusion of adsorbed oxygen on the Pt surface. Considering case (i), the electrode reaction can be described by,

\[
(6.3) \quad O_2(g) + 2V_{ad}(Pt) = 2O_{ad}(Pt)
\]

for which the rate equation is

\[
(6.4) \quad \nu = kP_0(1-\theta)^2 - k'\theta^2
\]

where \( \nu \) is the rate reaction per unit area of Pt surface, and \( k \) and \( k' \) are rate constants. Dissociative adsorption would only be rate limiting in cases where the diffusion of \( O_{ad} \) on the Pt is unimportant (for example, where the Pt particles are very small so that the diffusion length is always very short). In these cases, gas can be considered to be directly supplied to the Pt/solid electrolyte (SE) boundary. The rate limit then becomes how fast the oxygen molecules in the gas can dissociate and adsorb to be provided to the triple points. Denoting the activity of oxygen at the Pt/SE interface as \( a_O(SE) \), one obtains from Equation (6.2),

\[
(6.5) \quad \theta = \frac{a_O(SE)}{a_O(SE) + a_O^*}
\]
From this set of equations (6.3 - 6.5) (and a similar equation relating to the dependence of the overpotential on \( P_{O_2} \) (see [13])), one can obtain the following relation between the current, \( i \), and the overpotential (\( \eta \)),

\[
i = 4F\alpha k a^*_O P_{O_2} \left\{ \frac{1 - \exp\left(\frac{-4\eta F}{RT}\right)}{P_{O_2}^{3/2} \exp\left(\frac{-2\eta F}{RT}\right) + a^*_O} \right\}
\]

The electrode conductance is then given by

\[
G_E = \left( \frac{\partial i}{\partial \eta} \right)_{\eta=0} = \frac{16F^2 \alpha k a^*_O P_{O_2}}{RT \left[ P_{O_2}^{3/2} + a^*_O \right]^2}
\]

Now, if \( P_{O_2} \gg a^*_O \) (e.g. the surface is saturated with oxygen), then

\[
G_E = \frac{16F^2 \alpha k a^*_O}{RT} \neq f(P_0)
\]

Thus, \( G_E \) is independent of \( P_{O_2} \). According to [13], this is seen experimentally at \( T \approx 500 \) \(^\circ\)C and lower and \( P_{O_2} > 10^{-4} \) atm. As shown in Figure 5.7, the electrode conductance of the 10% Ca sample is clearly becoming independent of at \( T \leq 700 \) \(^\circ\)C. It is proposed that the 10% Ca sample is exhibiting electrode kinetics limited mainly by dissociative adsorption of oxygen on the Pt surface at \( T < 700 \) \(^\circ\)C and \( P_{O_2} > 10^{-4} \) atm.
However, this behavior is not seen at high temperature for the 10% Ca sample, and is not seen at all on the 2% Ca sample, where the electrode conductance begins to show a maximum at lower temperatures and high P$_{O_2}$ (see Figure 5.8). Mizusaki [13] also presented a model to explain this type of behavior, often seen experimentally at higher temperatures. This model is based on the surface diffusion of adsorbed oxygen molecules to the triple points becoming rate limiting as shown in Figure 6.1. A simple one dimensional model is presented where a concentration gradient develops in the area surrounding the active triple points. The surface flux of oxygen is assumed to proceed by successive jumps between neighboring adsorption sites given by,

$$j = -\lambda c \theta (1 - \theta) \frac{\partial \theta}{\partial x}$$

where $\lambda$ is a constant proportional to the mobility and $c$ is the concentration of total surface adsorption sites. The term $\theta(1 - \theta)$ represents the probability that a neighboring site will either be filled or empty. This yields a maximum flux at $\theta = 0.5$. Employing the Lagmuir isotherm (Equation (6.2)), integrating across the depletion area around the
Figure 6.1 Schematics of the Pt/SE/O$_2$(g) three phase boundary (triple point) and neighboring area. The reaction rate limiting step is assumed to be surface diffusion of oxygen to the triple points. After [13].
triple point, and inserting the result in the equation of $\eta$ as a function of $P_{O_2}$ (again, see [13]), one obtains the result for the electrode conductance,

$$G_E = \frac{4F^2 B \alpha a_{O_2} P_{O_2}^{1/2}}{\left(\alpha O + P_{O_2}^{1/2}\right)^2 \delta}$$

(6.10)

where $B$ is the length of the Pt/SE boundary per unit area of electrode and $\delta$ is the depletion width around each triple point.

The $P_{O_2}$ dependence of Equation (6.10) is such that $G_E$ shows a smooth maximum at $P_{O_2} = P_{O_2}^*$ with a linear drop-off on either side with a slope of $\pm/\frac{1}{2}$ (positive slope on the low $P_{O_2}$ side). The peak $P_{O_2}$ ($= P_{O_2}^*$) is dependent on temperature as confirmed experimentally [13]. It shifts to lower $P_{O_2}$ as the temperature decreases. At 800 °C Mizusaki measures $P_{O_2}^* = 1$ atm while at 600 °C, $P_{O_2}^* = 10^{-2}$ atm for Pt electrodes on stabilized ZrO$_2$. The data for the 2% Ca (Figure 5.8) appear to conform to this model. At high temperature (900 – 1000 °C), the log-log plot of $G_E$ vs. $P_{O_2}$ shows a slope of $+1/2$. This means that only the low $P_{O_2}$ regime of Equation (6.10) is being observed (e.g. $P_{O_2}^* >> 1$ atm). As the temperature is lowered, however, $G_E$ begins to exhibit the peak predicted by Equation (6.10), which becomes clear at 600 – 700 °C. The peak pressures ($P_{O_2}^*$) observed here correspond well with the data mentioned by Mizusaki (especially considering they worked with ZrO$_2$ as an electrolyte, while Ca...
doped GT was used in this study). The implication of this fact is that the electrode reaction is controlled solely by the interaction of the Pt with the gas phase, independent of the electrolyte composition. The 10% Ca material also exhibits this behavior at high $P_{O_2}$. However, it does not exhibit a maximum at the lower temperatures because it is controlled by dissociative adsorption instead of surface diffusion at those temperatures.

The fact that the 10% Ca doped material showed a shift in mechanism when going from high to low temperature at high $P_{O_2}$, while the 2% Ca material did not, may indicate something about the microstructure of the two sets of electrodes. Dissociative adsorption is rate limiting only under conditions where gas atoms are provided directly to the region around the triple point. This occurs where the surface diffusion becomes unimportant, such as when the Pt particles are so small that the diffusion becomes negligible in supplying oxygen to the reaction sites. There is no fundamental reason why the surface diffusion rate should vary on the Pt surface between the 10% and 2% Ca doped material. This leaves the conclusion that the Pt particles in the 10% electrode had a much smaller size (finer microstructure) than the 2% electrode. Though effort was made to make the processing steps as consistent as possible, it is possible that some differences may have occurred. For example, slightly more organic may have been used to dilute the Pt paste in either case, resulting in a different microstructure after being fired. It is unfortunate that no SEM micrographs of the electrode microstructures could be made. Upon removal from the test apparatus, the electrodes were destroyed. The author recommends that future studies make SEM micro-graphs before the samples are
placed in the test apparatus. See the "Future Work" chapter for more thoughts on this subject.

The low $P_{O_2}$ behavior shows an increase in the electrode conductance as $P_{O_2}$ decreases (negative slope) as shown in Figure 5.7 and Figure 5.8. It must be emphasized that the $P_{O_2}$ in this regime was established by the equilibrium between CO$_2$ and CO in the gas phase. The minimum in the electrode conductance always occurred at the lowest CO concentration in the gas (highest $P_{O_2}$). Based on a rate limiting mechanism involving the limited supply of O$_2$ (whether by adsorption or diffusion), the data shown in Figure 5.7 and Figure 5.8 are not consistent. In the case of a mechanism based on O$_2$, the conductance should continue to decrease as $P_{O_2}$ is decreased. However, the exact opposite occurs, indicating that either the CO or CO$_2$ is somehow involved in the electrode reaction. This has been seen in the literature by various researchers (as summarized in [75]). For example, Chebotin, et. al. [76] [77] presented a model based on an electrode reaction proceeding by the incorporation of CO and CO$_2$ into the electrolyte. Their model does explain a dependence of the electrode impedance on the ratio of CO/CO$_2$ with roughly the trends seen in the data of this work. However, the diffusion of CO and CO$_2$ within a solid electrolyte to any appreciable extent seems unlikely. More likely is a mechanism involving the reaction of oxygen adsorbed on the Pt with CO to form CO$_2$,

\begin{align}
(6.11) & \quad O_{SE}^{2-} \leftrightarrow O_{ad,Pt} + 2e^- \\
(6.12) & \quad CO(g) + O_{ad,Pt} \leftrightarrow CO_2(g)
\end{align}
Without a detailed model, the importance of the activation energies shown in Figure 5.9 and Figure 5.10 is unclear. One can say that the 10% Ca sample had a more facile electrode reaction than the 2% Ca sample at all but the highest temperature, both because of its higher overall electrode conductance and lower activation energy (with both P\textsubscript{O\textsubscript{2}} and CO/CO\textsubscript{2} fixed). This is an indication that perhaps the two samples experienced different electrode reaction mechanisms in the CO/CO\textsubscript{2} regime.

Further indication that the two samples experienced different mechanisms comes from the differing slopes between the 2% Ca sample (−1/4 slope) and the 10% Ca sample (−1/6 slope) in the CO/CO\textsubscript{2} regime. One difference between the two samples is increased electronic conduction in the 10% Ca electrolyte (as measured by Kramer [36]). This fact could have an effect only if electrons in the GT contributed in some manner to the electrode reaction. Given the above discussion, however, it appears that the limiting mechanism is confined to the Pt surface. The electrical conductivity in the bulk electrolyte is unlikely to affect the electrode kinetics. A more likely reason for the differences between the 2% and 10% Ca electrode reactions might be the possible difference in electrode microstructure between the two samples (as indicated in the high P\textsubscript{O\textsubscript{2}} data). It could be that this also has an effect on the mechanism at low P\textsubscript{O\textsubscript{2}}, thereby shifting the slopes and activation energies.
6.3 Conduction in $\text{Gd}_2(\text{Mo}_{1-y}\text{Mn}_y)\text{Ti}_{1-x}O_{7-\delta}$

6.3.1 Total Conduction Level

The total conductivity of $\text{Gd}_2((\text{Mo}_{1-y}\text{Mn}_y)x\text{Ti}_{1-x})_2O_{7-\delta}$ (GMMT) shown as a function of $x$ and $y$ in Figure 5.11 indicates that the maximum conductivity achieved in this work was about $10^{-0.9} = 0.12$ S/cm in air at 900 °C with $x = 0.3$, $y = 0.66$ (from this point forward, compositional values will be specified with the $x$ component only; they will correspond to $y = 0.66$ unless otherwise noted). This represents an over four order of magnitude increase in the total conductivity over undoped Gd$_2$Ti$_2$O$_7$ (GT). The only pyrochlore material previously fabricated with a higher conductivity in an oxidizing environment was a Ru, Bi co-doped compound prepared by Spears [42] (specifically, $(\text{Gd}_{0.8}\text{Bi}_{0.2})_2(\text{Ti}_{0.8}\text{Ru}_{0.2})_2O_7$). This compound exhibited a conductivity of about 1 S/cm at 900 °C in air with an activation energy of 0.3 eV. However, that material contained two unstable elements (Bi, Ru) that led to decomposition at low $P_{O_2}$. In addition, there was a problem in forming an ideal dense, uniform, single phase pyrochlore microstructure. Finally, Ru is considerably more expensive than either Mo or Mn. Thus, $x = 0.3$ GMMT may represent the best candidate material to serve as the MIEC cathode material for use in a monolithic pyrochlore fuel cell (as shown in Figure 2.5).
6.3.2 Microscopic Conduction Mechanism

6.3.2.1 Isolated Defects (x ≤ 0.05)

To isolate the microscopic mechanism responsible for these high conductivity values in GMMT, the conduction of the various compositions (x,y) were monitored as a function of P_{O_2} and temperature. This data was then compared to theoretically generated plots of the microscopic defect concentrations as a function of P_{O_2} and temperature developed according to the methods described in Chapter 3. By comparing the two plots, the defects responsible for conduction in the material can, in principle, be isolated.

Figure 6.2 shows a defect concentration plot for x = 0.01 GMMT at 900 °C. The experimental conduction behavior of the material is also shown for comparison. It is readily observed that electrons (n) exhibit a P_{O_2} dependence most similar to the conductivity behavior.
Figure 6.2 Plot of the mobile defects in Gd$_2$(Mo$_{1/3}$Mn$_{2/3}$)$_{0.01}$Ti$_{0.99}$O$_{7-\delta}$ at 900 °C as a function of $P_{O_2}$. Vertical bolded dotted lines indicate regions of different dominant charge neutrality control. The simplified neutrality equation for each regime is shown above the plot. The smaller plot shows the experimental conduction behavior of the same composition.
At high $P_{O_2}$, both the conductivity and theoretical electron concentration exhibit a decrease in conductivity with $P_{O_2}$ with a slope of $-1/4$. In this regime, the oxidation of Mo$^{4+}$ to Mo$^{6+}$ is charge compensated by the formation of oxygen interstitials. This is accompanied by an increase in the hole concentration ($p$) (because interstitials energetically act as acceptors in the material), which in turn must be compensated by an electron concentration drop to keep the internal electron hole generation product constant (Equation (3.9)).

At intermediate $P_{O_2}$, a “plateau” is exhibited where $n$ and the conductivity are independent of $P_{O_2}$. In this regime, which encompasses the stoichiometric point of the material (e.g. $[V_{O}^{**}] = [O^{/\prime}]$), the defects in the material are compensating. That is, the formation of Mo$^{6+}$ is charge compensated by the formation of Mn$^{3+}$. This compensation pins the Fermi energy near the Mn level, keeping $n$ independent of $P_{O_2}$. Taking the electron concentration from this regime and the total conductivity at 900 $^\circ$C, one can calculate the intrinsic electron mobility from Equation (2.2). The value calculated here at 900 $^\circ$C is roughly $1 \times 10^{-4}$ cm$^2$V$^{-1}$sec$^{-1}$. This is somewhat lower than earlier reports [78], which indicate that the electron mobility should be on the order of $10^{-2} - 10^{-1}$ cm$^2$V$^{-1}$ sec$^{-1}$. There could be several reasons for this discrepancy. The first is that the earlier reports were based on measurements made on Y$_2$Ti$_2$O$_7$ not GT. Also, the value of $n$ in Figure 6.2 are based on the estimation of many equilibrium constants which have an
exponential dependence. Minor differences in the activation energies and pre-exponentials can result in orders of magnitude differences in the various concentrations.

More likely may be the contribution of background fixed valent acceptors. These impurities can be fairly common in oxides [36], [79]. Relatively abundant elements such as Ca, Mg, Al, etc. may be incorporated into the material during processing. In GT, these elements tend to be acceptors as they tend to be either +3 or +2 (i.e., more negative than the host elements, Gd$^{3+}$ and Ti$^{4+}$). The presence of these elements has a particularly pronounced effect in pure or dilute doped GT ($x \leq 0.05$) because the impurities tend to be on the level of hundreds to thousands of ppm which approaches the level of the actual dopant in the material.

Figure 6.3 shows the effect of a background +2 acceptor impurity on the Gd site (such as Ca) in $x = 0.01$ GMMT at 1000 °C. Increasing acceptor concentration tends to depress the electron concentration and increase the oxygen vacancy concentration. With 6000 ppm acceptors, the electrons are depressed nearly two orders of magnitude. This could easily account for much of the mobility discrepancy calculated above.
Figure 6.3 Effect of background acceptor impurity on electron and oxygen vacancy concentration in x = 0.01, y = 0.66 GMMT at 1000 °C. Trend in acceptor concentration is shown on plot. The successive lines represent the following compositions: 0, 4000, 5000, 5500, 6000 ppm.
The activation energy of the $x = 0.01$ material in the plateau is 1.47 eV. Since the large majority of the mobile electrons in this regime exist in the conduction band, this energy should be a measure of the Mn ionization energy (e.g. the difference between the Mn defect level energy and the conduction band in GMMT). If Mn is viewed as lying at mid gap and weakly ionized, the $n$ in the plateau should be given by [34]:

\[
\begin{align*}
(6.13) \quad n \propto \exp\left(-\frac{E_{Mn}}{2kT}\right)
\end{align*}
\]

where $E_{Mn}$ is the Mn defect level energy (measured from the conduction band). Using this equation, $E_{Mn} \sim 3$ eV, which would place it as a deep acceptor, not at mid gap as proposed in [49]. However, as discussed above, the electron concentration may be affected by the presence of background acceptors. This affect is temperature dependent because the overall level of electrons and vacancies is temperature dependent and the background acceptors have more of an affect when the electrons and vacancies are more dilute in the material. This temperature variation could affect the measured activation energy of the conduction. As discussed below, the $x = 0.05$ shows similar properties to that of the $x = 0.01$ material. For this composition ($x = 0.05$), however, the background impurities must have less of an effect because the actual dopant concentration is much higher. The activation energy measured for the $x = 0.05$ in the plateau, around 1.3 eV, may therefore be more accurate. Using this activation energy, one calculates $E_{Mn} \sim 2.6$ eV, much closer to mid gap and the value obtained in previous works.
At low $P_{O_2}$, the conductivity again starts to increase with decreasing $P_{O_2}$. In this regime, oxygen vacancies are being created as the material is reduced. These vacancies are charge compensated initially by Mn$^{3+}$ (e.g. $2[Vo^*] = [Mn']$). In a short range of $P_{O_2}$, however, the vacancy concentration becomes high enough so that Mn$^{3+}$ can no longer compensate them. In this final regime, the vacancies are charge compensated by the generation of electrons via Equation (3.10) ($2[Vo^*] = n$). The slope of the theoretical electron density becomes $-1/6$, mirroring the dependence observed experimentally in the conductivity plot.

The activation energy for conductivity in the regime where $2[Vo^*] = [Mn']$ is 3.19 eV with a pre-exponential of about $6 \times 10^{12}$ S/cm. The reduction equilibrium constant can be extracted from these values by noting that $[Mn'] = [Mn_{tot}]$ in this regime. Substituting this value into the reduced electroneutrality equation and putting the resulting expression for the vacancy concentration ($2[Vo^*] = [Mn_{tot}]$) into Equation (3.11) yields the following expression for $n$,

$$n = \left( \frac{K_r}{Mn_{tot}} \right)^{1/2} P_{O_2}^{-1/4} \tag{6.14}$$

with $K_r = K_r^0 \exp(-E_r/kT)$ is the reduction equilibrium constant. If the relatively small activation energy of the electron mobility is ignored, the activation energy of conduction, $E_a$, becomes equal to $1/2$ the reduction energy, $E_r$. This gives $E_r = 6.4$ eV for $x = 0.01$ GMMT. This is comparable to values obtained on previous GT based materials, which
yielded reduction energies from 6-7 eV [38]. The pre-exponential for the reduction
constant becomes on the order of $10^{77}$ atm$^{1/2}$cm$^{-9}$ from Equation (6.14) (taking into
account $q$ and the pre-exponential of electron mobility) giving the following expression
for the reduction equilibrium constant,

$$K_r = 10^{77} \left( \frac{atm^{1/2}}{cm^9} \right) \exp\left(-\frac{6.4eV}{kT}\right) \quad (6.15)$$

This pre-exponential is somewhat higher than the previous values for the parameter,
which were on the order of $10^{69}$ atm$^{1/2}$cm$^{-9}$. This discrepancy could explain some of the
misalignment in the $P_{O_2}$ values between the model based on earlier reported values for $K_r$
and the experimental results in this thesis (a higher reduction pre-exponential shifts the
concentration curves to a higher $P_{O_2}$). The source of the discrepancies in the magnitude
of $K_r$ are not known.

The regime at high $P_{O_2}$ where $[Mo^\cdot] = [O_i^\cdot]$ can be used in a similar manner to
extract the Frenkel constant of the material. Noting that $[Mo^\cdot] = [Mo_{tot}]$ in this regime,
one can substitute the reduced neutrality equation into Equation (3.2), and then the
resulting expression into Equation (3.11) to obtain,

$$n = \left( \frac{K_r [Mo_{tot}]}{K_f} \right)^{1/2} P_{O_2}^{-1/4} \quad (6.16)$$
Combined with the value for $K_r$ obtained above, Equation (6.16) yields the value of the Frenkel constant. Analysis of the data in this regime indicates that the activation energy, $E_a$, of the conduction is 1.8 eV with a pre-exponential of about $7 \times 10^5$ S/cm. As above, if the small activation energy of the electron mobility is ignored, the activation energy in this regime becomes equal to $(E_r - E_f)/2$. Using the value of $E_r = 6.4$ eV calculated above, the Frenkel energy is calculated to be $E_f = 2.9$ eV. Analyzing the pre-exponential yields a value for $K_f^o = 2.6 \times 10^{53}$ cm$^{-6}$. The full expression for the Frenkel energy then becomes

$$K_f = 2.6 \times 10^{53} (cm^{-6}) \exp\left(-\frac{2.9 eV}{kT}\right)$$

This pre-exponential value corresponds well with previous values calculated on GT based systems [61]. However, the activation energy is well below the value of 5 eV reported previously on the GT systems. The Frenkel energies in the past were calculated with a more indirect method than the present case and may be inaccurate as a result.

The above discussion assumes that the conductivity is electronic over the entire range of $P_{O_2}$. At high $P_{O_2}$, it is obvious that the only mobile defect to fit the conductivity dependence on $P_{O_2}$ is electrons. However, at $P_{O_2}$ below where the plateau occurs, an alternative mobile defect is the oxygen vacancy. As observed in Figure 6.2, the vacancy concentration becomes higher than that of the electrons at low $P_{O_2}$, leading to possible ionic conduction. This would mean that the reduction in slope in the conductivity of $x = 0.01$ and 0.05 at the lowest $P_{O_2}$ is the result of flattening of the oxygen vacancy.
concentration in the regime where $2[V_0^-] = [Mn']$. It is not possible to distinguish which mechanism (ionic or electronic) is controlling at low $P_{O_2}$ from this data alone. The determination would rest on the ratio of the mobility of the electrons to the vacancies. This mechanism is even more probable if one takes into the account the possibility of background acceptors which may raise the vacancy concentration in this regime by orders of magnitude.

Figure 6.2 includes information regarding the location of the boundaries between the various regimes. When comparing the conductivity plots to the theoretical defect densities, the position of these boundaries differ appreciably. This appears to be a particular problem for the low $P_{O_2}$ boundary, which exhibits a shift of roughly 5-10 orders of magnitude in $P_{O_2}$ between the experimental and theoretical data. As with the defect concentrations, the $P_{O_2}$ at which these boundaries occur is a function of the various equilibrium constants. Minor variances in these constants can translate to large deviations in the theoretical plot. The discussion of background acceptors is relevant here as well. Since their presence suppresses $n$ and raises the vacancy concentration in the region of the low $P_{O_2}$ border, they will raise the $P_{O_2}$ at which the border occurs (see Figure 6.3).

The $x = 0.05$ GMMT material has a defect density plot very similar to Figure 6.2 (the conductivity plot is shown in Figure 5.14). The major difference is that the width of the electron plateau broadens. Figure 6.4 illustrates this point by plotting $n$ as a function of $P_{O_2}$ for increasing values of $x$. The plateau broadens successively with $x$ up to $x = 0.3$. 
Comparing the conductivity of $x = 0.05$ to $x = 0.01$ (Figure 5.14 to Figure 5.12), the main difference is that the high $P_{O_2}$ regime is independent of $P_{O_2}$ in the $x = 0.05$ material. This is the result of the broadening plateau regime. The high $P_{O_2}$ decline in $n$ is no longer
Figure 6.4 Plot of the electron density in Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7.5}$ as a function of $x$ (0.01 to 0.3, $y = 0.66$) and $P_{O_2}$. The width of the “plateau” increases with $x$. Note that the value of $n$ remains constant with $x$ in the plateau.
observed in the experimental range of \( P_{O_2} \). It can also be noted that the increase at low \( P_{O_2} \) starts at a lower \( P_{O_2} \) in the \( x = 0.05 \), again the result of the plateau broadening.

Figure 6.5 shows the plot of the variation in the oxygen vacancy concentration as a function of \( x \) and \( P_{O_2} \). At low \( P_{O_2} \), the vacancy concentration increases with \( x \) in the narrow \( P_{O_2} \) regime where they are compensated by \( Mn^{+3} \). If the low \( P_{O_2} \) conductive behavior of the \( x = 0.01 \) and \( x = 0.05 \) samples is due to vacancy motion, the conductivity in the low \( P_{O_2} \) regime should show a similar increase with \( x \). Indeed, if one compares the \( x = 0.01 \) and 0.05 conductivity plots closely at the same temperature and \( P_{O_2} \) (reducing), an increase in the conductivity can be detected. In addition, for the \( x = 0.05 \) sample, Figure 6.5 indicates that a second plateau should be approached as the vacancy concentration becomes independent of \( P_{O_2} \) (as opposed to the \( x = 0.01 \) sample, where the vacancies never fully plateau). Figure 5.14 shows a more extreme reduction in slope than Figure 5.12 at low \( P_{O_2} \), indicating that the \( x = 0.05 \) sample is indeed approaching a second plateau not exhibited by the \( x = 0.01 \) specimen. This argument appears to support the theory that GMMT becomes ionic under reducing conditions (for low values of \( x \)).
Figure 6.5 Plot of the oxygen vacancy concentration in Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7.5}$ as a function of x (0.01 to 0.3, y = 0.66) and P$_{O_2}$. The corresponding regime where the electron density achieves a P$_{O_2}$ plateau is noted.
If the conductivity values in the electron plateau regime are compared for the $x = 0.01$ and $x = 0.05$ samples, an increase of roughly $\frac{1}{2}$ order of magnitude is found. This is inconsistent with the model shown in Figure 6.4. The value of $n$ in the plateau regime is nearly independent of $x$. This is the result of the compensation between the Mo$^{+6}$ and Mn$^{+3}$ occurring at these $P_{O_2}$s. The Fermi energy of the material is pinned near the Mn level. Increasing the amount of Mn and Mo does not change this fact as the Mn level lies near the middle of the band gap. Thus, the concentration of electrons in the conduction band ($n$) does not change with $x$. However, the conductivity is experimentally observed to increase with $x$.

The problem becomes particularly noticeable when increasing from $x = 0.05$ to $x = 0.1$ (Figure 5.16). In the $x = 0.1$ sample, the conductivity is nearly $P_{O_2}$ independent over the entire $P_{O_2}$ range. Only at the very lowest $P_{O_2}$ is a slight increase in the conductivity noted. Over most of the $P_{O_2}$ range, this material is almost entirely in the electron plateau regime. However, the conductivity in this plateau increases nearly two orders of magnitude over the $x = 0.05$ sample, while the theoretical electron concentration remains nearly constant.

The conductivity continues to increase and become $P_{O_2}$ independent as $x$ is raised. The $x = 0.3$ sample (Figure 5.18) is observed to become independent of $P_{O_2}$ over the entire range of $P_{O_2}$ with a very high value of conductivity, over an order of magnitude higher than the $x = 0.1$ specimen. While the flattening of the plots can be explained by
the broadening of the electronic plateau with increasing x, the jumps in conductivity with x cannot be explained with the isolated defect model used thus far.

Further evidence of a shift in conduction mechanism with increasing x comes from Figure 5.20. The activation energy of GMMT is shown to decrease dramatically with increasing x (from nearly 1.5 eV in $x = 0.01$ to 0.6 eV in $x = 0.3$). This decrease is inconsistent with a model where the same process is occurring for all values of x. To solve these discrepancies, the isolated defect model must be modified to account for interactions between the transition metal elements (Mo, Mn) at high values of x.

6.3.2.2 Defect Band Formation ($x \geq 0.1$)

It is well known that transition metal elements substituted into oxides interact at high concentration values. As the extended d orbitals overlap, the degenerate electron energy levels split and form narrow “defect bands”. This has been discussed previously in transition metal substituted GT, including Ru [50], Mn [49], and Mo [8]. The electrons (or holes) in these bands form small polarons and move through the band by hopping from one equivalent site to the next. For example, in a Mn “one-electron” defect band, electrons proceed by hopping from Mn$^{3+}$ to Mn$^{4+}$ and vice versa, with the filled sites being Mn$^{3+}$ and empty sites Mn$^{4+}$. As the electrons act as small polarons, this motion is envisioned proceeding by a thermally activated hopping motion represented by,
where \( \sigma_{H,o} \) is a pre-exponential term based on the standard terms for activated motion (see Equation (2.6)), \( N \) is the total number of sites in the defect band, \( c \) is the fraction of these sites that are electrically filled, and \( E_H \) is the activation energy for the hopping process. The conduction is maximized when the band is half occupied, \( c = 0.5 \). This leads to a peak in the conduction profile that is often characteristic of defect band conduction, as emphasized in Figure 6.6. This figure shows the hopping conduction for a band composed of a hypothetical element, \( M \), existing in two valence states, +2 and +3. At \( c = 0 \), the band is empty and all of the \( M \) is +3. If some external influence (\( P_{O_2} \) for example) gradually changes the valence of \( M \) from +3 to +2, \( c \) increases. When \( c = 0.5 \), half of \( M \) is +3, and half is +2, and the conduction is maximized. As more of \( M \) becomes +3, the band depletes and the conduction decreases due to lack of carriers. At \( c = 1 \), all of the \( M \) is +2, and the conduction is again zero as the band is totally full. It should be emphasized that this peak is only observed if the valence distribution of \( M \) actually changes. If the valence distribution remains constant so will the conductivity.
Figure 6.6 Plot of hopping conduction for a one-electron defect band of a hypothetical element M existing in two valence states, +3 and +2. Note the peak in the conduction. The band is full when all of the M is +2, empty when it is all +3.
Another factor that strongly influences the hopping conduction is the migration energy, $E_H$. Very isolated elements will not experience much orbital overlap and will not create very many split energy states. The resultant defect band will therefore be very narrow. The limit, at very low concentrations, is the case of isolated defects discussed above where the dopant elements do not interact at all. As the dopant concentration is increased, the orbital overlap increases, and the levels diverge. The defect band becomes wider. In addition, the energy needed to hop from one dopant element to the next goes down due to the increased interaction between the elements. Eventually, at a high enough concentration, the band may become wide enough to support metallic or semi-metallic behavior where conduction is no longer activated ($E_H = 0$, such as in large polarons). This transition is in fact observed in Mo substituted GT at very high Mo concentrations (> 70%) [8].

The formation of these defect bands at the Mo and Mn levels in the band gap of GMMT are suspected to be the source of the large increases in conductivity seen for high $x$ ($\geq 0.1$). Figure 6.7 shows, schematically, the formation of defect bands in GMMT as a function of increasing $x$. It is expected that band formation occurs at both the Mo and Mn level based on previous work where defect band formation was observed for both Mn substituted GT [49] and Mo substituted GT [8].
Figure 6.7 Schematic of defect band formation in Gd$_2$((Mo$_{1-x}$Mn$_x$)$_x$Ti$_{1-x}$)$_2$O$_{7.5}$ as a function of increasing $x$ at both the Mn and Mo defect levels. Small spheres represent electrons.
Two trends can be expected in terms of defect band conduction with increasing $x$.  

The first is that the bands become wider leading to a decrease in $E_{Hi}$ and increase in level of conduction. In addition, the energy between the levels, $\Delta E$, can be expected to decrease with $x$ as the bands broaden. In the isolated defect case, most of the electrons lie in the Mn levels. As $\Delta E$ decreases however, more electrons will be excited into the Mo levels. This will bring the $c$ term for each band closer to 0.5 (raising the primarily empty Mo band and decreasing the primarily full Mn band) which will further optimize the conductivity. The large jumps in conductivity shown in Figure 5.11 as a function of $x$ can thus be described by the formation of defect bands as shown schematically in Figure 6.7.

The conductivity becomes independent of $P_{O_2}$ because the width of the compensation plateau regime (see Figure 6.4) becomes wider with increasing $x$. Within this regime, the dopant valence distributions are relatively fixed with $P_{O_2}$, and by extension the conductivity (via Equation (6.18)). If $c_{Mn}$ and $c_{Mo}$ are defined as

\[
(6.19) \quad c_{Mn} = \frac{[Mn^I]}{[Mn^I] + [Mn^{\ast}]} \\
(6.20) \quad c_{Mo} = \frac{[Mo^{\ast}]}{[Mo^{\ast}] + [Mo^{\ast\ast}]} 
\]
then a plot such as Figure 6.8 can be constructed. This shows the valence distributions for both Mo and Mn in GMMT with $x = 0.3$ at 1000 °C as a function of $P_{O_2}$ as predicted from the isolated defect model.

Also shown are the corresponding $c(1-c)$ terms relevant for hopping conduction for both Mo and Mn. The $c(1-c)$ terms are relatively independent of $P_{O_2}$ in the plateau regime. The small variations that do exist are exactly opposite in the Mo and Mn $c(1-c)$ terms. That is, as the Mn term increases with increasing $P_{O_2}$, the Mo term decreases by the same amount. Thus, the hopping conductivity will be roughly independent of $P_{O_2}$, as evidenced by the experimental conductivity plots of $x = 0.1$ (Figure 5.16) and $x = 0.3$ (Figure 5.18). It should also be noted that the $c$ terms presented in Figure 6.8 are from the isolated defect case. At $x = 0.3$, one would expect that the distribution of electrons would be more even between Mo and Mn. However, this would not affect the primary conclusion that the $c(1-c)$ term is independent of $P_{O_2}$ in the plateau. Defect band formation in GMMT also explains the trend in activation energy shown in Figure 5.20 with increasing $x$. At $x \geq 0.1$, the activation energy approaches $0.6 - 0.7$ eV, while at lower $x$, the activation energy is well above 1 eV. This drop is believed to be due to the widening defect bands and the decreased hopping activation energy that accompanies it.
Figure 6.8  Plot of both the valence distribution of Mo, Mn in Gd$_2$((Mo$_{1-x}$Mn$_x$)$_2$Ti$_{1-x}$)$_2$O$_{7.6}$ for $x = 0.3$, $y = 0.66$ at 1000 °C (left axis) and the corresponding c(1-c) term for both levels (right axis) as a function of $P_{O_2}$. 
The total conductivity of the GMMT material for \( x > 0.1 \) is the sum of the native conduction mechanisms (such as electrons in the conduction band, holes in the valence band, oxygen vacancies, and oxygen interstitials) and conduction in the defect bands. This can be expressed by the following

\[
\sigma_{\text{total}} = 2\left[ \nu_{\text{Mo}}^{2} \mu_{\text{Mo}} + \nu_{\text{O}}^{2} \mu_{\text{O}} + nq\mu_{n} + pq\mu_{h} \right] + 2N_{\text{Mo}}c_{\text{Mo}}(1 - c_{\text{Mo}}) \frac{\sigma_{\text{Mo}}}{T} \exp \left( \frac{-E_{\text{H,Mo}}}{kT} \right) + N_{\text{Mo}}c_{\text{Mo}}(1 - c_{\text{Mo}}) \frac{\sigma_{\text{Mo}}}{T} \exp \left( \frac{-E_{\text{H,Mo}}}{kT} \right)
\]

where \( N_{\text{Mn}} \) and \( N_{\text{Mo}} \) represent the total amount of Mo and Mn in solid solution. This equation simply represents the bulk portion of the conductivity (see Section 2.2) added to the defect band conductivity in both the Mo and Mn bands (see Equation (6.18)). The Mo band is treated here as a +4/+6 band. That is, \( \text{Mo}^{5+} \) is considered unstable, so that hopping can occur only by successive ionization of Mo from +4 to +6 and vice versa.

While no direct evidence of these valence assumptions was obtained in this thesis, they appear to be the most likely charge states based on their oxide compositions (\( \text{MoO}_{3}, \text{MoO}_{2} \)) under similar conditions of \( P_{02} \) and temperature. Directly isolating these values will be discussed in the “Future Work” chapter.

The concentrations of the above species can all be predicted by the model presented in this thesis. To model the conductivity via Equation (6.21), an estimation of the mobilities is needed and may be obtained from previous reports [49], [78] and are summarized here (see Table 6.1). The unknown values in the conductivity equation are
<table>
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<th>Carrier</th>
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<th>Activation Energy</th>
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</tr>
<tr>
<td>n</td>
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<tr>
<td>p</td>
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<tr>
<td>V₀⁻</td>
<td>1000/T</td>
<td>0.88</td>
</tr>
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</table>

Table 6.1 Values for the carrier mobilities used to model the conductivity of GMMT. From [78] and [49].
the pre-exponentials and activation energies of the defect band terms. The pre-
exponentials will be relatively invariant to temperature, $P_{O_2}$, and compositional changes
since they are fixed by the terms governing diffusive movement (see Equation (2.6)).

Values on the order of 1 to several hundred $Kcm^2V^{-1}s^{-1}$ [49], [80] are possible depending
on the estimations made to make the calculation. The best fits of the GMMT data are
performed with $\sigma_{0,Mn} \approx 10$ and $\sigma_{0,Mo} \approx 15 Kcm^2V^{-1}s^{-1}$.

Figure 6.9 shows the fit obtained for $x = 0.3$. The conductivity predicted by the
defect model concentrations has been shifted to higher $P_{O_2}$ by a factor of $10^8$ to correct
for differences with the experimental data due to possible inaccuracies in the estimations
of the equilibrium constants as discussed above. The free parameters used in the fitting
were the activation energies of the Mo and Mn defect levels. The values that yielded the
best fit were: $E_{a,Mn} = 0.19$ eV and $E_{a,Mo} = 0.22$ eV. This is somewhat lower than
previous values obtained for Mo doped GT at equivalent Mo concentration (10% Mo)
which gave $E_a$ on the order of 0.6 eV. This value was taken directly from the measured
activation energy of the total conduction, however. No attempt was made to take into
account the shifting of the Mo valence state, which is also thermally activated (which
makes the $c(1-c)$ parameter thermally activated in addition to the $E_H$ term). As a result,
the 0.6 eV report may be somewhat elevated.

The conductivity modeling also allows an estimation of the contribution of each
different conduction mechanism. This is shown for $x = 0.3$ at 900 °C in Figure 6.10.

This model predicts that the conductivity in the plateau is carried primarily by conduction

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Figure 6.9  Conductivity data of $x = 0.3$, $y = 0.66$ GMMT as a function of $P_{O_2}$ and $T$. Lines indicate fit from Equation (6.21) using the defect model presented in this work. The activation energies obtained for defect band hopping in the Mo and Mn bands are shown.

$E_H$ (Mn band) = 0.19 eV
$E_H$ (Mo band) = 0.22 eV
Figure 6.10  Conductivity of various defects in $x = 0.3$, $y = 0.66$ GMMT at 900 °C as a function of $P_{O_2}$, including the Mo and Mn defect band contributions.
in the Mo band. It can also be noted that the $P_{O_2}$-independence of the defect band conduction at intermediate $P_{O_2}$ is consistent with the experimentally observed $P_{O_2}$-independent conductivity and results from the fact that the valence distribution of the Mo and Mn are essentially fixed in the plateau region, thereby fixing the $c$ terms and the conductivity.

6.3.2.3 Variation of the Conductivity with $y$

Figure 5.19 shows the conductivity of GMMT with $x = 0.1$ and $y = 0.33$. This can be compared to $x = 0.1$ and $y = 0.66$ shown in Figure 5.16. The $y = 0.33$ material shows an increased conductivity with respect to the $y = 0.66$ material. Under oxidizing conditions, the increase is about $\frac{1}{2}$ order of magnitude. At lower $P_{O_2}$, however, this increase is over an order of magnitude. In addition to the increase in conductivity, the trend with $P_{O_2}$ changes in the $y = 0.33$ material. While in the $y = 0.66$ material, the conductivity is independent of $P_{O_2}$ over the entire $P_{O_2}$ range except the most reducing conditions, the $y = 0.33$ material shows an increase at much higher $P_{O_2}$ with the formation of a second plateau under reducing conditions. Under the most reducing conditions, it’s conductivity also shows an increase.

From the dilute solution defect model, decreasing $y$ tends to increase the level of the electron concentration in the plateau as shown in Figure 6.11. This increase would explain the slightly elevated conduction level under oxidizing environments. The formation of a second plateau under reducing conditions is not predicted based on a
Figure 6.11 Free electron and oxygen vacancy concentration as a function of y and $P_{O_2}$ at 900 °C in $Gd_2((Mo_{1-y}Mn_y)_xTi_{1-x})_2O_{7-δ}$ with $x = 0.1$. 
conduction mechanism controlled solely by free electrons.

It might be argued that the formation of the second plateau is due to a shift in control of conduction from free electrons to oxygen vacancies, which indeed show a plateau under reducing conditions. However, upon inspection Figure 6.11, it can be seen that the oxygen vacancy concentration is depressed upon decreasing $y$. In addition, the border where the two concentrations cross is at a lower $P_{O_2}$ in $y = 1/3$ than in $y = 2/3$, suggesting that a shift to oxygen vacancy conduction would occur at a lower $P_{O_2}$ for lower $y$ values. This is inconsistent with the experimental data which shows the high $P_{O_2}$ plateau ending at a higher $P_{O_2}$ with $y = 1/3$ than in $y = 2/3$.

One factor not incorporated in the defect model is that the replacement of Mn with Mo in GMMT tends to shift the valence distribution of the dopants under reducing conditions. In $y = 0.66$ under reducing conditions, the majority of the Mo is +6 and the Mn is +3. Reducing $y$ to 0.33 leads to the formation of $Mo^{4+}$ and $Mn^{3+}$ under reducing conditions. This shift in valence and redistribution of the dopant concentration leads to an increase in the average radius of the B site upon decreasing $y$ from 0.66 to 0.33 under reducing conditions ($Mo^{6+}_{1/3}Mn^{3+}_{2/3} = 0.626$, $Mo^{4+}_{2/3}Mn^{3+}_{1/3} = 0.648$). As discussed in Chapter 2, a decreasing radius ratio of the A to B site in the pyrochlore structure has been observed to increase the internal oxygen vacancy concentration as the material is driven towards the defect fluorite phase. This elevation in the vacancy concentration would effectively raise the Frenkel (stoichiometric) point of the material to a higher value. This
would in turn decrease the width of the plateau in the conduction with $P_{O_2}$. This would mean that the second plateau observed in the $y = 0.33$ material would in fact occur in the $y = 0.66$ material at a lower $P_{O_2}$. Raising the background vacancy concentration in the $y = 0.33$ material shifts the plateau such that it appears in the experimental range of $P_{O_2}$.

An alternative mechanism might be the formation of $\text{Mn}^{+2}$ in the Mo rich material under reducing conditions. As the Fermi level of the $y = 0.33$ material is higher than the $y = 0.66$ material, if a $\text{Mn}^{2+/3+}$ level exists above the $\text{Mn}^{3+/4+}$ level but below the Mo level, it could populate in the $y = 0.33$ material while remaining empty in the $y = 0.66$ material. The filling of these sites could potentially lead to a second plateau under reducing conditions. This mechanism could be checked by experimentally verifying the valence state distributions of the dopants as discussed in Chapter 8, "Future Work".

Though the above argument was stated in terms of the dilute defect model, the same principle would hold if the material were controlled primarily by defect band hopping. In this case, the high $P_{O_2}$ plateau would be due primarily to hopping in one of the defect bands, most likely the Mo band as it has a higher concentration at lower $y$. The slight increase in conductivity at high $P_{O_2}$ with lowering $y$ would be due to the lowering of $E_H$ in the Mo band experienced as the concentration of Mo was increased. The same argument as the case of the dilute defect model would hold under reducing conditions. That is, the elevated vacancy concentration due to the lowered radius ratio would lead to a shift to vacancy conduction at a much higher $P_{O_2}$ as $y$ was reduced.
6.3.2.4 Electronic Conductivity via Electronic Blocking Cell

The final experiment performed in evaluating GMMT as a mixed conductor was to separate the ionic and electronic conductivity. This was accomplished with the electronic blocking cell discussed in Section 4.3.2.

The desired result, the electronic transference number, is shown for \( x = 0.1 \) GMMT in Figure 5.27. The experimentally obtained value, about 0.9 to 0.95, indicates that the material is indeed a primarily electronic conductor at all temperatures for \( P_{O_2} \geq 10^{-4} \) atm. This confirms the discussion in the sections above, where the \( x = 0.1 \) material was shown to be an electronic conductor, primarily by conduction in the Mn and Mo defect bands. The ionic conductivity is then on the order of \( 10^{-3} - 10^{-2} \) S/cm for \( x = 0.1 \).

The dependence of the ionic conductivity \( (G_{\text{warburg}}) \) on \( P_{O_2} \) (Figure 5.26) shows an interesting positive slope at higher temperature. Figure 6.12 shows a plot of the concentrations of the ionic species in \( x = 0.1 \) GMMT at 900 °C as a function of \( P_{O_2} \). The
Figure 6.12 Concentration of ionic species in $x = 0.1$, $y = 0.66$ GMMT as a function of $P_{O_2}$ at 900 °C. The shaded region is the suspected range of the blocking cell experiment. As discussed in the text, this does not match the exact experimental $P_{O_2}$ due to possible inaccurate equilibrium constants in the defect model.
shaded region shows the $P_{O_2}$ over which the blocking cell measurements were made. This does not correspond to the exact experimental $P_{O_2}$ range because of the possible inaccuracies in the equilibrium constants in the defect model. As discussed above, this can shift the $P_{O_2}$ scale of the defect plots.

After inspecting Figure 6.12, it is apparent that the oxygen interstitials have a positive slope with $P_{O_2}$ in the experimental range. It should be noted, on the other hand, that all previous ionic conduction results for gadolinium titanate pyrochlores supported an oxygen vacancy conduction mechanism in both oxidizing and reducing environments, including the solid solution systems Mn GT [54] and Mo GT [8]. Even when oxygen vacancies are at a lower concentration than interstitials under oxidizing environments, the mobility advantage of vacancies over interstitials often gives them a higher conduction level than that of the interstitials. In GMMT, however, the difference in concentration is rather extreme, with the interstitials being up to $10^{10}$ times more concentrated than the vacancies (see Figure 6.12). This is a considerably larger difference than that for typical GT-based compounds (see undoped GT in Figure 3.2 for example). Thus the elevated interstitial concentration in GMMT could very well lead to interstitial conduction, overcoming the mobility advantage of the vacancies. The slope seen in Figure 5.26 of $+1/4$, is lower than the predicted slope of the interstitial concentration, which is $+1/2$. This would be consistent with the material entering the regime where the interstitials are starting to saturate at high $P_{O_2}$. The measured slope would then be $< 1/2$ as the curve leveled off. However, the other feature of Figure 5.26 is the gradual flattening of the
curves as the temperature decreased. This could point to the fact that, instead of nearing the plateau regime in interstitials, the material is still well into the regime where the interstitial slope is 1/2 but is experiencing a mixed ionic conduction due to both vacancies and interstitials. At 1000 °C, the material is primarily interstitial controlled but experiencing some vacancy movement. Since the vacancy concentration is coming up with a slope of -1/2 while the interstitials decline with a slope of +1/2 as P O_2 is decreased, the measured experimental slope is somewhat less than +1/2, but still positive. If the activation energy of interstitial movement is greater than vacancy motion, as the temperature is decreased, the material will move into a regime of vacancy control. Thus, the measured slope decreases, becoming essentially flat at 700 °C.

Since these measurements were made on the x = 0.1 GMMT material, the ionic conduction in the best conductor, x = 0.3, remains undetermined. From Figure 6.5, it can be seen that the ionic components does not appear to change with x in the region where the slope is +/- 1/2 (if the vacancy concentration is fixed, so is the interstitial by Equation (3.2)). This fact would suggest that the ionic conductivity of the x = 0.3 material would be similar to that of the x = 0.1 material.

The other interesting result of the electronic blocking cell was the observation of a high frequency arc in the impedance spectra of the cell (see response 2 in Figure 5.22). As discussed in Chapter 5, this arc could only be attributed to either the grain boundary resistance in the GMMT portion of the cell or to the internal interface between GMMT and Ca doped GT. It is unlikely that the arc is the result of the grain boundary resistance in GMMT for several reasons. First, many other samples of GMMT were made under
similar conditions with no evidence of such a large grain boundary resistance. Second, the dependence of this response on DC voltage as shown in Figure 5.23 is inconsistent with a grain boundary response. While a grain boundary response may be dependent on DC bias, it is unlikely to change by the amounts shown in Figure 5.23 because the voltage is distributed over so many individual boundaries. Finally, the arc is virtually a pure semi-circle with very little depression beneath the real axis. In a grain boundary response, a larger depression might be expected as the response is distributed over many elements (boundaries) in real space.

This leads to the conclusion that the large arc is due to the internal interface. This is very interesting as it implies the existence of an ionic junction similar to a pn junction in semiconductors. This means that some type of internal junction field may have formed that hinders the motion of ions in one direction and promotes it in the other direction under a DC bias (similar to reverse and forward biasing a pn junction). The small angular depression of the impedance spectra further indicates that this response is indeed due to only a single large junction.

The exponential change in the response with time (Figure 5.23) indicates that the change in this response with DC bias could be diffusive in nature. The time scale of the bias response and equilibration (on the order of hundreds to thousands of seconds) lends further credence to the idea that this is some sort of ionic junction, as ions would be expected to have a higher time constant associated with diffusion.
This response needs to be explored further before any definitive statement can be made about the mechanisms. Chapter 8, “Future Work” will present some possible ideas that might be used in this respect.

6.3.3 Review of Goals: Comparison to Mo Substituted GT and Mn Substituted GT

It is useful to note the differences between Mo substituted GT, Mn substituted GT, and GMMT at similar concentration values. Figure 6.13 shows the plots of the conductivity as a function of P\textsubscript{O\textsubscript{2}} and T for 10\% Mo substituted GT (Mo GT), 10\% Mn substituted GT (Mn GT), and x = 0.3 GMMT (which has 10\% Mo and 20\% Mn). The 10\% Mn substituted GT has a lower concentration of Mn than the x = 0.3 GMMT, which has 20\% Mn. This is the highest Mn concentration used in the past studies.

The x = 0.3 GMMT shows significantly higher total conductivity in oxidizing environments than either Mo GT or Mn GT. This is the result of two factors. The GMMT material enjoys the high conductivity offered by the defect band formation in Mo and Mn defect levels. However, the interplay of these elements compensating each other’s valence changes stabilizes this conductivity to a much higher P\textsubscript{O\textsubscript{2}}. The drop off experienced by the Mo material at higher P\textsubscript{O\textsubscript{2}} due to Mo oxidation to +6 is suppressed in
Figure 6.13  Conductivity of 10% Mn GT and 10% Mo GT compared against $x = 0.3$, $y = 0.66$ GMMT.
GMMT by the reduction of Mn to 3+. This was exactly the goal of this work as stated in Chapter 2, to stabilize the conductivity of the Mo doped GT material to oxidizing environments. In addition, if the conductivity of the Mo doped GT and GMMT are compared under reducing conditions, it is evident that the values are nearly identical. This is further evidence that the conductivity of the Mo doped GT has been stabilized to higher P$_{O_2}$ by addition of Mn.

Figure 6.14 shows a comparison of the concentration of Mo$^{6+}$ and O$_{i}^{--}$ for 10% Mo GT and $x = 0.3$ GMMT as a function of P$_{O_2}$ at 800 °C. In the 10% Mo GT, the elevated oxygen interstitial concentration at high P$_{O_2}$ resulted from the Mo oxidation to +6. The conduction was though to be primarily through a Mo defect band, which emptied as Mo shifted to +6 (thereby depressing $\sigma_{H}$ through the c(1-c) term). Figure 6.14 shows that the addition of Mn (GMMT) results in the full oxidation of Mo to +6 at a much lower P$_{O_2}$ while suppressing the oxygen interstitial concentration by several orders of magnitude. The oxygen interstitial saturation P$_{O_2}$ point is nearly five orders of magnitude higher than in the Mo GT. Thus, the decline in conductivity evidenced in the 10% Mo GT is not seen in the experimental P$_{O_2}$ range in GMMT (for high x).

The experimental results presented in Figure 6.13 are a confirmation of the theoretical predictions presented in Chapter 2. Figure 6.14 is a graphical representation of the discussion in Section 2.3.4. The addition of Mn indeed stabilizes the GMMT
Figure 6.14 Comparison of the Mo\(^{6+}\) and O\(_2\)\(^\prime\) concentrations as a function of P\(_{O_2}\) for 10% Mo substituted GT and x = 0.3, y = 0.66 GMMT at 800 °C.
material to a much higher $P_{O_2}$, thereby avoiding the conductivity declines and phase decompositions characteristic of Mo substituted GT in oxidizing environments. Taking into account the high ionic conduction value of GMMT (~ $10^{-3} - 10^{-2}$ S/cm), this work has largely been successful in creating a new pyrochlore material with a high mixed ionic and electronic conduction value under cathodic conditions.

It should also be emphasized here that the modeling and characterization methods used in this thesis have been very successful in predicting and controlling conduction in a very complex oxide system with five elements. The same basic modeling technique and ideas could, in principle, be applied to a wide variety of complex systems to help other researchers predict and control materials properties based on microscopic defect chemistry.

The conductivity values obtained here (approaching 1 S/cm) are still not high enough to compete with other leading mixed conductor candidates such as the lanthanum cobalt perovskites, however. These materials can exhibit conductivities greater than 100 S/cm with an ionic component as high as $10^{-1}$ S/cm. However, the author believes that further refinement of GMMT and related pyrochlore materials could lead to increased mixed conductivities. Ideas concerning this topic are presented in Chapter 8 – “Future Work”.

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6.4 Comparison of GMMT to State of the Art SOFC Cathode Materials

While this work has been successful in achieving the stated goals of extending the reasonably high mixed ionic and electronic conductivities in GT based pyrochlores to oxidizing environments, ultimately these materials must be compared to the current “state-of-the-art” MIEC materials. As this thesis focused on the application of MIEC materials as fuel cell electrodes (particularly the cathode), GMMT will be compared against the current fuel cell cathode materials, (La,Sr)MnO₃ (LSM) and (La,Sr)(Co, Fe)O₃ (LSCF).

Table 6.2 shows this comparison, as well as the parameters desired for the “ideal” fuel cell cathode. With respect to LSM, GMMT has a much higher ionic conductivity, but has a lower electronic conductivity. LSM is used in today’s SOFC because of its compatibility with ZrO₂. The GMMT would be used in a monolithic pyrochlore fuel cell and its stability with ZrO₂ would not be a primary concern.
Table 6.2 Comparison of $x = 0.3$ GMMT with other state of the art SOFC cathodes and the “ideal” cathode material \cite{3}. Several key parameters are compared. $(La,Sr)MnO_3$ and $(La,Sr)(Co,Fe)O_3$ data taken from \cite{23} and other sources.
Compared to LSCF, GMMT has a considerably depressed ionic and electronic conductivity. The main drawback of LSCF is its very high reactivity with respect to ZrO$_2$. The LSCF material begins to approach the ideal SOFC cathode, except in its stability with respect to the electrolyte. It can be seen that GMMT, while breaking new ground for the pyrochlore system, requires improvement when compared to the ideal cathode material. Several potential options for continuing the work on GMMT to achieve higher conduction values are presented in the “Future Work” chapter.

One area that was not explored for GMMT was its catalytic properties with respect to oxygen. This area needs to be explored. Ideas concerning how this could be done are presented in the “Future Work” chapter.
7 CONCLUSIONS

The pyrochlore material Gd$_2$((Mo$_{1-x}$Mn$_x$)$_y$Ti$_{1-y}$)$_2$O$_{7.8}$ (GMMT) was studied to evaluate the joint effects of x and y on its mixed ionic and electronic conduction (MIEC) properties. Particular emphasis was placed on its mixed conductivity under oxidizing environments. High mixed conductivities under oxidizing environments are very desirable in applications such as fuel cell cathodes. The conduction properties of the material were analyzed with the aid of a detailed microscopic defect and conduction model. This model allowed the identification of the dominant charge carriers as well as conclusions with respect to the dominant conduction mechanisms.

The electrode impedance of Pt electrodes on (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ was studied under both oxidizing and reducing atmospheres. Models describing the controlling kinetic steps were derived according to the theory presented in [13].

7.1 Properties of Gd$_2$((Mo$_{1-x}$Mn$_x$)$_y$Ti$_{1-y}$)$_2$O$_{7.8}$

This section summarizes the structure, conductivity, and defect modeling of the GMMT materials synthesized in this study. Compositions were made with $x = 0.01, 0.1, 0.2, and 0.3$ with $y = 0.66$. In addition, the composition $x = 0.1, y = 0.33$ was studied.

1. All of the compositions were of the pyrochlore ($x = 0.01$ to 0.33, $y = 0.66$) phase in air up to the highest temperature used in this study, 1000 °C.
2. The conduction of GMMT in oxidizing environments increased by over four orders of magnitude as $x$ increased from 0.01 to $x = 0.3$ ($y = 0.66$) (for example, at 900 °C in air, it increased from about $10^{-5}$ S/cm to 0.12 S/cm). The highest conductivity obtained in this study was for $x = 0.3$, $y = 0.66$ at 1000 °C, $\sigma = 0.12$ S/cm (the conductivity was $P_{O_2}$ independent). This is the highest conductivity obtained in a pyrochlore material in oxidizing environments apart from a Ru, Bi co-doped compound synthesized by [42]. Considering the cost of the Ru material, it is reasonable to propose this material as the most attractive candidate for mixed conducting applications in oxidizing environments (see below for the electronic and ionic component of the conductivity).

3. The conductivity as a function of $P_{O_2}$ and temperature was recorded and compared to a defect model created utilizing an approach enabling the analytical solution of the defect electroneutrality equation (see Chapter 3) used to identify the microscopic conduction mechanisms. At $x \leq 0.05$, the material behaved according to a dilute solution defect model. The conduction was found to be primarily electronic, with a possible contribution from vacancy conduction under reducing conditions. The main characteristic feature of the conductivity dependence on $P_{O_2}$ was a $P_{O_2}$ independent plateau regime at intermediate $P_{O_2}$. The activation energy of the conduction in this plateau was 1.46 eV for the $x = 0.01$ and 1.31 eV for the $x = 0.05$. This activation energy was suspected to arise primarily from ionization of electrons from the Mn defect levels to the
conduction band. The defect equilibrium under reducing and oxidizing conditions was used to calculate a reduction constant as

\[ K_r = 10^{77}(\text{atm}^{1/2}\text{cm}^{-9})\exp(-6.4\text{eV/kT}) \] and a Frenkel constant of

\[ K_f = 2.6\times10^{52}(\text{cm}^{-6})\exp(-2.9\text{eV/kT}). \]

4. For higher values of \( x \) (\( \geq 0.1 \)), the material exhibited sharp jumps in conductivity with \( x \) (up to several orders of magnitude) under oxidizing environments. In addition, the width of the conductivity plateau discussed above broadened so that the conductivity was independent of \( P_{O_2} \) over the entire experimental range. This was accompanied by a drop in the activation energy down to 0.66 eV for the \( x = 0.3 \) material. These trends were explained by the formation of defect bands at the Mo and Mn levels in the band gap of the Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}. These bands support a hopping type of conduction that increased in magnitude and became more weakly activated as \( x \) was increased. A conductivity model based on the defect model described above was used to explain and fit the conductivity properties described above for high values of \( x \). The fit yielded values for the hopping energies of electrons in the Mo band (0.22 eV) and Mn band (0.19 eV) for \( x = 0.3 \).

5. The ionic portion of the primarily electronic GMMT was isolated for \( x = 0.1, y = 0.66 \) using an electronic blocking cell. The electronic transference number was found to be between 0.9 and 0.95 in oxidizing environments (\( > 10^{-4} \) atm). The overall level of ionic conductivity was on the order of \( 10^{-3} - 10^{-2} \) S/cm at 900 °C.
The ionic conductivity was also found to have a positive dependence on $P_{O_2}$ implying, based on the defect model, oxygen interstitial movement. This is contrary to conclusions in previous work on other Gd$_2$Ti$_2$O$_7$ based materials, which supported predominant oxygen vacancy movement, even under oxidizing environments.

6. A key goal of this work was to extend the mixed conduction properties of the Mo doped Gd$_2$Ti$_2$O$_7$ into oxidizing environments. This work was very successful in meeting this goal. For equivalent Mo concentrations at $x = 0.3$, $y = 0.66$ GMMT and 10% Mo doped Gd$_2$Ti$_2$O$_7$, the conductivity of the GMMT material was roughly two orders of magnitude higher than the Mo doped Gd$_2$Ti$_2$O$_7$ material in air. This is a confirmation of the original hypothesis of this thesis as stated in Chapter 1 and 2.

7.2 Electrode Impedance

The electrode conductance of Pt electrodes on (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ (Ca doped GT) was monitored as a function of $P_{O_2}$ ($0.21$ atm > $P_{O_2}$ > $10^{-25}$ atm) and temperature ($600$ °C < $T$ < $1010$ °C) for $x = 0.02$ and $0.1$. The following features were observed:

1. The overall electrode conductance ($10^{-4}$ to $10^{-1}$ S) was very dependent on both $P_{O_2}$ and $T$ for both compositions. The maximum conductance was on the order or 0.1 S and occurred in the most oxidizing environment (0.21 atm) and highest
temperature (1000 °C). The minimum conductance occurred at intermediate 
\( P_{O_2} \) (at 600 °C) where the CO concentration of the CO/CO\(_2\) gas used to impart 
the lower \( P_{O_2} \) values was the lowest. The minimum in both cases was on the 
order of \( 10^{-4} \) S.

2. The slope of a log-log plot of the electrode conductance vs. \( P_{O_2} \) was +1/2 in 
oxidizing environments \( (P_{O_2} > 10^{-5} \) atm) and high temperature \( (T > 700 \) °C). 
This behavior was attributed to a rate limiting situation where surface diffusion 
of adsorbed O atoms on the Pt surface control the overall electrode reaction.

3. At lower temperature, the electrode conductance of the \( x = 0.1 \) Ca doped GT in 
oxidizing environments became roughly independent of \( P_{O_2} \). This was 
attributed to a shift in the rate limiting mechanism to one controlled by the 
dissociative adsorption of \( O_2(g) \) on the Pt surface. The conductance of the \( x = 
0.02 \) Ca doped GT electrodes did not experience this shift, being controlled by 
surface diffusion down to 600 °C in oxidizing environments. This could have 
been a result of finer Pt particles in the \( x = 0.1 \) electrode microstructure, which 
would lead to a situation where surface diffusion was less important.

4. In reducing conditions, the electrode conductance of both samples experienced a 
minimum followed by a increase with decreasing \( P_{O_2} \). The reducing 
atmospheres were imparted by varying CO/CO\(_2\) mixtures. The minimum in the 
conductance in both cases corresponded to the lowest CO concentration. The 
slope of the log-log plot of electrode conductance vs. \( P_{O_2} \) was \(-1/4\) for the \( x = \)
0.02 Ca doped GT and $-1/6$ for the $x = 0.1$ Ca doped. Though no detailed mechanism was presented for the electrode conductance under reducing conditions, from the dependence of the electrode conductance on the CO concentration, it seemed clear that the interaction of the CO with the Pt was involved.
8 FUTURE WORK

1. The conductivity of Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7.5}$ was only measured up to $x = 0.3$, $y = 0.66$. Further increases in the total conductivity may be obtained by increasing $x$. The end member Gd$_2$(Mo$_{1/3}$Mn$_{2/3}$)$_2$O$_7$ has a A site to B site radius ratio (RR) of 1.67 (assuming Mo is 6+ and Mn is 3+, the most likely combination under oxidizing environments), well within the pyrochlore limits ($1.46 < RR < 1.8$). Increasing $x$ should increase the contribution of defect band hopping in the material by lowering the hopping activation energy. This should lead to further increases in the total conductivity, which may bring the material to levels of conductivity more comparable to the perovskites (e.g. (La, Sr)(Co, Fe)O$_3$). Emphasis would need to be placed on identifying the regions of pyrochlore stability with respect to P$_{O_2}$.

2. Further optimization of the conductivity may also be obtained by further investigation of the effect of varying $y$ in Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7.5}$. There was some suggestion of increases in conductivity under both oxidizing and reducing conditions with decreasing $y$. However, it is expected that the stability of the material will decrease as $y$ approaches 0 (as evidenced by previous work on the $y = 0$ end member, Mo doped GT). A detailed study of the stability and conductivity of the material with variations in $y$ may result in a further optimization of the conductivity properties of GMMT.
3. Electronic blocking cell measurements could be made on more compositions to
isolate the ionic conductivity as a function of concentration. This would provide an
exact measure of the mixed ionic and electronic conduction value of each
composition. In addition, comparison of these results with the defect model may shed
further light on the evidence of oxygen interstitial conduction presented in this thesis.

4. The defect model used extensively in this thesis relied on educated guesses as to the
exact valence states of the Mo and Mn in the material. A direct experimental
confirmation of the predicted states would lend further credibility to the model.
Finding a technique to isolate the valence of each element independently in GMMT
would be extremely difficult as most techniques yield only an average valence of the
site (e.g. the B site in GMMT). Investigation into the various techniques used to
perform valence state measurements (e.g. iodometric titration, magnetic based
techniques) might yield a method to isolate the Mo and Mn valence states.

5. The conductivity measurements indicated that ionic conduction may dominate
\( \text{Gd}_2((\text{Mo}_{1-y}\text{Mn}_y)_{x}\text{Ti}_{1-x})_2\text{O}_{7.8} \) under reducing conditions for lower values of \( x \) (< 0.05)
and \( y \) (\( x = 0.1, y = 0.33 \)). This should be confirmed experimentally by taking
transference number measurements in the \( P_{O_2} \) ranges in question.

6. The defect model for high values of \( x \) in \( \text{Gd}_2((\text{Mo}_{1-y}\text{Mn}_y)_{x}\text{Ti}_{1-x})_2\text{O}_{7.8} \) (\( x = 0.3 \) for
example) indicated the domination of defect band hopping conduction. While a
successful model of the data was presented, the conductivity in the experimental \( P_{O_2} \)
range was independent of \( P_{O_2} \). Some of the more interesting features of the model
(such as the increase in conductivity under very reducing conditions) could potentially be observed by increasing the temperature of the measurements. At elevated temperatures, the plateau region will shrink, perhaps bringing some of the regions with distinctive trends in the conductivity with $P_{O_2}$ into the experimental range.

7. The catalytic properties of $\text{Gd}_2((\text{Mo}_{1-y}\text{Mn}_y)_x\text{Ti}_{1-x})_2\text{O}_{7.6}$ with respect to oxygen adsorption and dissociation need to be explored to predict its usefulness as a fuel cell cathode. This type of measurements could be made by $^{18}$O exchange measurements combined with SIMS measurements or relaxation methods. The key parameter to monitor would be the surface exchange coefficient, $k_s$.

8. The electronic blocking cell employed in this thesis showed a distinctive response in it’s AC impedance spectra suggesting the formation of an ionic junction at the internal interface between $\text{Gd}_2((\text{Mo}_{1-y}\text{Mn}_y)_x\text{Ti}_{1-x})_2\text{O}_{7.6}$ and $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$. Further investigation of this phenomena could be made. The key effects to monitor would be the variation of the junction resistance and capacitance as a function of DC bias. The standard theoretical predictions of a semiconducting junction could be expanded upon to determine key parameters about the junction (e.g. depletion width, barrier height, etc.).

9. The measurements of the electrode kinetics of Pt electrodes on $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ indicated that the microstructure of the electrode was important in determining the rate limiting mechanism of the kinetics. This could be confirmed by doing the
measurements again and paying especial attention to the microstructure of the electrodes with various microscopic techniques such as SEM or TEM.

10. The final measure of the utility of Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7.5}$ and other pyrochlore materials would rest in their performance in applications of interest, especially the monolithic pyrochlore fuel cell. Gd$_2$((Mo$_{1-y}$Mn$_y$)$_x$Ti$_{1-x}$)$_2$O$_{7.5}$ may be an adequate enough cathode material such that a cell could be constructed with (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ as the electrolyte and Gd$_2$(Ti$_{1-x}$Mo$_x$)$_2$O$_7$ as the anode. The utility of this structure as a fuel cell could be evaluated with standard DC i-V measurements under a P$_{O_2}$ gradient. AC impedance measurements could assist in determining the benefit of using mixed conductors as electrodes compared to metallic electrodes. One would also want to monitor any benefits in terms of chemical and thermal stability that such a cell would offer.
9 APPENDIX A: CITRATE MIX RECIPES

This Appendix lists recipes used to create the cation stock solutions used to prepare powders of $\text{Gd}_2((\text{Mo}_{1.2}\text{Mn}_y)_{x}\text{Ti}_{1-x})_2\text{O}_{7.5}$ via the “citrate” process (Section 4.1.1).

**Gd Stock Solution**

- 300 grams of Gd(NO$_3$)$_3$
- 900 ml of DI water
- 160 ml of NH$_4$OH
- 360 grams of Citric acid (anhydrous)
- 425 ml of Ethylene glycol

Gd(NO$_3$)$_3$ was dissolved in DI water. NH$_4$OH was added to precipitate Gd(OH)$_3$. The pH was checked with pH paper. If the pH was less than 10, more NH$_4$OH was added until it was slightly over 10. The solution was then filtered through a Buchner funnel. The resulting white cake of Gd(OH)$_3$ was washed continually over the funnel with DI water for 1-2 hours. The pH of the water draining through the funnel was checked with pH paper to ensure it was around 7. At this point, the cake was washed with isopropyl alcohol for another 0.5 to 1 hour. The cake of Gd(OH)$_3$ was set aside. Citric acid was dissolved in the ethylene glycol very slowly over very low heat in a separate beaker. Finally, the Gd(OH)$_3$ was dissolved in the citric acid solution. This solution was heated...
to about 110 °C, stirring constantly, for several hours to ensure complete mixing. The solution was dripped filtered into a plastic storage bottle and stored. The resulting clear solution was stable over a period of many months to years.

**Ti Stock Solution**

225 ml of Titanium Isopropoxide  
400 grams of Citric acid (anhydrous)  
500 ml Ethylene Glycol

Titanium isopropoxide was dissolved into ethylene glycol over very low heat. Citric acid was then slowly added to the solution. This mixture was heated to 100 °C and stirred several hours to ensure complete mixing. The solution was then dripped filtered and stored in a plastic jug. The resulting off-yellow solution was stable over months to years.

**Mo Stock Solution**

40 grams of MoCl₅  
260 grams of Citric acid  
400 ml of Ethylene Glycol

Citric acid was slowly dissolved into ethylene glycol over low heat (60 °C). MoCl₅ was then added to the solution while stirring vigorously. As a warning, MoCl₅ is a rather volatile and “dusty” material. This experiment should be performed in a hood while
wearing a breathing mask. The solution was stirred vigorously over high heat (100 °C) for 3-4 hours. The resulting very dark green (almost black) solution was stored in a plastic jug. The solution was stable over a period of months to years.

**Mn Stock Solution**

100 grams of Mn(NO₃)₂
120 grams of Citric acid (anhydrous)
150 ml of Ethylene Glycol

Citric acid and ethylene glycol were dissolved in a very large beaker (2000 ml). Without heating, Mn(NO₃)₂ was added very slowly. After it had dissolved, the solution was heated extremely slowly. After a short period of time, the nitrate group of the Mn began to react and boil off violently (hence the need for the oversized beaker). After the reaction, the solution was heated to over 100 °C and stirred for 0.5 to 1 hours to ensure complete mixing and evaporation of the nitrates. The solution was dripped filtered and stored in a plastic jug. The resulting dark red solution was stable over a period of months.
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