MIXED IONIC-ELECTRONIC CONDUCTION IN RARE EARTH TITANATE/ZIRCONATE PYROCHLore COMPOUNDS

by

Steve Andrew Kramer

B.S. Ceramic Engineering, University of Washington, Seattle (1987)
M.S. Ceramic Engineering, University of Illinois, Urbana (1989)

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Signature of Author

Department of Materials Science and Engineering, January 7, 1994

Certified by

Professor Harry L. Tuller
Thesis Supervisor

Accepted by

Carl V. Thompson II
Professor of Electronic Materials Chair, Departmental Committee on Graduate Students
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ABSTRACT

Electrical conductivity measurements have been performed on the pyrochlore compositions Gd$_2$Ti$_2$O$_7$, (GT), Y$_2$Ti$_2$O$_7$, (YT), Sm$_2$Ti$_2$O$_7$, (ST), Gd$_2$(Zr$_{0.25}$Ti$_{0.75}$)O$_7$ (GZT25) and La$_2$Zr$_2$O$_7$, (LZ), as a function of temperature, oxygen fugacity and aliovalent dopant concentration. A variety of "A" site (Ca, Sr, Mg, K), and "B" site (Al) acceptor dopants were incorporated substitutionally into the host A$_2$B$_2$O$_7$ lattice. Both the magnitude and type of conduction (ionic and/or electronic) were found to be influenced by dopant size, effective charge, site location ("A" or "B" cation sublattice) and net dopant density. For the "A" site Ca doped titanates, (GT, YT, ST), a concentration dependent ionic and electronic conductivity was observed. In (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$, the ionic conductivity $\sigma_i$ increased by over 2 1/2 orders of magnitude with increasing $x$ reaching a maximum value of 5x10$^{-2}$ S/cm at 1000°C and x=0.10. This value represents the highest ionic conductivity reported to date for a titanate based material. Accompanying the increase in $\sigma_i$ was a corresponding decrease in ionic activation energy E$_i$ which dropped from 0.94 to 0.63 eV in the composition range of x=0.00 to x=0.02. Similar effects were also observed in Ca doped ST and YT with the pre-exponential constant for ionic conduction, $\sigma_i$$^0$, also showing a steady increase.

The increase in $\sigma_i$ and decrease in E$_i$ was evident for "B" site Al doping (e.g., Al"Ti"), but valid only up to a doping level of 1.0 mole%. At higher dopant levels, $\sigma_i$ dropped sharply when the solubility limit was exceeded, as confirmed by x-ray diffraction lattice parameter measurements.

The effects of dopant-host size mismatch were examined by selecting the dopants Mg(r=0.89 Å), Ca(r=1.12 Å), Sr(r=1.25 Å), and K(r=1.51 Å) with a range of radii. Cation formulations were based on "A" site substitution with concentrations ranging from 0.0 to 10.0 mole%. In ST and GT, a well defined maximum in $\sigma_i$ vs. normalized radius ratio (r$_{\text{dopant}}$/r$_{\text{host}}$) was obtained with the
highest ionic conductivity found for the dopant with the smallest dopant-host size mismatch. Accompanying the increase in $r_{\text{dopant}}/r_{\text{host}}$ ratio, was a corresponding increase in ionic activation energy. We explain these results in terms of elastic strain energy which is an important component of the dopant-vacancy association energy. This term is minimized with a small size mismatch between host and dopant.

In similar fashion, acceptor doping in $\text{La}_2\text{Zr}_2\text{O}_7$ (LZ), and $\text{Gd}_2(\text{Zr}_{0.25}\text{Ti}_{0.75})_2\text{O}_7$ (GZT25), resulted in an increase in ionic conductivity. For Sr doped $(\text{La}_{1-x}\text{Sr}_x)_2\text{Zr}_2\text{O}_7$ both the pre-exponential and activation energy increased with increasing acceptor concentration with the increase in pre-exponential factor outweighing the increase in activation energy. For the pyrochlore solid solution GZT25, acceptor dopants were used to assist in extracting quantitative information regarding intrinsic ionic disorder. By comparing activation energies from the doped and undoped materials, a value for the Frenkel activation energy of $E_F=0.44 \text{ eV}$ (compared to 0.24 eV for GZT30) was obtained consistent with the expectation that intrinsic structural disorder increases with Zr in $\text{Gd}_2(\text{Zr}_{1-x}\text{Ti}_x)_2\text{O}_7$.

A primary objective of this work was to predict and control conditions under which pyrochlore materials exhibit mixed ionic-electronic conduction (MIEC). With the aid of a defect chemical model, explicit expressions for the ionic conductivity $\sigma_i$, electrolytic domain boundary positions ($P_n$,$P_p$) and domain boundary width ($P_D/P_n$) were derived under the limiting conditions of (a) intrinsic frenal disorder, (b) unassociated acceptor doping, and (c) associated acceptor doping. Trends for $\sigma_i$, $P_n$, $P_p$, and $P_D/P_n$ were evaluated for a variety of titanate and zirconate based pyrochlore compositions.

A final goal of this thesis was to experimentally measure mixed ionic-electronic conduction (MIEC) in a prototype material using a novel short circuit current method recently proposed by I. Riess. Preliminary measurements on $\text{Gd}_2\text{Ti}_2\text{O}_7$ with 0.25 mole% Ca demonstrated the viability of this method for the first time.
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1 INTRODUCTION

1.1 Purpose of Research

Ever since the pioneering work of Nernst in 1899 [1], solid oxides exhibiting high oxygen-ion conductivity have been the subject of numerous theoretical and experimental studies. Suitable materials have been successfully utilized in a variety of electrochemical applications including automotive oxygen sensors, sensors for combustion control, oxygen separation membranes, heating elements in high temperature furnaces and solid oxide fuel cells (SOFC) [2-5]. Still, there remains a demand for alternative oxygen ion and mixed ionic-electronic conductors with improved properties and enhanced structure-property relations. It is the purpose of this thesis to examine the oxygen ion and mixed ionic-electronic (MIEC) conduction of $A_2B_2O_7$ pyrochlore compounds. Specifically, it is the objective of this thesis to examine how defect properties and defect interactions control mass transport in several rare-earth titanate and zirconate based systems.

The rare-earth pyrochlores $Gd_2Ti_2O_7$, (GT), $Y_2Ti_2O_7$, (YT), $Sm_2Ti_2O_7$, (ST), $Gd_2(Ti_{0.75}Zr_{0.25})_2O_7$ (GZT25), and $La_2Zr_2O_7$, (LZ), were chosen for this study. These systems were selected for several reasons. First, while the structure-property relationship in "intrinsic" pyrochlores have been examined in some detail [6,7,8], few systematic studies have been performed on "extrinsic" doping and mass transport in ternary compounds. Highly ordered pyrochlores such as GT, YT, ST, and LZ are extrinsic in nature and thereby suitable for study with a variety of dopant substitutions. Mono, di or tri-valent acceptor dopants can be incorporated substitutionally into the host $A_2^{3+}B_2^{4+}O_7$ lattice thus providing an
excellent opportunity to study combined effects of dopant size, charge, and site location (either "A" or "B" cation sublattice) on the transport properties in ternary compounds. Secondly, certain titanate-zirconate pyrochlore solid solutions such as (GZT) and (YZT), contain substantial "intrinsic" structural disorder but still are susceptible to extrinsic aliovalent dopants. For example, the pyrochlore compound Gd$_2$Ti$_2$O$_7$ is an "ordered" pyrochlore structure in which both the "A" and "B" cation sublattice are susceptible to aliovalent dopants. Gd$_2$Zr$_2$O$_7$ on the other hand is a "disordered" pyrochlore in which the conduction mechanism is intrinsic. Solid solution of the two thereby provide an unique opportunity to explore the combined effects of extrinsic and intrinsic induced disorder on the electrical properties of pyrochlores.

Rare-earth pyrochlore oxides also are of technological interest. As pointed out later in the literature review, (section 2.1), pyrochlore compounds such as GZT and YZT are excellent oxygen ion conductors with conductivities approaching that of stabilized zirconia. Due to their ternary nature however, these compounds offer an additional thermodynamic degree of freedom when adjusting composition. Further, with several experimental routes available to manipulate $\sigma_{ionic}$, (e.g., intrinsic and/or extrinsic), the ratio of $\sigma_{ionic}/\sigma_{electronic}$ can be controlled over a wide spectrum. This provides an opportunity to explore mixed conduction, a feature of interest in developing electrodes with high oxygen exchange kinetics.

Finally, the experimental procedure for this work involved electrical conductivity tests using small signal ac complex impedance spectroscopy. This technique allowed deconvolution of bulk, grain boundary and electrode contributions to the total conductivity. Measurements were made as a function of temperature, oxygen partial pressure, and dopant concentration in conjunction with x-ray diffraction structural studies. These results, along with the aid of a
defect chemical model, provided the foundation for measuring mixed ionic-electronic conduction (MIEC) in a well characterized material. The feasibility of a novel short circuit current method of measuring MIEC could thus be tested.
2 LITERATURE REVIEW

The literature section begins with an applications overview for both ionic and mixed ionic-electronic conducting materials. In particular, a solid oxide fuel cell is described in which different specific material demands are placed on the electrode and electrolyte. Special emphasis is given to the $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore compounds and their potential as alternative oxygen ion and mixed ionic-electronic conducting materials. In the next section, (2.2) a review of fast oxygen ion conduction (FIC) is presented. Structure/transport properties for both defect fluorite and $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore compounds are addressed with the focus on extrinsic and intrinsic conduction mechanisms. Finally, a summary section (2.3) is provided which gives a basic outline for this research.

2.1 Mixed Ionic-Electronic Conduction: An Applications and Materials Overview

Solid electrolytes comprise a unique group of materials which exhibit high ionic conductivity and negligible electronic conductivity. Such materials are known as fast ion conductors (FIC) in which the predominant charge carrier is ionic and the ionic transference number, $t_i$, (i.e. the fraction of ionic conductivity to the total conductivity) is close to one. Another class of materials, mixed ionic-electronic conductors (MIEC) also exhibit FIC. This group is characterized as having both high ionic and electronic conductivities. Numerous examples of both FIC and MIEC are found in the literature, applications of which are shown in Table 2.1 [9]. In this thesis, a comprehensive overview of these applications will not be presented. Excellent reviews on the subject have been written by a number of authors with the work of West [9], Worrell [10], Steele [11], and Tuller
| Batteries, primary or secondary   |
| Sensors, gas pumps              |
| Fuel cells                      |
| Electrochemical reactors        |
| Supercapacitors                 |
| Synthesis of new materials by ion exchange |
| Waveguide fabrication by ion exchange |
| Optimization of superconductivity by oxygen |
| (de)intercalation                |
| Lithium (de)intercalation, solid electrodes |
| Electrochromics, smart windows, and displays |

Table 2.1 Applications of solid electrolytes and mixed ionic electronic conductors [9].
[12], strongly recommended to the interested reader. Instead, emphasis is placed solely on ionic and MIEC materials for use in electrochemical devices, particularly electrochemical devices used for energy conversion and storage. The objective is being to highlight materials requirements of ionic and MIEC materials in the same electrochemical device. Henceforth the solid oxide fuel cell (SOFC) is introduced in which different specific electrical demands are placed on the electrolyte and electrodes making up the device. Material properties of the $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore compounds are also discussed in relation to such devices.

2.1.1 SOLID OXIDE FUEL CELLS (SOFC): MATERIALS REQUIREMENTS

A fuel cell is an electrochemical device which produces electricity (and heat) from the electrochemical reaction of a fuel with an oxidant [13]. As shown in figure 2.1, a fuel cell consists of three primary components: an anode, cathode, and electrolyte. For an oxygen ion conducting fuel cell, neutral oxygen molecules pick up electrons at the cathode to form oxygen ions. These ions pass through the electrolyte and react with the fuel (e.g., hydrogen). The electrons released at the anode then flow back through an external (direct-current) circuit to completing the circuit. The electrolyte therefore functions to conduct oxygen ions between the two electrodes.

An unique aspect of a fuel cell is its high energy conversion efficiency. Since chemical energy is converted directly to electrical without intermediate thermal energy, its conversion efficiency is not subject to the limitation of the Carnot cycle. Minh [14] has recently compared the conventional power generation methods to that of fuel cells with fuel cells offering the following advantages: higher conversion efficiency, modular construction, high efficiency
Figure 2.1 Schematic of a Solid Oxide Fuel Cell (SOFC) [14].
at part load, minimal siting restrictions, potential for cogeneration, and lower production of pollutants.

Fuel cell performance differs by the materials selected. Figure 2.2 for example compares five fuel cell technologies listing the advantages and disadvantages of each [15]. Amongst all the fuel cells, the ceramic solid oxide fuel cell (SOFC) is shown to have several intrinsic features that makes it attractive. These include: (1) With the absence of a liquid phase, wetting of the electrode is avoided and therefore control of the water/fuel balance is easier with the composition of the electrolyte invariant. (2) Fabrication, operation, and maintenance of the system is made easier by reduced corrosion problems. (3) The high temperature cell operation (e.g., 1000°C) allows for methane (natural gas) to be used directly without reformation. (4) Generally, reduced electrode polarization at elevated temperature permits operation at higher current densities. Fuel conversion efficiencies of 50-60% are thereby obtainable with higher power output densities. (5) High-grade waste heat is produced, leading to possible combined heat and power applications for SOFCs.

The above features along with the added benefits of environmental safety (e.g., air pollution is reduced) lead one to believe the future of the SOFC is promising. Several key material problems still remain, however. Current SOFCs has been hindered both by electrode and electrolyte development. For the electrolyte, besides a high ionic conductivity $\sigma_l$, and ionic transference number $t_i$, the material must remain chemically and mechanically stable over the service temperatures and environments of interest. The ionic conductivity must also remain high enough to maximize cell voltages and minimize resistive losses. Further constraints are placed on the electrolyte's transference numbers. For $t_e$, (i.e. the fraction of electronic conductivity) its value must remain close to zero in
### Figure 2.2 A comparison of five fuel cell technologies. In each case, a different electrolyte material is given listing the advantage, disadvantage and application [15].
order to avoid cell discharge under open circuit conditions. For \( t_i \), its value must remain close to one over a wide range of partial pressures.

SOFC electrode materials also face severe material restrictions. One requires chemical and mechanical compatibility with the electrolyte over long periods of time at high temperature. For example, the composition of anode and cathode must be such as to avoid formation of chemical reaction products with the electrolyte while remaining invariant to the gas phase environment. A matching thermal expansion coefficient must also be provided to avoid cracking.

A further requirement for the SOFC electrode involves the concept of a three phase equilibrium. In order to achieve rapid reaction kinetics and avoid losses caused by overpotentials at the electrodes, the ionic, electronic, and gas phase species must all be rapidly supplied to, or removed from, the electrode/electrolyte interface.

2.1.2 SOFC: MATERIALS

The above section has demonstrated that there is a technological need to develop improved electrode and electrolyte materials for SOFC applications. We now discuss several oxygen ion conducting electrolytes and mixed conducting electrode materials emphasizing the limitations of each. In addition, the concept of compatible pyrochlore electrolyte - electrode materials is introduced.

Stabilized zirconia (e.g., \( \text{ZrO}_2 + 9 \text{ mole\% Y}_2\text{O}_3 \)) is the most common electrolyte material in SOFCs because of its high oxygen ion conductivity (e.g., \( \sigma = 10^{-1} \text{ S/cm at 1000}^\circ\text{C} \)) and excellent stability with respect to oxidation or reduction. However its operations has been limited by a number of factors. These include: (1) a relatively high ionic activation energy of 0.9 - 1.0 eV results in a sharp drop in electrolyte ionic conductivity at low temperatures. Below
1000°C, interfacial electrode resistance rapidly increases and the efficiency of the device drops. (2) Cell lifetime is limited by chemical reactions between the electrolyte and the electrode materials. For example, interactions between zirconia, Ni-ZrO$_2$ and LaMnO$_3$ (current anode and cathode) results in resistive intermediate phases. (3) The requirement of an extrinsic dopant adds another limitation. Since the electrical properties are subject to dopant-defect interactions, long term "aging" or degradation occurs over time. (4) Achieving a matching electrode/electrolyte thermal expansion coefficient also presents a problem. Cracking due to thermal-mechanical stresses arises due to the expansion mismatch between the different materials in contact.

Although most present applications utilize stabilized zirconia as the electrolyte, other oxygen ion conducting materials are available. Figure 2.3 for example shows both δ-Bi$_2$O$_3$ and CeO$_2$ have higher ionic conductivities than zirconia. However these materials are limited by other problems. δ-Bi$_2$O$_3$ is easily reduced under low oxygen partial thereby limiting the size of the PO$_2$ independent electrolytic domain [16]. Similarly, CeO$_2$ undergoes large departures from stoichiometry in reducing atmospheres resulting in electronic conduction [17].

A third electrolyte material shown in figure 2.3 is the $A_2B_2O_7$ pyrochlore. Although generally not as conductive as stabilized zirconia at elevated temperatures, the material does offer several advantages. Moon and Tuller [6,18], have demonstrated that a pyrochlore compound such as Gd$_2$Zr$_2$O$_7$ is an intrinsic fast ionic conductor which requires no dopant. Since this phase is an equilibrium phase, no long term aging affects are expected as is the case for stabilized zirconia. Further, Gd$_2$Zr$_2$O$_7$ offers an additional advantage of compositional flexibility. For example, solid solutions of Gd$_2$(Zr$_y$Ti$_{1-y}$)$_2$O$_7$, (GZT), may be formed [18] with both end members oxygen ion conductors.
Figure 2.3 The temperature dependence of conductivity for several oxygen ion conducting electrolyte materials [11].
However, while the end member Gd$_2$Zr$_2$O$_7$ (GZ) is an intrinsic oxygen ionic conductor, the other, Gd$_2$Ti$_2$O$_7$ (GT), is extrinsic. Several experimental routes, either intrinsic substitution or extrinsic doping, are thereby available to manipulate ionic conductivity.

But perhaps the most interesting facet of a pyrochlore material is the flexibility one has in controlling mixed ionic-electronic conduction (MIEC). As pointed out in section 2.1.1, in order to achieve rapid reaction kinetics and avoid losses caused by overpotentials at the electrodes, the ionic, electronic, and gas phase species must all be rapidly supplied to, or removed from, the electrode-electrolyte interface. A MIEC electrode whose surface is everywhere catalytically active is one such approach. In this case, the charge transfer reaction occurs over the entire electrode surface with gas molecules reaching the three phase (electrolyte-reactant-electrode) interface readily.

Although all solids possess some degree of mixed conduction, only a limited number of materials have been investigated in detail. Included among these are stabilized zirconia (YSZ), CeO$_2$ and ThO$_2$ which crystallize in the cubic fluorite structure [17,19,20]. However due to the binary nature of these systems, the flexibility in controlling MIEC is somewhat limited. Hence the advantage of a ternary MIEC pyrochlore oxide.

In a recent study, Spears et al. [21] examined both ionic and MIEC in the pyrochlore compositions Gd$_2$(Zr$_y$Ti$_{1-y}$)$_2$O$_7$ (GZT) and Y$_2$(Zr$_y$Ti$_{1-y}$)$_2$O$_7$ (YZT). For large values of "y", an ionic conductor was obtained with the magnitude of $\sigma_i$ increasing with increasing y. For low values of y a MIEC was obtained. Thus by varying "y", the ratio of $\sigma_i/\sigma_e$ could be controlled over a wide spectrum, providing an opportunity to develop electrode and electrolyte materials from the same base composition.
2.2 Oxygen Ion Conduction

2.2.1 GENERAL COMMENTS

The total electrical conductivity of a solid ($\sigma_t$) is the sum of the partial conductivities associated with each type of charge carrier and given by:

$$\sigma_t = \sum \sigma_j$$  \hspace{1cm} (2.1)

Each partial conductivity $\sigma_j$, which may represent transport of either ionic or electronic carriers, is defined by:

$$\sigma_j = [N_j] \mu_j e z_j$$  \hspace{1cm} (2.2)

where $j$ refers to the charge carrying species, $[N_j]$ the number of carriers per unit volume, $\mu_j$ the mobility of species $j$, $e$ the charge of an electron, and $z_j$ the valence of the species. The fraction of conductivity by species $j$ is then expressed by its transference number $t_j$ such that:

$$t_j = \sigma_j / \sigma_t$$  \hspace{1cm} (2.3)

Both $[N_j]$ and $\mu_j$ may be functions of temperature, pressure, composition or structure. For ionic conduction, transport may occur by the jumping of ionic species from one site to another, such as vacancies on normal lattice sites or ions in interstitial positions. The carrier density per unit volume can be rewritten as:
\[ [N_j] = [N_0]^\dagger (1 - n_\nu) \]  

where  
\( [N_0] = \) number of energetically equivalent lattice sites  
\( n_\nu = \) fraction of vacancies on the sites  
\( (1 - n_\nu) = \) fraction of occupied lattice site

In some cases, \([N_j]\) maybe temperature dependent and follow an Arrhenius-type relationship:

\[ N_j = N_j^0 \exp(-\Delta G_f/kT) \]  

with \( \Delta G_f \) the Gibbs free energy of formation. This topic will be described more thoroughly in section 2.3.3.1.

The mobility \( \mu_j \), can be related the diffusivity \( D_j \) by the Nernst-Einstein relation:

\[ \mu_j = D_j z_j e/kT \]  

Using a random walk model for diffusion, the diffusivity of a lattice atom moving by vacancies is given by an Arrhenius type expression of the form:

\[ D_j = \gamma d_o^2 n_\nu \Gamma \]  
\[ = \gamma d_o^2 n_\nu v_o \exp\{-\Delta G_m/kT\} \]

where  
\( \gamma = \) geometric constant  
\( d_o = \) jump distance  
\( \Gamma = \) the jump frequency = \( v_o \exp\{-\Delta G_m/kT\} \)  
\( v_o = \) the Debye frequency
Combining equations (2.1 - 2.7) yields an Arrhenius-type ionic conductivity of the form:

\[ \sigma_i = \{[N_0](ze)^2 \gamma d_0^2 v_0 n_v(1-n_v)/kT\} \exp[-\Delta G_m/kT] \]

\[ = (\sigma'_O/T) \exp(-H_m/kT) \]

with the pre-exponential for ionic conductivity \( \sigma'_O \), given by:

\[ \sigma'_O = \{[N_0](ze)^2 \gamma d_0^2 v_0 n_v(1-n_v)\exp[\Delta S_m/k]\}/k \]

In the above expressions \( \Delta G_m \), the activation energy is given as the difference between enthalpy and entropy terms \( (\Delta H_m - T\Delta S_m) \). The ionic conductivity \( \sigma_{ion} \) is shown to be nonzero only when the product \( n_v(1-n_v) \) is nonzero i.e., for \( n_v \) not equal to one or zero. [22].

2.2.2 STRUCTURAL REQUIREMENTS

Fast ion conduction in crystalline solids requires large defect concentrations and ion mobilities. It is clear then that structure plays a dominant role both in the generation of carriers and in their motion. These structural effects may be geometrical or connected with the type of bonding. For example, "intrinsic" fast ion conductors have structural disorder which is crystallographic in nature [23]. Thermally induced disorder places normal lattice ions in interstitial positions (Frenkel mechanism) or vacancies are simultaneously created on the cation and anion sublattices (Schottky mechanism). In either case, the structure
provides a highly ordered, immobile sublattice with continuous channels for ion transport. Interwoven among this sublattice is a mobile carrier sublattice which contains a random distribution of carriers over an excess number of equipotential sites. For uninhibited ion motion this framework must provide tunnels the diameter of which are the same order of magnitude as the ions themselves. If the bottlenecks are too small, the ion have difficulty getting through while if too large the ion will "stick" to the walls of the tunnels thereby limiting their motion.

Bonding effects are reflected in the relative contributions of (1) ion polarization, (2) lattice strain, and (3) electrostatic interactions to the total conductivity. Each of these variables affects the magnitude of the migration energy for ion transport. The difficulty however, is in separating these factors. One such attempt has recently been performed by van Dijk et al. [24] on pyrochlore and fluorite related structures. In this work, the authors attempted to deconvolute the strain contribution to ion transport by correlating the strain component to cation size. Figure 2.4 shows the edge-sharing cation tetrahedra in the pyrochlore structure type. Here, the strain enthalpy is considered only for the passage of oxygen ions through cation planes. The jumping oxygen ion has a choice of two routes: through the shared edge (route 1) or through the tetrahedral faces (route 2). Van Dijk's et al.'s. model predicts route 2 is energetically more favorable with the strain enthalpy simply determined by the free space in the triangular tetrahedron face. From these results, the authors conclude that the strain energy associated with ion transport may be correlated to cation size.

Polarization is also linked to ion size. Specifically, if the charge cloud of the mobile ion is deformable, the energy barrier associated with the saddle point of the jump will be smaller. Kleppmann and Bilz [25] have demonstrated that
Figure 2.4 The edge-shared cation tetrahedron in pyrochlore oxides showing two possible jump mechanisms (1) through the shared edge and (2) through the tetrahedral faces. [24].
deformable ions with high quadrupolar polarizability (e.g., Pb, Bi) are relatively more mobile than ions with lower quadrupolar polarizability.

Finally, one must consider electrostatic effects on the migration energy. We defer our discussion of this topic to section 2.3.3.1 where a detailed analysis of impurity-defect interactions in fluorite-type oxides is presented.

2.3 Structure/Property Relations in $\text{A}_2\text{B}_2\text{O}_7$ Pyrochlores

Compounds with the pyrochlore structure encompass a wide variety of properties, one of which is fast ion conduction. This section describes the structural requirements for ionic and/or MIEC in rare earth pyrochlore compounds. We begin with a discussion of the pyrochlore crystal structure and phase stability in relation to the order-disorder phenomena. A detailed analysis of the electrical properties is then presented with transport mechanisms in both extrinsic and intrinsic oxygen ion conductors. Since similarity with fluorite compounds is evident, the review highlights both pyrochlore and fluorite structure/property relations.

2.3.1 PYROCHLORE CRYSTAL STRUCTURE

Pyrochlore compounds are named after the mineral pyrochlorite $(\text{Ca,Na,Ce,Th})_2(\text{Nb,Ta,Ti})_2\text{O}_6(\text{OH,F})$. Its structure consists of a cubic unit cell (space group $\text{Fd3m}$), a lattice constant $\approx 10$ Å and a general molecular formula of $\text{A}_2\text{B}_2\text{O}_6\text{X}$ were $\text{A}$ and $\text{B}$ are cations and $\text{O}$ and $\text{X}$ are anions.
Any discussion of the $A_2B_2O_7$ pyrochlore compounds benefits from an analysis of the fluorite crystal structure as well. Shown in figure 2.5 are fluorite and pyrochlore unit cells with the corresponding atomic positions in each [7]. For ideal fluorite, (space group Fm3m) two cells are shown in which the stoichiometric MO$_2$ array consists of an anion array of simple cubic packing with the cations occupying every other cube center. When the oxide is doped with lower valent cations such as $A^{3+}$ or $A^{2+}$, the dopant ion substitutes for the host ion creating charge-compensating anion vacancies. The "defect" fluorite structure that results when equivalent amounts of tri-valent and quadravalent host ion are mixed, consists of seven oxygen ions randomly distributed over eight available sites, each of which are in tetrahedral coordination. The cations also are randomly distributed over all the available 8 coordinated sites.

In contrast to fluorite, the $A_2B_2O_7$ pyrochlore compound may be viewed as an ordered superstructure with a cell edge double that of "defect" fluorite. Its structure is derived from fluorite by removing one eighth of the oxygen ions such that the newly formed vacancies are arranged in a diamond-like array, and by separately ordering each of the two cations in alternating rows along <110> [27]. Figure 2.5 depicts two octants of the structure implying eight molecules per unit cell.

Besides ordering of the cation sublattice, pyrochlore oxides are characterized by additional ordering of the anion sublattice including an additional displacement of selected oxygen ions. To highlight this point, figure 2.6 gives the <100> projection of a pyrochlore unit cell. Here the larger A cations are shown to occupy the 16(c) sites and the smaller B cations the 16(d) sites. The coordination number of these two sites are 8 and 6-fold respectively. In addition, the anion sublattice is characterized by three different oxygen sites. Six oxygen ions occupy the 48(f) sites which are surrounded by two A and two B
Figure 2.5 Schematic of the fluorite and pyrochlore unit cells with the corresponding atomic positions in each [7]. For fluorite (left) two cells are shown while for pyrochlore (right) two octants are given.
Figure 2.6 (100) projection of a portion of the pyrochlore unit cell [18].
cations. The seventh oxygen occupies the 8(a) site which is in a tetrahedrally coordinated by four A neighbors. The vacant 8(b) site, also in tetrahedral coordination, is surrounded by B cations. Unique to the 48(f) site is the positional parameter x which describes the relaxation of this ion towards the vacant 8(b) site.

2.3.2 PHASE STABILITY

Phase stability for the $A_2B_2O_7$ pyrochlores is determined by three main parameters - the ionic radii, the temperature, and deviation from stoichiometry. We begin by discussing the effects of ionic radii on phase stability.

All pyrochlore compositions must meet certain constraints of ionic charge and radii. For the rare-earth $A_2^{3+}B_2^{4+}O_7$ pyrochlores, one such constraint is the cation radius ratio, $(R_A^{3+} / R_B^{4+})$, which requires that the radii of the "A" and "B" site cations remain within certain limits for the pyrochlore phase to exist. This ratio has been defined by a number of authors [28,29] the magnitude of which is determined by the source of the values assigned to the radii. Moon for example [18], based his results on the atomic radii of Shannon [28]. In this case an upper and lower limit for the tri- and quadrivalent ions are based on 8 and 6-fold coordinated radii. Knop [29,30] however, used only the 6-fold coordinated radii of Ahrens. Comparing the two cases, upper and lower $(R_A^{3+} / R_B^{4+})$ limits of 1.50 and 1.22 (Ahrens) and 1.80 and 1.47 (Shannon) are obtained for titanate-zirconate based materials. In remaining parts of this thesis, only the ionic radii of Shannon will be used.

The effects of ionic radii $(R_A^{3+}, R_B^{4+})$, becomes apparent in figure 2.7. Here, a two-dimentional stability field defined by the parameters $r_A$ and $r_B$ is given for
Figure 2.7 Pyrochlore stability field for $r_{\text{Lu}} \leq r_{A} \leq r_{\text{La}}$ and $r_{\text{Tl}} \leq r_{B} \leq r_{\text{Zr}}$ with the solid lines representing solid solutions [18].
Clearly, the pyrochlores $\text{Gd}_2\text{Zr}_2\text{O}_7$ (GZ), $\text{Y}_2\text{Ti}_2\text{O}_7$ (YT), $\text{Sm}_2\text{Ti}_2\text{O}_7$ (ST), and $\text{La}_2\text{Zr}_2\text{O}_7$ (LZ), lie entirely within the pyrochlore phase field while the compounds $\text{Y}_2\text{Zr}_2\text{O}_7$ (YZ), and $\text{Nd}_2\text{Ti}_2\text{O}_7$ (NT), do not.

In explanation, we examine two extremes, (NT) and (YZ). For (NT), (for which $\frac{R^{3+}_A}{R^{4+}_B} > 1.80$), the size difference between the "A" and "B" site cations is large enough that thermodynamics favors a change in structure. A distorted pyrochlore phase with an extra degree of order on the oxygen sublattice results, ultimately leading to distorted cubic symmetry [31]. At the other extreme, (e.g., $\frac{R^{3+}_A}{R^{4+}_B} < 1.47$), the "A" and "B" site cations will substitute easily for one another and the driving force for cation ordering is lost. $\text{Y}_2\text{Zr}_2\text{O}_7$ therefore represent a case where the enthalpy difference between the pyrochlore and fluorite phases is relatively small and an anion-deficient defect fluorite phase is stable [18].

Although the cation radius ratio gives a good first order approximation of phase stability, many unresolved issues involving the order-disorder phenomenon remain. These include: the sharpness of the order-disorder phase boundary, degree of cation and anion sublattice order, correlation's between the two sublattices, long vs. short range ordering, and ordering effects on the positional parameter "x". All of these issues have been addressed using a variety of spectroscopic and diffraction experiments. In this thesis a comprehensive overview of these results will not be given. Instead, we refer the reader to the work of Subramanian [26], and Heremans [27].
2.3.3 EXTRINSIC DOPING AND OXYGEN ION CONDUCTION

Although few systematic doping experiments have been performed on $\text{A}_2\text{B}_2\text{O}_7$ pyrochlores, numerous studies have been completed on related fluorite structures [32,33]. In most of these studies attention has been paid to the role of dopant-vacancy interactions which determine the conductivity parameters. In interpreting these experimental results, theoretical considerations and computer simulation techniques have established that dopant ion radii, effective charge and concentration are all important variables in determining the interaction energies [34,35]. The goal of this section, therefore, is to review these variables emphasizing how defect interactions control mass transport in both fluorite and pyrochlore based materials.

2.3.3.1 Defect Association

The basic equation governing ionic conductivity has already been present by an Arrhenius relation of the form:

$$\sigma_i = \{[N_0] (ze)^2 \gamma d_0^2 v_0 n_v (1-n_v)/kT \} \exp[-\Delta G_m/kT]$$

$$= (\sigma'_O / T) \exp(-\Delta H_m / kT)$$

with the pre-exponential $\sigma'_O$, containing the temperature dependent formation term and the exponential the defect migration enthalpy $\Delta H_m$. We may generalize this expression even further such that:

$$(\sigma''_O / T) \exp(-\Delta H'_O / kT)$$

(2.9)
where the activation enthalpy term $\Delta H_\sigma$ now contains contributions from migration and other processes such as defect formation and association.

Equation 2.9 forms the basis of the "conductivity plot" defined by Nowick [33]. In this work, the author established three regions to the log $\sigma T$ vs. $1/T$ plot shown schematically in figure 2.8. At high temperatures, region I, the intrinsic range is obtained where intrinsic ionic disorder, either Frenkel or Schottky control defect equilibria. In this case, both defect formation and migration must be considered (e.g., for Frenkel defects $n_V \propto \exp(-H_f/2kT$ with the activation energy given by $\Delta H_\sigma = \Delta H_m + \Delta H_f/2$). Because of the high melting point and the presence of impurities, this region is typically not observed for highly doped oxides.

At intermediate temperatures one obtains region II, the extrinsic dissociated range, in which all vacancies, which compensate the dopants, are available for conduction. In this case, $n_V$ is a constant proportional to the dopant concentration $n_o$ and the activation energy is given by $\Delta H_\sigma = \Delta H_m$.

Finally, at low temperatures, because the defect and dopant are of opposite charge, an attractive coulombic force exists between them and impurity-vacancy association takes place. This ultimately leads to Stage III, the extrinsic associated range.

The behavior of stage III differs with the type of dopant selected. Assuming the dopant is immobile and randomly distributed, initially only dimers will form. The reaction is described by:

$$(I-D)^{x-y} \rightleftharpoons I^x + D^y$$  \hspace{1cm} (2.10)

in which I is the impurity with net charge $(\pm)x$ and D is the defect with net charge $(\mp)y$. In this expression, the factor $x/y$, defined as $\beta$, is commonly either equal to
Figure 2.8 Schematic log $\sigma T$ vs. $1/T$ plot for an ionic conductor. Three regime are represented: (I) intrinsic (II) extrinsic dissociated and (III) extrinsic associated [33].
unity (e.g., $\text{Ca}^{\text{\textsuperscript{2}}}\text{Zr}$) or less than one (e.g., $\text{Y}^{\text{\textsuperscript{3}}}\text{Zr}$). For the case of $\beta=1$, it can be shown [36] that the concentration of mobile defects is given by the expression:

$$n_v = (\eta I K_\text{A}^*)^{1/2} \exp(-\Delta H_\text{A}/2kT)$$  \hspace{1cm} (2.11)

where $n_v$ is the net vacancy density, $\eta I$ the impurity density, and $K_\text{A}^*$ and $H_\text{A}$ the association pre-exponential and activation energy, respectively. For the latter case of $\beta<1$ one obtains a vacancy density of:

$$n_v = [(1-\beta)/\beta] K_\text{A}^* \exp(-\Delta H_\text{A}/kT)$$  \hspace{1cm} (2.12)

Equations (2.11) and (2.12) show that for both $\beta=1$ and $\beta<1$ the activation energy for ionic conduction consists of a migration plus an additional association energy term. However for the case of $\beta=1$, the activation energy is given as $\Delta H_\sigma = \Delta H_\text{m} + \Delta H_\text{A}/2$, while the pre-exponential constant, $\sigma_0$, (e.g., the concentration of defects) follows a square root dependence on dopant density. For $\beta<1$ on the other hand, $\Delta H_\sigma = \Delta H_\text{m} + \Delta H_\text{A}$ with the pre-exponential surprisingly independent of dopant concentration.

Experimentally, the $\beta=1$ case has been evaluated both at high and low temperatures by a number of authors [37-39]. For di-valent Ca doped CeO$_2$ (e.g., Ce$_{1-x}$Ca$_x$O$_{2-x}$) several points emerge. Nowick [37] measured the isothermal bulk conductivity below 500 K and found that for the composition range of $x = 0.003 - 0.15$, the activation energy remained essentially constant at 0.93 eV. El Adham [38] confirmed the independence of activation energy and $x$ but found a slightly smaller activation energy of 0.8 eV. In both cases, the conductivity followed a square root dependence with $x$ as predicted by equation 2.11. The square root dependence along with the constant activation energy.
suggests that the primary defect is not free but is bound to the dopant cation to form associates. At high temperatures however, this result is not necessarily true. Figure 2.9 shows the isothermal conductivity of Ce(Ca)O_{2-x} measured by Blumenthal et al. [39]. For the composition range of 1.0 - 14 mole% CaO, the conductivity was found to follow a linear dependence with x instead of the predicted square root dependence. Further, a maximum in isothermal conductivity is shown at higher Ca concentration. This result along with a lower activation energy of 0.6 eV indicates that the defects are unbound free vacancies.

For the case of β<1, we cite the work of Hammou [40] and Nowick [41]. Figure 2.10 shows an Arrhenius plot for Ce(Y)O_{2-x} in the composition range of 0.05 - 1.0 mole% Y_{2}O_{3}. Several observations can be made. First, equation 2.12 predicts that in the associated regime, both the conductivity and activation energy should be independent of dopant concentration. Clearly, the figure shows that a composition dependence is observed. Secondly, all four compositions are shown to deviate from linear straight line behavior. This indicates that in the temperature range of 150 - 700 K, a transition exists between the associated and dissociated regimes. Similar results have been obtained for Th(Y)O_{2-x} although interpretation of the high temperature data tends towards associated not free defects [42]. Another surprising result is shown in figure 2.11. Here, the isothermal conductivity and activation energy are plotted together as a function of Y_{2}O_{3} content showing that the maximum in conductivity corresponds to a minimum in activation energy. Similar to the β=1 case, the activation energy is not constant as predicted by theory but actually decreases up to ≈2 mole% Y_{2}O_{3} followed by a sharp increase. To explain these results Wang et al [43] suggested that the compositional dependence results from the incomplete compensation by Y'Ce for V_{O}⁻ in a (Y'Ce-V_{O}⁻)⁻ complex. With two Y'Ce
Figure 2.9 The isothermal conductivity of Ce(Ca)O$_{2-x}$ solid solutions [39].
Figure 2.10 Conductivity versus temperature curves for dilute CeO$_2$:Y$_2$O$_3$ solid solutions [41].
Figure 2.11 Variation of the activation enthalpy, ($E_{\text{act}}$), with composition plotted on a logarithmic scale for $\text{CeO}_2:\text{Y}_2\text{O}_3$ solid solutions [41]. Also shown is the conductivity data at 182°C.
acceptors for every $V_O\cdot\cdot$, the uncompensated $Y'_{Ce}$ provides favorable transport paths which do not require full dissociation. As the total $[Y'_{Ce}]$ increases, an increasingly large overlap between the potential well of the yttrium-oxygen vacancy pair ($Y'_{Ce}$-$V_O\cdot\cdot$) and the isolated yttrium ion $Y'_{Ce}$ occurs, thereby narrowing the energy difference between the bound and free states of the oxygen vacancy, $V_O\cdot\cdot$. This results in the first stage, a steadily decreasing association energy. At sufficiently high $[Y'_{Ce}]$, deep traps for $V_O\cdot\cdot$ arise, presumably due to long range ordering.

2.3.3.2 The Concentrated Range

Any treatment of defect association based on mass action principles requires a discussion of association under conditions of high solute concentrations. The equations outlined above are valid only under conditions of dilute solutions. For concentrated solution it is no longer meaningful to consider association between a single defect and a single dopant even with a random distribution of dopant ions. Although there is no clear break between the two regimes, a common denominator possessed by all fluorite type oxides is the peak in conductivity and corresponding minimum in activation energy with increasing dopant density. Taking these results into account, Hohnke [44] defined the activation energy minimum as a good first order approximation for the dilute to concentrated transition. For the Zr(M)O$_{2-x}$ (M=Yb, In, Y, Ca) solid solutions shown in figure 2.12, several observations were made. First, for anion vacancy concentrations greater than x=0.08, the activation energy becomes concentration-dependent with a slope of 6 eV/mole. Secondly, when the
Figure 2.12 Activation energy vs. anion vacancy concentration for various Zr(M)O$_{2-x}$ (M = Yb, In, Y, and Ca) solid solutions [44].
activation energy is plotted versus the pre-exponential factor, a straight line is observed which increases with dopant concentration. Hohnke has shown that this variation is consistent with the introduction of an extra Gibbs free energy-like term which depends on composition. This term is associated with the free energy of long-range ordering.

2.3.3.3 Dopant-Host Size Mismatch

Following the work on Y-doped ceria, similar conductivity measurements were carried out to evaluate dopant size effects on the conductivity parameters [45,46]. In these studies, the authors showed that both conductivity and association enthalpy vary as the size mis-match between the host and the dopant cation is varied. For example, Gerhart-Anderson and Nowick [45] measured the association enthalpies between trivalent dopant cations and oxygen vacancies in CeO$_2$. There results are shown in figure 2.13 along with computer-simulated binding energies calculated by Butler et al. [46]. Excellent agreement between calculation and experiment is observed. In each case, the lowest association energy is found when the size difference between dopant and host ion is minimized.

To explain these results, Kilner and Brook [47] concluded that the elastic strain energy provides an important component of the dopant-vacancy association energy. This term is minimized when there is a small size mismatch between host and dopant. Noted in figure 2.13 is that the effects on association energy are greater for a smaller dopant radii (relative to the host) than a larger one. These result have been observed in other systems as well [48,49]. The net result is to shift the minimum slightly to the right. For example, on the basis of
Figure 2.13 The experimental and calculated binding energy for Ce(Mf)O$_{2-x}$ solid solutions [45,46].
size effects Y^{3+} (r=1.01\,\text{Å}) is a better size match to Ce^{4+} (r=0.97\,\text{Å}) than Gd^{3+} (1.06\,\text{Å}). However substitution of Y^{3+} causes a slight contraction of the lattice and the minimum shifts to the right. Kilner [50] suggested that better qualitative data are obtained by examination of a lattice parameter map. Figure 2.14 shows such a map in which electrostatic effects (e.g., lattice expansion or contraction) are more evident.

2.3.3.4 Doping Experiments in Pyrochlores

Doping studies (either experimental or theoretical) on ternary compounds such as the rare-earth pyrochlores are severely lacking. Of a limited number of experimental studies, the lanthanide zirconate pyrochlores Gd_2Zr_2O_7, Sm_2Zr_2O_7, and Nd_2Zr_2O_7 [7,8,18] have received most attention. In these studies the role of "A" site dopants on the conductivity parameters has been evaluated. For the pyrochlore composition \((\text{Gd}_{1-x}\text{Ca}_x)\text{Zr}_2\text{O}_7\), \((\text{GZ})\), Moon [18] has established that Ca^{2+} acceptors have no effect on the ionic conductivity for dopant concentrations between 0 and 2 mole\%. This results can be explained by the fact that GZ is an intrinsic fast ion conductor in which aliovalent dopant addition in small amounts have no effect. At higher doping levels (e.g., 5 - 15 mole\% Ca) Fournier et al. [51] have shown that the total conductivity drops. Since the decrease in conductivity corresponds to an increase in activation energy, the lower \(\sigma_1\) has been attributed to defect association.

In contrast to GZ, Factor et al. [7] have shown the Ca^{2+} doping (0 - 10 mole\%) in \((\text{Nd}_{1-x}\text{Ca}_x)\text{Zr}_2\text{O}_7\), \((\text{NZ})\), results in dopant dependent conductivity. This result is not surprising if one considers the stability map shown in figure 2.7. Here, NZ is recognized as an ordered pyrochlore somewhat off the order-
Figure 2.14 Lattice parameter vs. composition for the systems CeO$_2$ - M$_2$O$_3$ (M = La, Nd, Sm, Gd, Dy, Y and Yb) [50].
disorder phase boundary. NZ therefore may be considered as an extrinsic pyrochlore suitable for doping. Figures 2.15 - 2.17 show the trend in activation energy, pre-exponential constant, and bulk conductivity with increasing Ca²⁺ concentration. Although both pre-exponential and activation energy are shown to increase, as was the case for GZ, the net result is an increase in conductivity. Thus while the activation energy increases from ≈0.73 to 0.88 kJ/mole, the increase in pre-exponential factor outweighs the increase in activation energy resulting in significantly higher ionic conductivities.

Here an interesting observation may be made. For both GZ and NZ the activation energy and pre-exponential factor increase at high dopant concentrations. However, only Ca²⁺ doped NZ results in an increase in σ₁. The relative contributions of order and lattice strain thus becomes apparent. Table 2.2 gives the trends in activation energy, pre-exponential, and lattice parameter for several rare earth zirconates. Noted are the generally lower activation energies for larger "A" site ions. The question remains whether compositions with a lower activation energy and larger "A" site ion (e.g., "A" = Sm) will, upon doping, exhibit a higher conductivity than GZ and NZ. In this study, the pyrochlore compositions \((La_{1-x}A_x)_2Zr_2O_7\) (A=Sr,Ca), have been chosen to address this issue.

Of the experimental data on doped titanate pyrochlores only the work of Moon [18] can be cited. Here, Moon found that the conductivity of Gd₂Ti₂O₇, (GT), increased with the addition of 1 mole% Ca. In striking contrast to the zirconates however the activation energy decreased from approximately 1.0 eV to 0.5 eV for the doped material. In this study however, caution was taken in evaluating the results as only one concentration of dopant was studied. In any case, these preliminary results provide a strong foundation for a systematic
Figure 2.15 The activation energy for ionic conduction in \((\text{Nd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\) as a function of Ca doping [7].
Figure 2.16 The pre-exponential factor for ionic conduction in \((\text{Nd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\) as a function of Ca doping [7].
Figure 2.17 The ionic conductivity of $(\text{Nd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7$ as a function of Ca doping at 500°C [7].
<table>
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<tr>
<th>COMPOSITION</th>
<th>Lattice Parameter</th>
<th>E&lt;sub&gt;i&lt;/sub&gt;</th>
<th>Log σ&lt;sub&gt;i&lt;/sub&gt;&lt;sup&gt;o&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd&lt;sub&gt;2&lt;/sub&gt;Zr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>10.63 Å</td>
<td>0.75 eV</td>
<td>2.3 S/cm K</td>
</tr>
<tr>
<td>Sm&lt;sub&gt;2&lt;/sub&gt;Zr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>10.57 Å</td>
<td>0.65 eV</td>
<td>3.0 S/cm K</td>
</tr>
<tr>
<td>Gd&lt;sub&gt;2&lt;/sub&gt;Zr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>10.53 Å</td>
<td>0.87 eV</td>
<td>5.0 S/cm K</td>
</tr>
<tr>
<td>Y&lt;sub&gt;2&lt;/sub&gt;Zr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
<td>10.41 Å</td>
<td>1.26 eV</td>
<td>5.5 S/cm K</td>
</tr>
</tbody>
</table>

Table 2.2 Lattice Parameter, activation energy, and pre-exponential constant for A<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (A=Nd, Sm, Gd, and Y) pyrochlores [6,7,8].
investigation of the role of dopants in an extrinsic titanate-based pyrochlore such as GT.

Although experimental work on titanate-zirconate pyrochlores is limited, computer simulations have recently begun on the $A_2B_2O_7$ pyrochlores by Wilde and Catlow [52]. Here the effects of dopant-host size mismatch have been investigated. For the compositions Gd$_2$Ti$_2$O$_7$ (GT) and Gd$_2$Zr$_2$O$_7$ (GZ), the authors have shown that Ca$^{2+}$ has the lowest solution energy as an "A" site dopant (figure 2.18). This result is not surprising considering the size match between dopant and host (Gd$^{3+}$ - 1.06 Å and Ca$^{2+}$ 1.12 Å). However, one surprising result is that the solution energies are consistently lower for the substitution at the trivalent cation site than at the tetravalent cation site. Thus a dopant such as Mg$^{2+}$, whose ionic radii is close in size to that of Ti$^{4+}$, is still predicted to substitute on the "A" site.

2.3.4 INTRINSIC DISORDER AND OXYGEN ION CONDUCTION

As outlined earlier in section 2.3.2, a stability map in the cation radius field, $(R_A^{3+}, R_A^{4+})$, can be used to identify various degrees of intrinsic structural disorder in pyrochlore oxides. This disorder can be manipulated in several ways, namely by systematic substitution on the "A" cation sublattice, "B" cation sublattice or both "A" and "B" sublattices. With this in mind, we begin our review of intrinsic fast ion conduction in pyrochlore oxides.
Figure 2.18 Solid solution energy calculations for the dopants Mg, Ca, Sr, and K in Gd₂Ti₂O₇, Gd₂Zr₂O₇, Y₂Ti₂O₇ and Y₂Zr₂O₇ [52].
2.3.4.1 "A" Site Substitution in Zirconates

The effects of "A" site substitutions on the electrical properties of pyrochlores is best demonstrated by the zirconate-based systems. Both Gd$_2$Zr$_2$O$_7$ (GZ) and Nd$_2$Zr$_2$O$_7$ (NZ) have been characterized in detail [7,18] and, as expected, GZ has a higher degree of intrinsic structural disorder due to its location just inside the pyrochlore/fluorite phase boundary. Again, we refer to equation 2.8 showing that the conductivity parameters are dependent on the pre-exponential constant (i.e. carrier concentration) and activation energy (i.e. mobility). Also noted are the earlier results of table 2.2 which show that for Ln$_2$Zr$_2$O$_7$ pyrochlores, both pre-exponential and migration enthalpy decrease with increasing size of the lanthanide ion. Hence, for zirconia based compounds located near the phase boundary, two opposing forces, ($\sigma_0$) and (E$_H$) control the overall conductivity. An example of this is shown in figure 2.19. Here the conductivity of GdO$_{1.5}$ - ZrO$_2$ and NdO$_{1.5}$ - ZrO$_2$ is given as a function of composition. For the stoichiometric pyrochlore (e.g., 50 mole% ZrO$_2$) the conductivity of Gd$_2$Zr$_2$O$_7$ is maximized while that for Nd$_2$Zr$_2$O$_7$ is minimized. Even though the larger "A" ion reduces the bottle neck strain enthalpy (activation energy), the intrinsic carrier concentration ($\sigma_0$) is reduced so much that the net result is a decrease in $\sigma_{ionic}$. The question still remains, however, as to whether Gd$^{3+}$ has the optimum radius for ionic conduction in the zirconates. For example, it might be possible to substitute a larger "A" site ion than Nd$^{3+}$ thereby decreasing the activation energy while having only a small effect on the pre-exponential, $\sigma_0$. If so, the pre-exponential can then be enhanced by extrinsic dopants (e.g., section 2.3.3.4).
Figure 2.19 The ionic conductivity as a function of composition for Gd$_2$O$_3$-ZrO$_2$ and Nd$_2$O$_3$-ZrO$_2$ solid solutions [18].
2.3.4.2 "B" site Substitution in Titanates

The effect of isovalent "B" site substitution is represented by the results for Gd$_2$Ti$_2$O$_7$-Gd$_2$Zr$_2$O$_7$, GZT, and Y$_2$Ti$_2$O$_7$-Y$_2$Zr$_2$O$_7$, YZT, pyrochlore solid solutions. Moon and Spears [18,53] have recently performed a systematic investigation of the role of "B" site Zr substitutions on the electrical properties of these compounds. Figure 2.20 summarizes their findings. For both YZT and GZT, a dramatic increase in ionic conductivity is observed with increasing Zr content. Again we refer to the stability map for an explanation. The stability map shows that pyrochlore solid solutions of Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ and Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ with low values of $x$ are entirely within the pyrochlore phase field, while those with higher $x$ values (e.g., Gd$_2$Zr$_2$O$_7$, Y$_2$Zr$_2$O$_7$) are near or within the fluorite boundary. It is therefore reasonable to expect that highly disordered compositions such as Gd$_2$Zr$_2$O$_7$ and Y$_2$Zr$_2$O$_7$ are better intrinsic oxygen ion conductors, ultimately yielding a higher $\sigma_i$. Figures 2.21 and 2.22 show that the measured activation energy and pre-exponential term are consistent with this hypothesis. For both YZT and GZT the pre-exponential increases with increasing Zr but the activation energy (for $x>0.3$) remains nearly constant. Moon also used dopants to calculate the "quasi" Frenkel constant for the intermediate composition $x=0.3$. The relatively high value of $E_F= 1.0\times 10^{39}\text{exp}(-0.24 \text{ eV } \pm 0.03 \text{eV})$ cm$^{-6}$ was consistent with the concept of high intrinsic structural disorder. The experimental formation energy of 0.24 eV however needs to be compared to other GZT compositions to verify the trend of increasing structural disorder with increasing $x$. 

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Figure 2.20 Conductivity as a function of mole% Zr substitution in Gd$_2$(Zr$_y$Ti$_{1-y}$)$_2$Ti$_2$O$_7$ and Y$_2$(Zr$_y$Ti$_{1-y}$)$_2$Ti$_2$O$_7$ solid solutions [53].
Figure 2.21 Activation energy for ionic conductivity for Gd$_2$(Zr$_y$Tl$_{1-y}$)$_2$Ti$_2$O$_7$ and Y$_2$(Zr$_y$Tl$_{1-y}$)$_2$Ti$_2$O$_7$ solid solutions as a function of y. [53].
Figure 2.22 Pre-exponential for ionic conductivity for Gd$_2$(Zr$_y$Ti$_{1-y}$)$_2$Ti$_2$O$_7$ and Y$_2$(Zr$_y$Ti$_{1-y}$)$_2$Ti$_2$O$_7$ solid solutions as a function of $y$. [53].
2.4 Literature Review Summary and Overview of Planned Research

The literature review has outlined several aspects of oxygen ion and mixed ionic-electronic conductors both from a materials science and theoretical point of view. First, while few systematic doping experiments have been performed on $A_2B_2O_7$ pyrochlores, numerous studies have been completed on fluorite-related structures. In most of these studies, attention has been paid to the role of dopant-vacancy interactions which determine the conductivity parameters. In interpreting these results, it has been established that the dopant ion radius, relative charge, and concentration are important parameters. A logical extension of this work, therefore, is to examine dopant size, charge, and concentration effects in ternary $A_2B_2O_7$ pyrochlore compounds. Given the high levels of oxygen ionic conductivity found in acceptor doped GT (e.g., $(\text{Gd}_{0.99}\text{Ca}_{0.01})_2\text{Ti}_2\text{O}_7$), [18], the "extrinsic" end member $\text{Gd}_2\text{Ti}_2\text{O}_7$ (GT) will be used as the host material. The acceptor dopants $\text{Ca}^{2+},\text{Sr}^{2+},\text{Mg}^{2+}$, will be incorporated substitutionally into the host ($\text{Gd}^{3+}$) lattice in order to investigate dopant size effects on the conductivity parameters. Similarly, $\text{K}^{1+}$, only marginally larger than $\text{Ca}^{2+}$, but possessing a net negative charge of two, allows analysis of the effect of charge on the conductivity.

Of special interest to $A_2B_2O_7$ pyrochlores are the additional degrees of freedom available for investigating dopant effects on transport. In contrast to fluorite oxides, the pyrochlores have two cation sublattices onto which dopants can be added. A question to resolve is whether "B" site doping is equivalent to "A" site doping. $\text{Al}^{3+}$ will be substituted for $\text{Ti}^{4+}$ to investigated this effect. A related question is the effect of co-doping on both "A" and "B" sites on the
conductivity. Several \( (\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_1{\gamma}\text{Al}_y\text{O}_7 \), compositions will be prepared to investigate this aspect.

The combined effects of doping and host lattice size (e.g., "A" site ion) on the conductivity parameters will also be investigated. Here, trends in Ca doped YT, GT, and ST will be evaluated in order to investigate the role of lattice strain on ionic conductivity and MIEC.

Doping studies in zirconia based pyrochlores also have highlighted several interesting issues. The observation that dopants affect the conductivity parameters of \( \text{Nd}_2\text{Zr}_2\text{O}_7 \), leads one to believe that pyrochlores with larger "A" site ions (e.g., \( \text{La}^{3+} \)) will also be affected by dopant additions. The pyrochlore composition \( (\text{La}_{1-x}\text{A}_x)\text{Zr}_2\text{O}_7 \) (\( \text{A} = \text{Sr}, \text{Ca} \)) will be prepared in order to examine dopant size and concentration effects in the zirconates. Also of relevance are doping effects in "intrinsic" based pyrochlores such as \( \text{Gd}_2(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_7 \) solid solutions. As pointed out by Moon [18], dopant additions in these compounds may be used to quantify the degree of intrinsic structural disorder. For example, in the pyrochlore composition GZT \( x=0.30 \), Moon found a relatively high frenkel constant with an activation energy of 0.24 eV. However, a value for \( E_F \) was obtained only for this one GZT composition. Experimentally, it is of interest to investigate the trend in Frenkel formation energy with increasing structural disorder (i.e. "x"). In this work, the pyrochlore composition GZT \( x=0.25 \) will be examined.

Finally, certain rare-earth pyrochlore compounds such as GZT and YZT have been noted to be of potential technological importance as well. As outlined in section 2.1 these compounds are excellent oxygen ion conductors with conductivities approaching those of stabilized zirconia. Under certain circumstances, these materials also possess a substantial level of electronic conduction. For the GZT and YZT based compositions, the electronic
conductivity was found to decrease with increasing \( x \) due to an increase in reduction enthalpy and narrowing of the Ti 3d conduction band [53]. It is also of interest, therefore, to monitor the trends in reduction enthalpy and band gap for various dopant additions. A defect chemical model will be used for such an analysis.

Table 2.3 summarizes the various dopants and composition that will be studied.
<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>&quot;A&quot; site dopants</th>
<th>&quot;B&quot; site dopants</th>
<th>&quot;A&quot; and &quot;B&quot; Co-dopants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd₂Ti₂O₇</td>
<td>Ca, Sr, Mg, K</td>
<td>Al</td>
<td>Ca-Al</td>
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<td>Y₂Ti₂O₇</td>
<td>Ca</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm₂Ti₂O₇</td>
<td>Ca, Sr, Mg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La₂Zr₂O₇</td>
<td>Ca, Sr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd₂(Zr₀.25Ti₀.75)O₇</td>
<td>Ca</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3  List of the A₂B₂O₇ titanate and zirconate pyrochlores examined in this thesis. Included are the "A" site, "B" site, and co-dopants.
3 THEORY

In this section we begin the theoretical analysis of ionic and mixed ionic-electronic conduction (MIEC) in pyrochlore oxides. General topics of MIEC are first described in section 3.1 with emphasis on nonstoichiometry and electronic transport in oxygen ion conductors. The concept of defect chemical modeling is then introduced in section 3.2 with a specific defect model for zirconia and titania based pyrochlores. The model we present here enables improved predictability on how MIEC varies with composition, dopant, temperature, and atmosphere. Finally, the last section (section 3.3) describes limitations in evaluating MIEC along with MIEC measurement techniques.

3.1 Mixed Ionic-Electronic Conduction (MIEC)

While solids are often categorized as ionic or electronic conductors (i.e. semiconductors and metals) they all exhibit some degree of mixed ionic-electronic conduction (MIEC). Generally speaking, only one type of carrier dominates charge transport and contributions from minority carriers are often ignored. However for a small subgroup of oxides, by circumstances of crystal structure, band gap, composition, and temperature, both ionic and electronic carriers contribute simultaneously in a major way to the overall electrical conductivity. Such mixed conductors are the subject of this section.
3.1.1 DEFINITIONS AND REQUIREMENTS FOR MIEC

Referring to the discussion of MIEC by Tuller [54], the total conductivity of a solid can be expressed by the superposition of partial conductivities:

$$\sigma_t = \Sigma j \sigma_j$$

with the electronic and ionic contributions given by:

$$\sigma_e = \Sigma N_e(j) \mu_j e z_j$$  \hspace{1cm} (3.1)

$$= n q \mu_e + p q \mu_H$$

and

$$\sigma_i = \Sigma N_i(j) \mu_j e z_j$$  \hspace{1cm} (3.2)

where \(N_e(j)\) and \(N_i(j)\) are the number of electronic and ionic charge carriers per unit volume respectively.

In the above expressions, the electronic conductivity, \(\sigma_e\), is given as the sum of the partial electron and hole conductivities while the ionic conductivity, \(\sigma_i\), is the conductivity carried by one predominate ionic carrier (e.g., anions migrating via a vacancy mechanism). In a similar manner, one may designate the fraction of total conductivity contributed by each type of charge carrier by its transference number \(t_j\). One defines the electronic and ionic transference numbers as:

$$t_e = \sigma_e / \sigma_t$$  \hspace{1cm} (3.3)
\[ t_i = \sigma_i/\sigma_t \] (3.4)

where \( t_e \) and \( t_i \) represent the ratio of electronic and ionic conductivity to the total conductivity respectively.

When dealing with MIEC, one is generally concerned with the relative magnitudes of \( t_e \) and \( t_i \). By definition, the sum of the individual transference numbers must be unity with neither value being truly zero. In practice however it is useful to speak of MIEC only when both ionic (\( t_i \)) and electronic (\( t_e \)) contributions to the total conductivity are "significant". What is "significant" depends on the subject of interest. For example, the use of solid electrolytes in fuel cells requires that the electronic contribution be such that \( t_e < 10^{-3} \). For sensors, however, approximately 1/10 of this value is termed significant. Solid electronic-conducting electrodes on the other hand allows \( t_i \) to be as low as \( 10^{-6} \).

Assuming only one type of ionic and electronic carrier predominates such as vacancies and electrons, it is next of interest to examine the specific case of \( t_e = t_i = 1/2 \). Under these conditions, equations 3.1 - 3.4 may be re-written as:

\[ N_v \mu_i = N_e \mu_e \] (3.5)

or

\[ N_v/N_e = \mu_e/\mu_i >> 1 \]

since electronic mobilities are typically \( 10^4 \) - \( 10^8 \) times greater than ionic mobilities.
Equation 3.5 has important consequences for all MIEC materials. The equation states that the ionic carrier concentration must be $10^4$-$10^8$ times greater than the electronic carrier concentration for "significant" levels of MIEC. This condition is satisfied only in a select group of oxides in which high densities of mobile ions can be induced either by doping, crystallographic disorder, or deviation from stoichiometry. In the next section, we describe such defect generation reactions.

3.1.2 CARRIER GENERATION AND DEFECT FORMATION

The electrical response of a material to temperature and atmosphere excursions depends both on the manner in which the electronic and ionic carriers are generated and the way in which they move.

In oxides, three types of mechanisms for defect formation need to be considered. These are (1) thermally induced intrinsic disorder, (2) redox, and (3) impurity-induced defects. We will illustrate these for the specific case of a binary oxide of composition MO.

In the first category, intrinsic disorder can be predicted from statistical thermodynamics. Since solids tend to disorder at high temperatures, lattice defects are intrinsically created. Two important types of ionic intrinsic disorder exist. Schottky disorder in a divalent oxide MO corresponds to a cation - anion pair leaving the interior of the crystal leaving vacant sites:

$$O \rightarrow V_M^{\prime\prime} + V_O^{\prime\prime}$$  \hspace{1cm} (3.6)
while Frenkel disorder involves a cation or anion leaving a normal lattice site to
an interstitial position:

\[ \text{O} \rightarrow V_{\text{O}^\text{\textsuperscript{\textbullet}}} + \text{O}^\text{\textsuperscript{\textbullet\textbullet}} \quad (3.7) \]

or

\[ \text{O} \rightarrow V_{\text{M}^\text{\textsuperscript{\textbullet\textbullet}}} + \text{M}^\text{\textsuperscript{\textbullet\textbullet}} \]

Generally, only one of these two mechanisms needs to be considered for a given
material, with the choice being determined by the crystal structure (i.e. open
structures encourage Frenkel disorder while closed-packed structures favor
schottky disorder). For fluorite and pyrochlore type oxides, Frenkel disorder on
the oxygen sublattice is the favored mechanism [18]. One may express Frenkel
oxygen disorder by:

\[ \text{O}^\text{\textsuperscript{\textbullet\textbullet}} \rightarrow V_{\text{O}^\text{\textsuperscript{\textbullet}}} + \text{O}^\text{\textsuperscript{\textbullet\textbullet}} \quad K_F = [V_{\text{O}^\text{\textsuperscript{\textbullet}}}][\text{O}^\text{\textsuperscript{\textbullet\textbullet}}] \quad (3.8) \]

where \( K_F \) represents the mass action equilibrium constant.

Statistical thermodynamics also requires that intrinsic electronic defects
be considered. The reaction:

\[ \text{nil} \rightarrow \text{e}^+ + \text{h}^- \quad K_e = np \quad (3.9) \]

describes the formation of electron (\( \text{e}^+ \)) - hole (\( \text{h}^- \)) pairs by thermal excitation
across the band gap. Here, the np product is constant and represented by the
mass action constant \( K_e \).
In a second type of carrier generation reaction, both ionic and electronic defects are created by equilibration of the solid with the gas phase. Assuming full ionization of defects, the oxidation reaction at high oxygen partial pressure describes the dissolution of oxygen into the lattice producing holes:

$$\frac{1}{2}O_2(g) \rightarrow O_1^{\cdot\cdot\cdot} + 2h^+ \quad K_{ox}=[O_1^{\cdot\cdot\cdot}]p^2PO_2^{-1/2}$$  \hspace{1cm} (3.10)

Conversely, at low oxygen partial pressures, the reduction reaction involves oxygen ions leaving the lattice thereby generating electrons and oxygen vacancies:

$$O_0^{X} \rightarrow V_0^{\cdot\cdot\cdot} + 2e^+ + \frac{1}{2}O_2(g) \quad K_{r}=n^2[V_0^{\cdot\cdot\cdot}]PO_2^{1/2}$$  \hspace{1cm} (3.11)

Both oxidation and reduction reactions described above are shown to result in the generation of ionic and electronic carriers or MIEC. However distinct to MIEC in oxides is that oxides do not always maintain the composition in which they are fabricated but can instead exchange oxygen with the ambient oxygen partial pressure. Thus the redox reactions described above lead to an imbalance in the ideal cation-to-anion ratio or "nonstoichiometry."

A third type of carrier generation reaction involves the addition of altervalent impurities. In this case, dopant impurities induce the formation of either charged electronic or ionic defects. To maintain charge balance, one may write an electroneutrality condition (ignoring defects on the cation sublattices) as:

$$2[V_0^{\cdot\cdot\cdot}] + p + [D^\cdot] = [A^\cdot\cdot\cdot] + n + 2[O_1^{\cdot\cdot\cdot}]$$  \hspace{1cm} (3.12)

in which $D^\cdot$ and $A^\cdot\cdot\cdot$ are donor and acceptor impurities respectively.
3.2. **Defect Chemical Modeling**

As outlined earlier, a main objective of this thesis is to gain insight into the mechanism of ionic and electronic conduction while extracting various key thermodynamic parameters. The concept of defect chemical modeling is one such approach where detailed information may be obtained. In this section, therefore, we present a defect chemical model for rare earth titanate/zirconate pyrochlore oxides with the following objectives in mind:

(a) deconvolute the ionic, n, and p type semiconductive components from the total conductivity

(b) determine the nature of the mobile oxygen species

(c) derive a number of key thermodynamic parameters including those related to intrinsic disorder

(d) describe several limiting boundary conditions for electrolyte application.

3.2.1 GENERALIZED MIXED CONDUCTION MODEL

For purposes of describing MIEC in pyrochlore oxides, it is sufficient to begin with equations (3.8), (3.9), (3.11), and (3.12) which provide four simultaneous equations for the four mobile defect concentrations $e^\prime$, $h^\prime$, $V_{o}^-$ and
\( \text{O}_1^{-} \). Under circumstances for which \( t_i \) is substantial, the conductivity data have been shown to conform to a defect model in which acceptor or donor impurities or quasi-Frenkel equilibrium between oxygen interstitials and oxygen vacancies control the minority electronic defects [6,18]. The key defect reactions are therefore described by anion Frenkel formation, reduction, and intrinsic electron-electron-hole formation:

\[
\begin{align*}
\text{O}_0^{-x} &\rightarrow \text{V}_0^{-} + \text{O}_1^{-} \\
\text{O}_0^{-x} &\rightarrow \text{V}_0^{-} + 2e^+ + 1/2\text{O}_2(\text{g}) \\
\text{nil} &\rightarrow e^+ + h^+
\end{align*}
\]

\[
\begin{align*}
K_F &= [\text{V}_0^{-}][\text{O}_1^{-}] \\
K_r &= [\text{V}_0^{-}][\text{n}^2\text{P}_2]^{1/2} \\
K_e &= \text{np}
\end{align*}
\]

For each of the above reactions, the equilibrium constant \( K_j \) is thermally activated and has an Arrhenius form of \( K_j = K_{j0}\exp(-E_j/kT) \) in which \( E_j \) represents the enthalpy of the reaction.

The fourth equation, electroneutrality, becomes:

\[
2[\text{V}_0^{-}] + p + [\text{D}^{-}] = [\text{A}'] + n + 2[\text{O}_1^{-}]
\]

in which \( \text{A}' \) and \( \text{D}' \) are, respectively, the singly ionized acceptors and donors.

Routinely, one often solves equations (3.8 - 3.12) piece-wise by employing the Brouwer approximation. Here, we wish to define more precisely the defect densities which account for both intrinsic and extrinsic conduction mechanisms.

Combining equations (3.8-3.12) and solving for \( [\text{V}_0^{-}] \) (\( n \) and \( p \) are assumed negligible) yields:
\[ [V_{O^{-}}] = \frac{1}{4} [I + (I^2 + 16K_I)^{1/2}] = R \] (3.13)

where \( I = [A^+] - [D^-] \) is the net acceptor impurity concentration. Substituting equation (3.13) into (3.9) and (3.11) gives:

\[ n = \left( \frac{K_r}{R} \right)^{1/2} \text{PO}_2^{-1/4} \] (3.14)

\[ p = K_e \left( \frac{R}{K_r} \right)^{1/2} \text{PO}_2^{1/4} \] (3.15)

For the three mobile species, the corresponding partial conductivities are:

\[ \sigma_i = 2q[V_{O^{-}}] \mu_i \] (3.16)

\[ \sigma_e = q\eta \mu_e \] (3.17)

\[ \sigma_h = q\rho \mu_h \] (3.18)

where \( \mu_i, \mu_e, \) and \( \mu_h \) are the oxygen vacancy, electron, and hole mobilities respectively. Combining equations (3.13-3.15) with (3.16-3.18) gives an expression for the total conductivity:

\[ \sigma_{\text{tot}} = \sigma_i + \sigma_e + \sigma_h \] (3.19)

\[ = A + B(\text{PO}_2)^{-1/4} + C(\text{PO}_2)^{1/4} \]

in which the coefficients \( A, B, \) and \( C \) are obtained from equations (3.13 + 3.16), (3.14 + 3.17) and (3.15 + 3.18), respectively.
By using such a defect model, experimental data can be fit to equation (3.19) to reveal the regimes where electrons, ions, or holes dominate [55]. Figure 3.1 shows one such fit for the pyrochlore composition $(\text{Gd}_0.9975\text{Ca}_0.0025)^2\text{Ti}_2\text{O}_7$. The solid line in the figure represents an iterative fit to equation 3.19 while the dashed lines represent the individual contributions of $\sigma_e$, $\sigma_i$ and $\sigma_h$ to the total conductivity.

3.2.2 ACCEPTOR DOPED TITANATE PYROCHLORES

As noted in equation (3.13), the oxygen vacancy concentration $[\text{V}_o^{-}]$ is not a simple function of one variable but instead a function of both the Frenkel equilibria ($K_F$) and the extrinsic net acceptor-donor density ($I$). With this in mind, one must express the defect concentration in the form of a polynomial [56] or define specific limiting cases for the conductivity parameters. One such limiting case applies for the extrinsic pyrochlores $A_2\text{Ti}_2\text{O}_7$ with $A=$Sm,Gd,Y which exhibit low levels of frenkel disorder. In these materials, aliovalent impurities dominate the mixed conduction model such that several simplifications can be made. First, with $16K_F << I^2$, the electroneutrality expression may be simplified to:

$$2[\text{V}_o^{-}] = I = [A']$$  \(3.20\)

in which $A'$ is a singly ionized acceptor. Combining equations (3.11) and (3.9) with (3.20) and solving for $[\text{V}_o^{-}]$, $n$, and $p$ yields:

$$[\text{V}_o^{-}] = [A']/2$$  \(3.21\)
Figure 3.1 Log $\sigma$ vs log $PO_2$ plot for the pyrochlore composition $(Gd_{0.9975}Ca_{0.0025})_2Ti_2O_7$ at 1000°C. The solid line in the figure represents an iterative fit to equation 3.19 while the dashed lines represent the individual contributions of $\sigma_e$, $\sigma_i$ and $\sigma_h$ to the total conductivity.
\[ n = (2K_T[A'])^{1/2}PO_2^{-1/4} \]  
(3.22)

\[ p = K_e([A']/2K_T)^{1/2}PO_2^{+1/4} \]  
(3.23)

in which \( V_{O^2} \), \( n \), and \( p \) are shown only to be a function of \( A' \) and/or \( K_T \). The mobility expression also may be simplified. Assuming a dilute (unassociated) solution, the vacancy concentration is fixed by acceptor impurities, and \( \mu_i \) is given by:

\[ \mu_i = \sigma_i/q[A'] \]  
(3.24)

Next it is of interest to examine the activation energies connected with the conductivities. Given that ionic conduction is always activated, \( \mu_i \) has the form:

\[ \mu_i = \mu_i^0/T \exp(-E_m/kT) \]  
(3.25)

where \( E_m \) is the migration energy. If the electrons are small polarons, they will have a similar expression for their mobility:

\[ \mu_e = \mu_e^0/T \exp(-E_h/kT) \]  
(3.26)

where \( E_h \) is the so-called hopping energy. Consequently, from Eqs. (3.16-3.18), (3.21-3.23) and 3.25-3.26 one obtains the following expressions for the activation energies for ionic and \( n \) and \( p \)-type conductivities respectively:

\[ E_{ion} = E_{mig} \]  
(3.27)
\[ E_{\text{electron}} = E_{r}/2 + E_{h} \quad (3.28) \]

\[ E_{\text{hole}} = E_{g} \cdot E_{r}/2 - E_{h} \quad (3.29) \]

where \( E_{\text{mig}}, E_{r}, E_{h}, \) and \( E_{g} \) represent the activation enthalpies for migration, reduction, electron hopping and band gap respectively.

### 3.2.3 INTRINSIC CONDUCTION AND FRENKEL ENERGY

A second limiting case to be considered is one of intrinsic control. In previous publications, Moon and Tuller [6,18] demonstrated that intrinsic disorder controls the ionic conductivity in undoped \( \text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7 \) (GZT) solid solutions with \( x>0.3 \). Given that GZT \( x>0.3 \) represent intrinsic disorder alone, the condition arises such that \( 16K_F \gg I^2 \). Equations 3.13, 3.14 and 3.15 can then be simplified to read:

\[ [V_{O^{2-}}] = (K_F)^{1/2} \quad (3.30) \]

\[ n = (K_F^{1/2}K_F^{-1/4})P_{O_2}^{-1/4} \quad (3.31) \]

\[ p = K_0(K_F^{-1/2}K_F^{1/4})P_{O_2}^{+1/4} \quad (3.32) \]

In GZT \( x>0.3 \) Moon and Tuller also observed that the degree of intrinsic disorder is reflected in the pre-exponential term \( \sigma^0 \) rather than in the ionic activation energy, \( E_i \). By employing an atomistic model for ionic conduction one therefore obtains a direct expression for \([V_{O^{2-}}]\):
\[ \sigma_0 = \frac{4ae^2d^2N_0v_0[V_o^-]_{\exp}[\Delta S_m/k]}{k} \]  
(3.33)

where

\[ \sigma_0 \] = the pre-exponential constant for ionic conduction
\[ \alpha \] = geometrical factor
\[ e \] = the elementary charge,
\[ d \] = the carrier jump distance
\[ v_0 \] = the jump attempt frequency
\[ N_0 \] = the number of oxygen 48f sites per unit volume
\[ V_o^- \] = the fractional oxygen 48f site vacancy concentration
\[ S_m \] = the migration entropy
\[ k \] = Boltzmann's constant.

Similar to the doped case, one may also examine the activation energies for intrinsic conduction. By combining equations (3.16-3.18), (3.30-3.32), and (3.25-3.26) one obtains the following expressions for the activation energies for ionic and n and p-type conductivities:

\[ E_{\text{ion}} = E_F/2 + E_{\text{mig}} \]  
(3.34)

\[ E_{\text{electon}} = E_r - E_F/4 + E_h \]  
(3.35)

\[ E_{\text{hole}} = E_e - E_r/2 + E_F/4 - E_h \]  
(3.36)

Thus by comparing activation energies obtained from the doped and undoped cases, one should be able to extract quantities for \( E_{\text{mig}}, E_F, \) and \( E_r \). In section
6.1.3.2 we obtain such quantities for the pyrochlore composition
Gd₂(Ti₀.75Zr₀.25)₂O₇ (GZT25).

3.2.4 MIEC DOMAIN BOUNDARIES

Until now, we have used a defect chemical model to obtain generalized
expressions for σᵢ and σₑ under several limiting conditions. However little has
been said about the relative importance of the ionic/electronic carrier ratio or the
extent of the electrolytic domain. In this section we extend our defect chemical
model to derive quantitative expressions for electrolytic domain boundaries to
predict how the relative mix of ionic and electronic defects are dependent on
intrinsic defects, extrinsic dopants, and dopant-charge association.

Expressions for the ionic and electronic conductivities σᵢ and σₑ have
been derived from the "A", "B", and "C" fitting parameters of equation 3.19. To
obtain expressions for the electrolytic domain boundary, one sets the ratio of the
ionic and n-type or ionic and p-type conductivity to a particular value, such as
unity, and solves for the PO₂. If we define Pₙ as the PO₂ at which σᵢ=σₑ and Pₚ
at which σᵢ=σ_p, we can, with the aid of equation 3.19 derive the following
expressions:

\[ \ln Pₙ = -4[(Eᵦ - Eᵢ)/k]1/T + 4\ln(Bₒ/Aₒ) \]  \hspace{1cm} (3.37)

and

\[ \ln Pₚ = -4[(Eᵦ - E_p)/k]1/T + 4\ln(Aₒ/Cₒ) \]  \hspace{1cm} (3.38)
where $A_0$, $B_0$, and $C_0$ are the pre-exponential terms and $E_i$, $E_n$, and $E_p$ are the exponent terms in $A$, $B$, and $C$, respectively. Similar to the conductivity expressions in section 3.2.1, equations (3.37) and (3.38) may be simplified for several limiting conditions. For extrinsic (unassociated) controlled conductivity, equations (3.37) and (3.38) may be re-written as:

$$P_n = 4K_r^2[A']^{-6}(\mu_i/\mu_e)^4$$  \hspace{1cm} (3.39)

and

$$P_p = 4K_r^2[A']^2/K_i^4(\mu_i/\mu_e)^4$$ \hspace{1cm} (3.40)

where $n$ and $p$-type domain boundary positions are shown to depend only on the parameters, $[A']$, $K_r$, $K_i$, $\mu_i$, and $\mu_e$.

Similar expressions for the domain boundary positions ($P_n$, $P_p$), domain boundary width ($P_p/P_n$), and ionic conductivity ($\sigma_i$) under the three limiting case of (a) intrinsic Frenkel disorder, (b) unassociated acceptor doping, and (c) associated acceptor doping are summerized in table 3.1 [57]. Although a detailed analysis of these expressions will not be presented here, they will be further addressed in the results and discussion sections of this thesis.
<table>
<thead>
<tr>
<th></th>
<th>$\sigma_i$</th>
<th>$P_n$</th>
<th>$P_p$</th>
<th>$P_p/P_n$</th>
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<tr>
<td><strong>Case #1</strong></td>
<td><em>Intrinsic</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2e(K_F)^{1/2} \mu_i$</td>
<td>$\frac{K_R^2}{16K_F^3} \frac{\mu_e}{\mu_i}$</td>
<td>$\frac{16K_R^2K_F}{K_i^4} \frac{\mu_i}{\mu_h}$</td>
<td>$\frac{256 K_F^4}{K_i^4} \frac{\mu_i^2}{\mu_e \mu_h}$</td>
</tr>
<tr>
<td><strong>Case #2</strong></td>
<td><em>Dopant</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2e(\frac{A'}{2}) \mu_i$</td>
<td>$\frac{4K_R^2}{[A']^6} \frac{\mu_e}{\mu_i}$</td>
<td>$\frac{4K_R^2[A']^2}{K_i^4} \frac{\mu_i}{\mu_h}$</td>
<td>$\frac{[A']^8}{K_i^4} \frac{\mu_i^2}{\mu_e \mu_h}$</td>
</tr>
<tr>
<td><strong>Case #3</strong></td>
<td><em>Associated</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2e(K_A) \mu_i$</td>
<td>$\frac{K_R^2}{16K_A^6} \frac{\mu_e}{\mu_i}$</td>
<td>$\frac{16K_R^2K_A^2}{K_i^4} \frac{\mu_i}{\mu_h}$</td>
<td>$\frac{256 K_A^8}{K_i^4} \frac{\mu_i^2}{\mu_e \mu_h}$</td>
</tr>
</tbody>
</table>

Table 3.1 Expressions for the ionic conductivity ($\sigma_i$) electrolytic domain boundary positions ($P_n$, $P_p$) and width ($P_p/P_n$) under the limiting cases of (a) intrinsic f renkel disorder, (b) unassociated acceptor doping, and (c) associated acceptor doping.
3.3 Limitations in Evaluating MIEC

3.3.1 MEASUREMENT TECHNIQUES

Surprisingly, only a small subgroup of oxides has been identified as MIEC materials. Part of the reason, as outlined above, is due to the high mobility of electrons relative to ions. However other limitations can arise. One such limitation develops in determining MIEC experimentally.

Whether the material of interest is primarily an ionic or MIEC it is nevertheless of interest to separate out the individual ionic and electronic contributions from the total conductivity. The method outlined above (e.g., defect chemical modeling) is one such "indirect" method in which the contributions of the majority and minority charge carriers can be extracted by measuring the atmosphere dependent electrical conductivity. However this technique requires that both $P_{O_2}$ independent and dependent conductivities are obtainable and that the ratio of $\sigma_{\text{electronic}}/\sigma_{\text{ionic}}$ is easily evaluated. Otherwise, thermodynamic equilibrium constants for the minority carriers become difficult or impossible to extract.

In principle, a number of other "direct" experimental techniques are available. These include: (1) the use of blocking electrodes (e.g., Hebb-Wagner) [58,59], (2) measurement of open circuit voltages under oxygen activity gradients [60], (3) permeation currents [61], and (4) diffusion measurements [62]. Although any of these methods may be used to obtain quantitative information on majority and minority charge carriers, we note several drawbacks. For example, each of the above techniques are used primarily for determining the electronic conductivity in the ionic domain of a mixed conductor. For the reciprocal case (i.e. determining the ionic conductivity in a semiconducting oxide)
the measurements are often inaccurate [63]. With the Hebb-Wagner approach for example, a blocking electrode is used to block the predominant charge carrier and thus enables measurement of the minority carriers. However for the specific case of a semiconducting MIEC, a suitable blocking electrode must exist that conducts the same ionic specie as the MIEC and has high resistance to electronic current. Further, this electrode must be mechanically and chemically compatible with the MIEC and allow no leakage of oxygen ions or gas species within or around the sample.

Leakage also presents a problem in the open circuit EMF technique. In this method, one measures the open circuit EMF under a chemical activity gradient and compares its value to the theoretical Nernst voltage \( V_{th} \) given by:

\[
V_{th} = \frac{RT}{4F} \ln \left( \frac{PO_2^+/PO_2^-}{} \right)
\]

where \( R \) is the universal gas constant and \( F \) is the Faraday constant. However if leaks occurs, the ratio of \( PO_2^+/PO_2^- \) is unknown. Further, when the sample is an electronic or mixed conductor, the open circuit potential may be too small for reliable measurements and surface polarization problems are more likely to effect the analysis.

Finally, with diffusion and permeation techniques, difficulties may arise due to experimental limitations. In diffusion experiments for example, besides being costly and time consuming, the rate controlling step often results from surface exchange or grain boundary diffusion. In the permeation method, instrument control may present a problem. For example, if the permeation flux is low, as is the case for a semiconductive oxide with oxygen ions the minority carriers, a highly accurate gas flow regulator is required.
3.3.2 SHORT CIRCUIT CURRENT TECHNIQUE

In this thesis, a primary objective is to determine the ionic conductivity in a semiconducting oxide (i.e. Gd$_2$Ti$_2$O$_7$). Thus, for the first time, a novel measurement technique known as the short circuit current or "zero driving force" method is applied. The new method, as proposed by I. Riess [64] enables the determination of the partial conductivities $\sigma_e$, and $\sigma_i$, in a semiconducting oxide without the use of blocking electrodes. Like the traditional blocking Hebb - Wagner method, an ionic or electronic dc current is passed through the MIEC. However, the removal of the undesired charge carriers is not accomplished with a blocking electrode but rather by eliminating their driving force by shorting the electrical potential that makes those species flow through the MIEC. A chemical driving force however maintains an ionic flow between the two electrodes.

Riess derived an expression for the total current $I_t$ flowing through a MIEC under a chemical gradient given by

$$\mu_X^L - \mu_X^0 = -qV_{th}$$  \hspace{1cm} (3.42)

where $\mu_X^L$ and $\mu_X^0$ are the chemical potentials of $X$ at electrodes $x=0$ and $L$, respectively, and $V_{th}$ is the theoretical Nernst voltage. The expression for $I_t$ is given by

$$I_t = (V_{th} - V)/(R_i + R_{i,c}) - V/(R_e + R_{e,c})$$  \hspace{1cm} (3.43)

where $V$ is the measured voltage across the cell, $R_i$ and $R_e$ are the ionic and electronic resistivities of the MIEC and $R_{i,c}$ and $R_{e,c}$ the respective ionic and
electronic "contact" resistances. By short circuiting the cell such that $V=0$ and thus the electronic current $I_e=0$ one obtains

$$I_{SC} = \frac{V_{th}}{(R_i + R_{i,c})}$$  \hfill (3.44)

where the short circuit current, $I_{SC}$, is now solely the ionic current. Under conditions of negligible contact resistance

$$R_i = \frac{V_{th}}{I_{SC}}$$  \hfill (3.45)

The basic experimental set up for the short circuit current method is given in figure 3.2. The diagram shows that $I_{SC}$ may be obtained experimentally from an external resistor ($R_{ext}$) in series with a measuring voltmeter (i.e. $I_{SC}$ in equation 3.45 is given by $I_{SC} = \frac{V_{SC}}{R_{ext}}$). Riess [64] however has pointed out that for this expression to be valid, the voltage $V$ across the measuring device must be much less in magnitude than the open circuit voltage $V_{OC}$. This condition is satisfied when the electronic resistance of the sample is much greater than the external resistor in parallel. This condition and the significance of the contact resistance $R_{i,c}$ will be further examined in the results and discussion parts of this thesis.
Figure 3.2 A schematic of the experimental set-up for the "short circuit current" method [64].
4 EXPERIMENTAL METHODS

4.1 Sample Preparation and Characterization

4.1.1 POWDER PREPARATION

Powder processing was performed using a "liquid-mix" technique known as the Pechini processing method [65]. Such a "liquid-mix" technique was chosen since it provided homogeneous air-stable stock solutions with well-defined cation mole ratios and near atomic scale mixing.

According to the Pechini process, a compound of the desired metal is first dissolved in a citric acid-ethylene glycol mixture. One such solution is made for each of the desired elements which, for our particular case, involved solutions of gadolinium, samarium, yttrium, titanium, zirconium and citrates for the dopants Ca$^{2+}$, Mg$^{2+}$, Sr$^{2+}$ and Al$^{3+}$. As shown schematically in figure 4.1, the first step in preparing the transition metal and dopant-based mixtures was to dissolve an alkoxide or carbonate directly into a citric acid-ethylene glycol solution. However for the rare earth elements, care was taken to remove the nitrate anions. In this case, by dissolving the rare earth metal nitrate in water followed by precipitation with ammonia, a hydroxide was formed. Upon filtration, this hydroxide was then dissolved directly into the ethylene glycol and citric acid mixture.

After "stock" solution preparation, the solutions were assayed and mixed in the required proportions to produce the desired oxide stoichiometry. Although no precipitate was observed, we note the solutions were often viscous and therefore mixed for several hours to ensure homogeneity. After mixing, the solutions were heated to condense the acid and alcohol groups. The crosslinked polyester polymer mass that formed was further heated to drive off water and
Figure 4.1 The Pechini powder processing method used for preparation of pyrochlore oxides.
excess ethylene glycol. This resulted in a hard crosslinked polymeric solid. The solid was then charred in air at 400 °C to partially burn off the organic material followed by comminution of the solid into powder. Finally, the powder was calcined at 700°C - 850°C to form the appropriate oxide phase.

4.1.2 PREPARATION OF PELLETS

Calcined powders were pressed into cylindrical pellets using a 3/4" diameter stainless steel die, under a pressure of 5 kpsi. The surfaces of the pellets were then cleaned by lightly rubbing them with SiC paper (grit No. 1200). The resulting pellets were put in a latex bag, evacuated, and isostatically pressed at 45 kpsi.

Sintering of the pellets involved placing the samples in platinum-lined alumina boats and heating in air at 3°/min to a temperature of 1600°C. After soaking for 12 -16 hours the pellets were slowly cooled at 2°/min to room temperature. A programmable Lindberg tube furnace (model #54434) was used for the heat treatment.

4.1.3 DENSITY MEASUREMENTS

To measure the density of the pellets, two methods were used. In the first, the physical dimensions were measured with a micrometer followed by weighing on a microgram balance. In the second, Archimedes Principle was applied. In this case, the pellets were suspended from a spring balance with a thin piece of thread and weighed both in air and immersed in water. The density of the sample was found from the relation:
\[ \rho_{\text{sample}} = \frac{m_{\text{air}}}{(m_{\text{air}} - m_{\text{water}})} \times \rho_{\text{water}} \]  \hspace{1cm} (4.1)

### 4.1.4 X-RAY DIFFRACTION

A Rigaku RU-300 powder diffractometer in line with a Digital Equipment Corp. MicroVax host computer was used for the diffraction measurements. The diffractometer had a rotating anode with a maximum electron beam power of 18kW. Typical operating parameters were \( \lambda = \text{CuK}_\alpha \), a graphite diffracted-beam monochromator, x-ray tube voltage of 40kV, tube current of 200 mA, scan rate of 1° 2θ/minute and a scan range of 10° to 130°.

Lattice parameters were determined for several of the Al doped compositions. In this case, a Si standard was mixed in with the powders and high angle scans (70° - 130°) were performed. The Si standard provided a reference for calibrating the exact location of the peaks as a linear extrapolation of the sample peak was made from two nearby Si reference peaks. The accuracy of this method is noted as ±0.0001 Å.

### 4.1.5 MICROSTRUCTURE/COMPOSITIONAL ANALYSIS

In order to examine sample porosity and homogeneity, both fractured and diamond cut surfaces were periodically viewed under a scanning electron microscope. An ISI SMS Super II tabletop SEM equipped with Energy Dispersive X-ray analysis (EDAX) and back-scattered imaging was used for the analysis. These two features provided qualitative checks of cation distribution and phase homogeneity.
To quantify the cation stoichiometry, further analysis was performed using Wavelength Dispersive Spectrometry (WDS). A JEOL Superprobe 733 microprobe equipped with a Tracer Northern TN-550 x-ray system was used to determine atomic percentages and weight percentage of oxides. All analysis was done on bulk samples which first were polished to 1µ and then coated with a thin film of carbon. The concentration and distribution of metallic elements were checked using Gd metal, TiO₂ and a homogeneous Ca-silicate glass as standards.

4.2 Electrical Measurements

4.2.1. TEST CONFIGURATION AND MEASUREMENT CONDITIONS

The majority of electrical tests were made on polycrystalline sintered-compact bars approximately 2mm x 3mm x 8mm. These bars were cut from sintered pellets using a diamond saw. Notched groves were placed on each end of the bars onto which sputtered Pt and Pt paste was deposited. (In most cases both deposition methods were employed to ensure a large, reproducible contact area). A chemically pure Pt wire (0.001") was twisted inside each groove for electrical contact.

The sample holder for conductivity measurements was designed to be gas-tight and accomodate bar shaped samples. The apparatus consisted of 3 parallel Al₂O₃ four-bore tubes (1/8") into which platinum wires were added. These wires were then spot welded to the twisted wires on the sample. The

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sample temperature was monitored with a platinum/rhodium thermocouple located within 1 mm of the sample.

For the bar-shaped samples, electrical tests were made in a temperature range of 300 - 1100°C. Samples measurements were taken every 50°C on cooling. For the \( \text{PO}_2 \) dependence, either pre-mixed (Matheson) oxygen/argon or carbon dioxide/carbon monoxide mixtures were used in which the oxygen fugacity was calculated from the thermodynamic values and periodically checked with a stabilized \( \text{ZrO}_2 \) galvanic cell. The \( \text{PO}_2 \) range was 1 atm to approximately \( 10^{-20} \) atm.

4.2.2 IMPEDANCE SPECTROSCOPY

Electrical conductivity measurements were made using a variety of techniques, with the vast majority of measurements performed via complex impedance spectroscopy. Impedance spectroscopy allows for separation of grain-boundary, intragrain and electrode resistivities in polycrystalline ceramics by obtaining an ac frequency dependent response [66]. In our case, a Hewlett Packard 4192a LF Impedance Analyzer was used to monitor the sample response in the frequency range of 5 Hz to 13 mHz. In order to interpret experimental data however, one must develop a theoretical model for comparison. Since each component (bulk, grain boundary, and electrode) represents a distinct dielectric relaxation process with a characteristic relaxation time \( \tau = RC \), our model consists of a series of parallel resistor-capacitor (RC) networks. For a single RC component, the impedance is given by:

\[
Z(w) = Z'(w) + iZ''(w) \tag{4.2}
\]
with

$$Z'(w) = \frac{(1/R)}{(1/R)^2 + (wC)^2}$$

(4.3)

and

$$Z''(w) = \frac{(wC)}{(1/R)^2 + (wC)^2}$$

(4.4)

where $w$ is the angular frequency, $Z'$ the real and $Z''$ the imaginary part of the impedance $Z$. A plot of $Z''$ vs. $Z'$ should thus yield a semicircle with radius $R/2$ with the peak of the semicircle occurring at the Debye relaxation frequency, $w_0 = 1/(RC)$ [66]. If the relaxation frequencies of the three distinct processes are far apart, a series of semicircles will be observed. The equivalent circuit and deconvoluted semicircles under such conditions is shown schematically in figure 4.2.

Experimentally, however, obtained spectra are often quite distinct from the idealized spectra of figure 4.2. For example, if the semicircles overlap or sample heterogeneity exists, (i.e. a statistical distributions of relaxation processes) a depressed semicircle may result. Several researchers have modeled this depression by a depression angle $\alpha \pi/2$ [67]. In this case, $\alpha \pi/2$ represents the degree of semicircle depression below the $Z'$ axis as shown schematically in figure 4.3.

In addition to impedance spectroscopy, both 2-probe and four-probe dc techniques were used to separate electrode contributions. A Hewlett Packard 4140b Picoammeter Programmable voltage source and a Keithley multimeter were used for this analysis.
Figure 4.2 The equivalent circuit and deconvoluted semicircles for three distinct processes (e.g., bulk, grain boundary, and electrode). If the relaxation frequencies of the three processes are far apart, a series of semicircles will be observed [66].
Figure 4.3 Two semicircles, depressed below the $Z'$ axis by different amounts. The depression angles are marked $\alpha_1 \pi/2$ and $\alpha_2 \pi/2$ respectively [67].
4.2.3 Short Circuit Technique

As noted earlier, the short circuit current method is a new experimental approach recently developed by I. Riess to measure the minority ionic conducting species in mixed conducting oxide [64]. In this technique, the removal of the undesired charge carrier is not accomplished with a blocking electrode but rather by eliminating the driving force that makes those species flow through the MIEC.

The experimental apparatus used for the Riess method is shown schematically in figure 4.4. The set-up consists of two separated quartz tubes (an inner an outer sealed tube) in which two different gases are used. Separating the gases is a platinum gasket which is compressed against the cylindrical specimen. Gases of controlled PO$_2$ are then passed over each face of the sample, which had been previously electroded by painting and firing-on Pt paste. Contacts to each face are then made by pressing a thermocouple tube with a Pt/ Pt-10% Rh thermocouple bead at its end against the sample to which a Pt mesh is welded to each electrode.

For the zero driving force "test condition", the parameters measured were the short circuit current $I_{SC}$, in the external circuit, and the open circuit voltage voltage $V_{OC}$. In calculating $I_{SC}$, the sample electrodes were shorted through an external resistor (under a chemical activity gradient) such that the contribution of electrons/holes to the current was set to near zero. In the actual experiment resistors ranging from 1-500 $\Omega$ were used with a Keithley voltmeter measuring the induced voltage across them. Stable and reproducible voltages were obtained for $R$ values between 10-500 $\Omega$. This condition also satisfied the requirement of $R_e$(MIEC) $>> R_{ext}$ with the electronic resistance of the sample, $R_e$(MIEC) between $10^8$ - $10^6$ $\Omega$ in the temperature range of interest.
Figure 4.4 The experimental apparatus used in the short circuit current measurement.
In calculating $V_{OC}$, several approximations were made. In this case, the open circuit voltage $V_{OC}$ was taken to be equivalent to the actual imposed $V_{th}$ given by equation 3.41. This assumption was valid provided that the experimental conditions fall mostly within the electrolytic domain [64]. Secondly, gas leaks through or around the sample must be minimized for this assumption to be accurate.
5 RESULTS

The results section is broken into three main parts. Section 5.1 describes the effects of aliovalent dopants on transport properties of titanate pyrochlores. In particular, we examine the role of dopant size, charge, site location, and concentration in the pyrochlore oxides Gd$_2$Ti$_2$O$_7$, (GT), Y$_2$Ti$_2$O$_7$, (YT), and Sm$_2$Ti$_2$O$_7$, (ST). Section 5.2 then describes dopant effects in zirconate pyrochlores. We examine La$_2$Zr$_2$O$_7$ along with the pyrochlore solid solution Gd$_2$(Zr$_{0.25}$Ti$_{0.75}$)O$_7$. Finally, in section 5.3 we present our short-circuit current results for (Gd$_{0.975}$Ca$_{0.025}$)$_2$Ti$_2$O$_7$.

5.1. ACCEPTOR DOPED TITANATE PYROCHLORES

5.1.1 "A" SITE (Ca) DOPING IN Gd$_2$Ti$_2$O$_7$

5.1.1.1 Solubility and Phase Characterization

We begin by examining several structural features associated with the "A" site substitution of Ca for Gd in (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$. Figures 5.1 - 5.3 give x-ray powder diffraction patterns for nominally undoped and Ca-doped compositions. For the undoped sample (figure 5.1), a total of nineteen diffraction peaks are observed in the 2θ range of 10-100° with all peaks indexed to the pyrochlore phase. Figures 5.2 shows the diffraction patterns for (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ with x=0.05. Similar to the undoped sample, all peaks in the pattern are identified as
Figure 5.1  X-ray powder diffraction pattern for Gd$_2$Ti$_2$O$_7$.
Figure 5.2  X-ray powder diffraction pattern for $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ with $x=0.02$. 
Figure 5.3  X-ray powder diffraction pattern for \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\) with \(x=0.15\).
pyrochlore with no extra peaks or evidence of second phase. Such a single phase diffraction pattern was found reproducible in each of the Ca doped compositions with $x=0.0$, 0.0025, 0.05, and 0.10. The sole noted exception was found for $x=0.15$. In this sample (figure 5.3), extra diffraction peaks were observed at $33^\circ$, $47^\circ$, $76.5^\circ$, $87^\circ$ and $97^\circ$. These peaks were indexed by the JCPDS files as CaTiO$_3$.

Lattice parameters for each Ca doped composition were obtained from high angle peaks in the diffraction patterns. Values ranged from 10.190 Å to 10.195 Å with no apparent trend with Ca doping. Caution however is noted in interpreting these results. Since no reference standard was used in the powders (i.e. Si standard), it would seem inappropriate to draw any conclusions about the dependence of lattice parameter on Ca content. We do note that the relatively small difference in size between Ca$^{2+}$ and Gd$^{3+}$ ($r=1.12$ Å vs $1.06$ Å) should result in a correspondingly small change in lattice parameter. In fact, the predicted lattice parameter change for a Ca$^{2+}$ substitution for Gd$^{3+}$ is similar in magnitude to the quoted error margin of the instrument; $\pm 0.002$Å.

We next examine several microstructural features of (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$. Figures 5.4 and 5.5 show scanning electron micrographs for the $x=0.02$ and 0.15 samples. Both are characterized by a high degree of porosity estimated at 10 - 20 volume%. This value is considerably higher than that found from dry weight or the Archimedes method which yielded densities of 89 - 94% theoretical. The deviation between the techniques is not yet clear. However, the high porosity in the SEM micrographs appears to reflect the poor sintering characteristics of the samples. Since the pores are primarily intergranular, further densification is believed possible.

A second feature noted in the micrographs is the grain size which varies between 1 - 10 µm. The grains appear to be equiaxed and uniformly distributed.
Figure 5.4 Scanning electron micrograph of (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ with $x=0.02$
Figure 5.5 Scanning electron micrograph of $(\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7$ with $x=0.15$
throughout the samples. No apparent trend of grain size versus Ca concentration was established.

Quantitative analysis of the cation distribution was performed using wavelength dispersive spectroscopy (WDS). Figures 5.6 and 5.7 show WDS backscattered images of the Ca distribution in \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\) with \(x=0.02\) and 0.15. (The white dots in these photos represent the Ca concentration as obtained after calibration of the elements). For the \(x=0.02\) sample, the distribution is uniform throughout except in dark regions which were later identified as voids or polishing pull outs. The concentration of Ca was found to be 0.35 atom\% or 2.0 mole\%, in excellent agreement with the expected stoichiometry. In contrast, the \(x=0.15\) sample (figure 5.7) shows several regions which are Ca rich. These regions which are found in the middle and right side of the photo are approximately 1 - 2 nm in size and not interconnected. All compositions with Ca concentrations greater than 5.0 mole\% showed these Ca-rich regions.

The results of chemical analyses for each of the \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\) compositions is summarized in table 5.1. Of special note is the maximum "bulk" Ca concentration of 7.0 mole\% even in the \(x=0.10\) and \(x=0.15\) samples. This result appears to reflect a solubility limit of 7.0 mole\% Ca. The 10.0 and 15.0 mole\% Ca samples show a second Ca rich phase which the WDS calibration identified as \((\text{Ca}_{1-x}\text{Gd}_x)\text{TiO}_3\) with \(x=0.3\).

5.1.1.2 Partial-Pressure Dependence of Conductivity

We begin by describing the oxygen partial-pressure dependence of the conductivity for \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\). (In this section and throughout this thesis,
Figure 5.6 Wavelength Dispersive Spectroscopy (WDS) dot map image of the Ca distribution in $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ with $x=0.02$. 
Figure 5.7 Wavelength Dispersive Spectroscopy (WDS) dot map image of the Ca distribution in \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\) with \(x=0.15\).
<table>
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<th>COMPOSITION</th>
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<th>Ti atom%</th>
<th>Ca atom%</th>
<th>O atom%</th>
</tr>
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<tr>
<td>((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7) x=0.0025</td>
<td>19.07</td>
<td>18.61</td>
<td>0.06</td>
<td>62.24</td>
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<tr>
<td></td>
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<td></td>
<td>0.22 mole%</td>
<td></td>
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<tr>
<td>((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7) x=0.02</td>
<td>19.08</td>
<td>18.65</td>
<td>0.35</td>
<td>61.92</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>2.0 mole%</td>
<td></td>
</tr>
<tr>
<td>((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7) x=0.10</td>
<td>17.91</td>
<td>18.66</td>
<td>1.27</td>
<td>62.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.0 mole%</td>
<td></td>
</tr>
<tr>
<td>((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7) x=0.15</td>
<td>18.18</td>
<td>18.75</td>
<td>1.25</td>
<td>61.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.9 mole%</td>
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</tr>
</tbody>
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Table 5.1 WDS chemical analysis for Ca doped \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\).
we first present the partial pressure dependence followed by a more detailed
description of ionic and electronic conductivities in subsequent sections).

Figures 5.8 - 5.14 give log \( \sigma \) vs log PO\(_2\) plots for \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\) with
\(x=0.0\) (#1) [68], 0.0 (#2), 0.0025, 0.02, 0.05, 0.10, and 0.15. The solid lines in the
figures represent interactive least squares fits to equation 3.19. In each case, the
experimental data (symbols) are shown to fit the defect model quite well. The
noted exceptions are found for \(x=0.0\) and 0.0025. In these samples, a -1/4 to
-1/6 transition is observed at low PO\(_2\)'s which represents a transition from
acceptor doped to redox controlled (i.e. the material is oxygen deficient with the
conductivity expressed by equation 3.11 and \(n=2[V_{0\cdot}\cdot]\)). The data points in these
transition regions were not used in the model fit.

The log \( \sigma \) vs log PO\(_2\) plots in figures 5.8 and 5.9 are representative of
nominally undoped \(\text{Gd}_2\text{Ti}_2\text{O}_7\). Two such plots are given in order to highlight an
important feature of the undoped material - namely its "extrinsic" behavior.
Although both samples were processed under nominally the same conditions
(i.e. calcination/pressing/firing) the starting batch powders were different. With
different levels of background impurities and/or cation stoichiometry, striking
differences in electrical properties were observed. While the first sample shows
only n-type electronic conductivity the second shows both n-type electronic and
PO\(_2\)-independent conductivity. The magnitude of \(\sigma\) is also different. The
difference in background impurity concentration results in a much higher
conductivity for the latter sample.

As Ca\(^{2+}\) is successively added to \(\text{Gd}_2\text{Ti}_2\text{O}_7\), several observations are
apparent. First, while nearly all samples exhibit an n-type conductivity at low
PO\(_2\) followed by a PO\(_2\)-independent conductivity at intermediate PO\(_2\)'s and p-
type conduction at high PO\(_2\), the extent of each partial pressure regime changes
with increasing Ca. Most striking is the growth of the PO\(_2\) independent
Figure 5.8 Log conductivity as a function of log oxygen partial pressure for Gd$_2$Ti$_2$O$_7$ (sample#1).
Figure 5.9 Log conductivity as a function of log oxygen partial pressure for Gd$_2$Ti$_2$O$_7$ (sample#2).
Figure 5.10 Log conductivity as a function of log oxygen partial pressure for $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ with $x=0.0025$. 
Figure 5.11 Log conductivity as a function of log oxygen partial pressure for \((\text{Gd}_{0.98}\text{Ca}_{0.02})_2\text{Ti}_2\text{O}_7\) with \(x=0.02\).
Figure 5.12 Log conductivity as a function of log oxygen partial pressure for \((\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\) with \(x=0.05\).
Figure 5.13 Log conductivity as a function of log oxygen partial pressure for \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\) with \(x=0.10\).
Figure 5.14  Log conductivity as a function of log oxygen partial pressure for $(\text{Gd}_{0.85}\text{Ca}_{0.15})_2\text{Ti}_2\text{O}_7$ with $x=0.15$. 

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(electrolytic) regime. For example, while a substantial n-type electronic conductivity is observed in the x=0.0025 material, the remaining samples show a nearly PO₂-independent behavior. The magnitude of σ also increases in this regime. We now examine these features in more detail.

5.1.1.3 Oxygen Ion Conduction

Figure 5.15 gives the Arrhenius temperature dependence of the ionic conductivity for the Ca doped samples. In each case, the data have been extracted from the "A" fitting parameter in equation 3.19. In the temperature range of 800-1100°C, a single straight line is observed in the log σ vs 1/T plot indicating a single conduction mechanism. However a concentration independent conductivity, as predicted by the dilute solution association model of equation 2.12 is clearly not observed. A large jump in σ_i is shown between 0.25 and 2.0 mole% Ca followed by a further increase between 2.0 and 10 mole%. The ionic conductivity as a function of Ca concentration is plotted in figure 5.16. The conductivity is found to increase by over 2 orders of magnitude, reaching a maximum at 10.0 mole% Ca and gradually decreases thereafter. The conductivity value of 5 x 10⁻² S/cm at the maximum at 1000°C represents the highest reported ionic conductivity to date for a titanate-based material.

The extracted activation energies and pre-exponential constants for ionic conduction are next presented in figure 5.17. As shown in the figure, the activation energy is not constant but drops to a minimum value of 0.63 eV at 2.0 mole% Ca. Correspondingly, for x=0.0 to 0.01, the pre-exponential constant shows a slow rise from log σ₀=2.9 to log σ₀= 4.5 (S/cm)⁻¹ K.
Figure 5.15 The temperature dependence of ionic conductivity for $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ between 1100 - 800°C.
Figure 5.16 The ionic conductivity as a function of $x$ in $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ at 1000°C.
Figure 5.17 The activation energy for ionic conduction and pre-exponential constant, $\sigma_0$, as a function of $x$ in $(\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7$. 
5.1.1.4 Grain Boundary Conduction

Analysis of the low temperature (<800°C) conductivity data becomes complicated due to interface and grain boundary contributions to the total conductivity. Figure 5.18 shows the conductivity vs temperature data extracted for \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\) with \(x=0.02\) and 0.10 as obtained from ac complex impedance spectroscopy. At temperatures of \(\approx750^\circ\text{C}\), curvature is clearly evident in both samples with the activation energy changing from \(\approx0.67\) eV to 1.0 eV. Caution, however, is noted in interpreting these results. As shown in the representative complex impedance plot of figure 5.19, the intercept which is marked \(R_1\) has been taken as the bulk resistance. Noted is the depressed semicircle \((\alpha\pi/2 = 22^\circ)\) from which the data has been obtained. This depression, which was common in all Ca doped samples, is believed to be related to grain boundary conduction.

To confirm the presence of interfacial or grain boundary effects, several Ca-doped compositions were re-electroded for both 4-probe dc and 2-probe ac measurements. Additional Pt was sputtered and painted on these samples to improve interface kinetics. Figure 5.20 shows a complex impedance plot for a re-electroded GT 2.0 mole% Ca sample at 507°C in air. A second semicircle (marked \(R_2\)) is clearly visible which became evident at all temperatures below 750°C. When the intercept of this circle \((R_2)\) is plotted vs temperature, a single slope of 0.63 eV is obtained, in excellent agreement with the high temperature data. A single bulk conduction mechanism in the temperature range of 1100 - 400°C can therefore be assumed with an activation energy of 0.63 eV.

The next figure (figure 5.21) shows an Arrhenius plot of the 4-probe dc results compared to the bulk ac conductivity values. The curvature in the dc data indicates a low temperature grain boundary contribution. Figure 5.22 shows the
Figure 5.18 The temperature dependence of ionic conductivity for \((\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\) with \(x=0.02\) and \(x=0.10\) between 1100 - 400°C.
Figure 5.19 A complex impedance plot of (Gd$_{0.9}$Ca$_{0.1}$)$_2$Ti$_2$O$_7$ at 405°C in air. The "assigned" bulk resistance is marked $R_1$. 
Figure 5.20 A complex impedance plot of Gd$_{0.98}$Ca$_{0.02}$Ti$_2$O$_7$ at 507°C in air. The "assigned" bulk resistance is marked $R_2$. 
Figure 5.21 Temperature dependence of $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ with $x=0.02$. Both "bulk" ac impedance and 4-probe dc data are shown in the temperature range of 1100 - 400°C.
Figure 5.22  The temperature dependence of grain boundary conduction for (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ $x=0.02$. 
grain boundary conductivity as a function of temperature. The results are characterized by a slope of 1.1 eV.

5.1.1.5 Electronic Conduction

Given the validity of the defect model derived in section 3, it becomes possible to extract two additional conductivity parameters from the partial pressure dependence, namely the electron and hole conductivities (σₑ, σₕ). Figure 5.23 shows the temperature dependence of the electron conductivity at a partial pressure of 10⁻²⁰ atm. Similar to σᵢ, a single conduction mechanism (i.e. linear behavior) is observed in the temperature range of 800 - 1100°C. Scatter in the data at high Ca levels is attributed to difficulties in separating out the small electronic contribution. The electronic activation energies and pre-exponentials are summarized in table 5.2. Both Eₑ and σₑ⁰ are shown to decrease with increasing Ca.

The next figure (5.24) depicts the hole conductivity as a function of temperature. Only values for x=0.0, 0.0025, and 0.02 were obtained since the p-type contribution for higher Ca levels was difficult to extract. Again, linear behavior is observed with the corresponding activation energies and the pre-exponentials summarized in table 5.2. Like Eₑ, Eₕ appears generally to decrease with increasing Ca.

In Figure 5.25 we plot the electron and hole conductivity as a function of Ca. The calculated slopes of log σ vs. log[Ca'] gave values of -0.36 for σₑ and +1.17 for σₕ , respectively.
Figure 5.23 The temperature dependence of n-type electronic conduction, $\sigma_e$, for $(\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7$ at $10^{-20}$ atm.
<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>$E_e$ (eV)</th>
<th>Log $\sigma_e^0$ (S/cm K)</th>
<th>$E_h$ (eV)</th>
<th>Log $\sigma_h^0$ (S/cm K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ $x=0.00$</td>
<td>2.91</td>
<td>5.82</td>
<td>0.78</td>
<td>0.752</td>
</tr>
<tr>
<td>(Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ $x=0.0025$</td>
<td>2.79</td>
<td>4.97</td>
<td>0.82</td>
<td>0.305</td>
</tr>
<tr>
<td>(Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ $x=0.02$</td>
<td>2.69</td>
<td>4.34</td>
<td>0.42</td>
<td>0.745</td>
</tr>
<tr>
<td>(Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ $x=0.05$</td>
<td>2.34</td>
<td>2.68</td>
<td>0.56</td>
<td>0.134</td>
</tr>
</tbody>
</table>

Table 5.2 The activation energies and the pre-exponentials for electron and hole conductivity as a function of Ca in (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ at 1000°C and 1 atm.
Figure 5.24 The temperature dependence of hole conduction, $\sigma_h$, for $(Gd_{1-x}Ca_x)_{2}Ti_2O_7$ at 1 atm.
Figure 5.25 The electron and hole conductivities ($\sigma_e$, $\sigma_h$) as a function of Ca doping in ($\text{Gd}_{1-x}\text{Ca}_x$)$_2\text{Ti}_2\text{O}_7$ at 1000°C and 1 atm.
5.1.1.6 Domain Boundaries

The applicable working range of an electrolyte material may be described by its electrolytic domain boundary position $P_n$ (i.e. for our particular case, the $PO_2$ for which $\sigma_i=\sigma_e$). In figure 5.26 we plot the domain boundary position under reducing conditions for $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$. As the temperature is lowered, the boundary position shifts to lower $PO_2$'s. Log $P_n$ also is shown be Ca dependent, decreasing with increasing Ca. In figure 5.27 log $P_n$ versus log [Ca] content is plotted at a fixed temperature of 1000°C. An increase of over 10 orders of magnitude is observed with a calculated slope of -6.4. This value is in good agreement with the predicted slope of -6 (equation 3.39).

5.1.2 "B" SITE Al DOPING

5.1.2.1 Solubility

In this section we present data for Al doping on the "B" site i.e. $\text{Gd}_2(\text{Ti}_{1-y}\text{Al}_y)_2\text{O}_7$. Figures 5.28 and 5.29 show Cu k$\alpha$ x-ray diffraction patterns for $\text{Gd}_2(\text{Ti}_{1-y}\text{Al}_y)_2\text{O}_7$ with $y=0.01$ and 0.10. For the $y=0.01$ sample, no extra peaks are observed indicating, within experimental error, a single phase microstructure. However for $y=0.10$, several additional peaks were found. These peaks have been indexed by the JCPDS files as $\text{GdAlO}_3$.

Further confirmation of a second phase comes from the lattice parameter measurements. The calculated lattice parameter as a function of Al concentration is plotted in figure 5.30. For each composition a Si reference standard was mixed in with the powder to insure accuracy of $\pm 0.0001\text{Å}$. Since
Figure 5.26 The electrolytic domain boundary position, $P_n$, as a function of temperature for $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$. 
Figure 5.27 The electrolytic domain boundary position, $P_n$, as a function of $x$ for $(Gd_{1-x}Ca_x)_2Ti_2O_7$. 
Figure 5.28 X-ray powder diffraction pattern of Gd$_2$(Ti$_{1-y}$Al$_y$)$_2$O$_7$ with y=0.01.
Figure 5.29  X-ray powder diffraction pattern of Gd$_2$(Ti$_{1-y}$Al$_y$)$_2$O$_7$ with $y=0.10$. 
Figure 5.30 Lattice parameter as a function of y (mole%) in Gd$_2$(Ti$_{1-y}$Al$_y$)$_2$O$_7$. 
Al$^{3+}$ is smaller than Ti$^{4+}$ it is expected to contract the lattice thereby decreasing the lattice parameter. This is indeed the case as a significant drop of $0.002\text{Å}$ is observed between 0.0 and 1.0 mole% Al. For concentrations greater than $y=0.01$, no apparent change in lattice parameter is observed. We therefore conclude that the solubility limit of Al$^{3+}$ in Gd$_2$(Ti$_{1-y}$Al$_y$)$_2$O$_7$ is $y \leq 0.01$.

5.1.2.2 Partial-Pressure Dependence of Conductivity

The partial-pressure dependence of electrical conduction for Gd$_2$(Ti$_{1-y}$Al$_y$)$_2$O$_7$ is given in figures 5.31 - 5.33. As in the case of an "A" site dopant, acceptor doping on the "B" site (e.g. Al'$^+$Ti) results in a large increase in conductivity relative to the undoped sample. Comparing the isotherms of figure 5.31 to figure 5.9 (i.e. undoped GT), the magnitude of the PO$_2$-independent conductivity is seen to increase with Al doping.

For dopant levels higher than $y=0.01$, we note an opposite trend. Figures 5.32 and 5.33 show that the magnitude of the PO$_2$ independent conductivity drops for Al concentrations of $y=0.05$ and $y=0.10$. Accordingly, the electronic conductivity is more apparent. In particular, p-type conductivity is clearly observed in both samples.

5.1.2.3 Oxygen Ion Conduction

In figure 5.34 we compare the ionic conductivities of the "B" site Al dopant to that of the "A" site Ca dopant. In each case, a steady increase in $\sigma_i$ is observed for dopant levels up to 1.0%. For higher doping levels, the ionic
Figure 5.31 Log conductivity as a function of log oxygen partial pressure for Gd$_2$(Ti$_{0.99}$Al$_{0.01}$)$_2$O$_7$ with $y=0.01$. 
Figure 5.32 Log conductivity as a function of log oxygen partial pressure for Gd$_2$(Ti$_{1-y}$Al$_y$)$_2$O$_7$ with $y=0.05$. 
Figure 5.33 Log conductivity as a function of log oxygen partial pressure for Gd$_2$(Ti$_{1-y}$Al$_y$)$_2$O$_7$ with $y=0.10$. 
Figure 5.34 Ionic conductivity of $\text{Gd}_2\text{Ti}_2\text{O}_7$ at 1000°C as a function of acceptor doping on the "A" (Ca\textsuperscript{3+}Gd) and "B" (Al\textsuperscript{3+}Ti) cation sublattices.
conductivity for Al doped Gd₂Ti₂O₇ drops sharply while that for Ca continues to increase. The corresponding activation energies and pre-exponentials are plotted in figure 5.35. Between 0.0 and 10.0 mole%, similar behavior in activation energies is observed. For Al, the activation energy drops from 0.94 eV to 0.74 eV between 0.0 and 5.0 mole%. However in contrast to Ca, the pre-exponential for Gd₂(Ti₁₋ₐAlₐ)₂O₇ shows a drop at 1.0 mole% instead of a steady increase.

5.1.2.4 Electronic Conduction and Domain Boundaries

Plots of σₑ and σₜ as a function of temperature are given in figures 5.36 and 5.37. Several features worth noting are σₑ decreases and σₜ increases as Al is substituted for Ti in Gd₂(Ti₁₋ₐAlₐ)₂O₇. However the increase in σₜ with Al is observed only up to 1.0 mole%. This drop in σₜ is further viewed in the domain boundary plot of figure 5.38. Of the three Al doped samples, the 1.0 mole% Al sample is shown to have the widest electrolytic domain.

5.1.3 Al/Ca CO-DOPING

5.1.3.1 Solubility

To address the question of whether combined "A" and "B" site dopants are additive, several co-doped Ca/Al samples were prepared. The compositions studied were (Gd₀.₉₉Ca₀.₀₁)₂(Ti₀.₉₉Al₀.₀₁)₂O₇ (1Ca/1Al) and (Gd₀.₉₀Ca₀.₁)₂Ti₀.₉₉Al₀.₁)₂O₇ (10Ca/10Al). For the former, a single phase
Figure 5.35 Ionic activation energy and pre-exponential constant of Gd$_2$Ti$_2$O$_7$ at 1000°C as a function of acceptor doping on the "A" (Ca' Gd) and "B" (Al' Ti) cation sublattices.
Figure 5.36 The temperature dependence of n-type electronic conduction, $\sigma_e$, for $\text{Gd}_2(\text{Ti}_{1-y}\text{Al}_y)_2\text{O}_7$ at 1 atm.
Figure 5.37 The temperature dependence of hole conduction, $\sigma_h$, for $\text{Gd}_2(\text{Ti}_{1-y}\text{Al}_y)\text{O}_7$ at 1 atm.
Figure 5.38 The electrolytic domain boundary as a function of temperature for \( \text{Gd}_2(\text{Ti}_{1-x}\text{Al}_x)_2\text{O}_7 \).
diffraction pattern was observed. For the latter, several additional peaks were observed, again indicating a solubility limit for Al concentrations greater than 1.0 mole%.

5.1.3.2 Partial-Pressure dependence of Conductivity

Figures 5.39 and 5.40 give log σ vs log PO2 plots for the co-doped samples (Gd0.99Ca0.01)2Ti0.99Al0.01)2O7 (1Ca/1Al) and (Gd0.9Ca0.1)2Ti0.9Al0.1)2O7 Gd2Ti2O7 (10Ca/10Al). Again, two features commonly observed with acceptor-doped material are observed; namely an increase in total conductivity and an extended PO2-independent electrolytic regime with increasing acceptor concentration.

5.1.3.3 Oxygen Ion Conduction

Figure 5.41 compares the extracted ionic conductivity of the co-doped samples to that of the individual "A" and "B" site doped samples. As shown in the figure, σi for 1Ca/1Al is greater than 1.0 mole% Al but slightly less than that of 2 mole% Ca. In figures 5.42 and 5.43 we compare the ionic pre-exponentials and activation energies. Although the pre-exponent for 1Ca/1Al and 2.0 mole% Ca are the same, the activation energy for the co-doped sample is slightly higher.
Figure 5.39 Log conductivity as a function of log oxygen partial pressure for 
$\text{(Gd}_{1-x}\text{Ca}_x)\text{2(Ti}_{1-y}\text{Al}_y)\text{2O}_7}$ with $x=0.01$ and $y=0.01$. 
Figure 5.40 Log conductivity as a function of log oxygen partial pressure for (Gd_{1-x}Ca_x)\textsubscript{2}(Ti_{1-y}Al_y)\textsubscript{2}O\textsubscript{7} with x=0.10 and y=0.10.
Figure 5.41 Ionic Conductivity of $(\text{Gd}_{1-x}\text{Ca}_x)_{2}(\text{Ti}_{1-y}\text{Al}_y)_{2}\text{O}_7$ as a function of acceptor doping on the "A" (x), "B" (y), and co-doped (x and y) cation sublattice.
Figure 5.42 Ionic pre-exponential of \((\text{Gd}_{1-x}\text{Ca}_x)_2(\text{Ti}_{1-y}\text{Al}_y)_2\text{O}_7\) as a function of acceptor doping on the "A" (x), "B" (y), and co-doped (x and y) cation sublattice.
Figure 5.43 Ionic activation energy of \((\text{Gd}_{1-x}\text{Ca}_x)_{2}(\text{Ti}_{1-y}\text{Al}_y)_{2}\text{O}_7\) as a function of acceptor doping on the "A" (x), "B" (y), and co-doped (x and y) cation sublattice.
5.1.4 DOPANT SIZE AND CHARGE EFFECTS

5.1.4.1 Phase Characterization

Dopant size and charge are two additional parameters believed to effect the ionic and MIEC properties of titanate pyrochlores. To examine these features, several additional acceptor-doped materials were prepared with various dopant size and charge. The dopants chosen were Sr\(^{2+}\) (\(r=1.25\ \text{Å}\)), Mg\(^{2+}\) (\(r=0.89\ \text{Å}\)), and K\(^{1+}\) (\(r=1.51\ \text{Å}\)). In each case, formulation was based on the assumption that the dopants substitute for the "A" site ion, following the solution energy calculations of Catlow et. al. [52]. See section 2.3.3.4.

A total of five compositions were prepared: \((\text{Gd}_{0.98}\text{Mg}_{0.02})_2\text{Ti}_2\text{O}_7\), \((\text{Gd}_{0.95}\text{Mg}_{0.05})_2\text{Ti}_2\text{O}_7\), \((\text{Gd}_{0.98}\text{Sr}_{0.02})_2\text{Ti}_2\text{O}_7\), \((\text{Gd}_{0.95}\text{Sr}_{0.05})_2\text{Ti}_2\text{O}_7\), and \((\text{Gd}_{0.98}\text{K}_{0.02})_2\text{Ti}_2\text{O}_7\). Diffraction patterns for each showed a single phase indexed to the pyrochlore phase. A noted exception was found in the \(x=0.05\) Sr sample. In this case, several unidentifiable peaks were observed.

The densities of the samples were measured by the dry weight method and found to be 93-95% of theoretical. For \((\text{Gd}_{0.98}\text{K}_{0.02})_2\text{Ti}_2\text{O}_7\) the density was only 70% of theoretical. This sample was visibly porous and structurally weak.

5.1.4.2 Partial-Pressure Dependence of Conductivity

Log \(\sigma\) vs Log PO\(_{2}\) plots for the Mg\(^{2+}\), Sr\(^{2+}\) and K\(^{1+}\) doped samples are shown in figures 5.44 - 5.48. Comparing these results to the undoped samples (figures 5.8 and 5.9), each dopant causes an increase in total conductivity. However, Mg and Sr doped samples are noticeably more conductive than
Figure 5.44 Log conductivity as a function of log oxygen partial pressure for $(\text{Gd}_{0.98}\text{Mg}_{0.02})_2\text{Ti}_2\text{O}_7$ with $x=0.02$. 
Figure 5.45 Log conductivity as a function of log oxygen partial pressure for (Gd$_{1-x}$Mg$_x$)$_2$Ti$_2$O$_7$ with x=0.05.
Figure 5.46 Log conductivity as a function of log oxygen partial pressure for (Gd_{1-x}Sr_x)\_2Ti_2O_7 with x=0.02.
Figure 5.47 Log conductivity as a function of log oxygen partial pressure for \((\text{Gd}_{1-x}\text{Sr}_x)\text{Ti}_2\text{O}_7\) with \(x=0.05\).
Figure 5.48 Log conductivity as a function of log oxygen partial pressure for $(\text{Gd}_{1-x}\text{K}_x)\text{Ti}_2\text{O}_7$ with $x=0.02$. 
(Gd$_{0.98}$K$_{0.02}$)$_2$Ti$_2$O$_7$. Further, the conductivity of (Gd$_{0.98}$K$_{0.02}$)$_2$Ti$_2$O$_7$ is almost entirely n-type while the Sr and Mg samples are primarily ionic. For the Mg and Sr doped samples a concentration dependent conductivity is also noted.

5.1.4.3 Oxygen Ion Conduction

In figure 5.49 we plot the extracted ionic conductivity at 1000°C for each acceptor dopant as a function of normalized radius ratio ($r_A/r_{Gd}$). At a fixed dopant level of 2.0 mole%, Ca$^{2+}$, the dopant closest in size to Gd$^{3+}$ is shown to have the highest ionic conductivity. Although $\sigma_i$ for the Sr doped sample is comparable in magnitude, the other two dopants are noticeably less conductive. Table 5.3 summarizes the extracted activation energies and pre-exponentials. The drop in $\sigma_i$ is accompanied by an increase in activation energy $\sim$0.1 eV for Sr and Mg and 0.6 eV for K relative to Ca. Also noted in the table is a drop in pre-exponential for the 2.0 mole% Mg sample.

The ionic conductivity as a function of acceptor concentration for the dopants Mg, Sr, and Ca are plotted in figure 5.50. While the Ca doped samples show a steady increase in $\sigma_i$ up to 10.0 mole%, $\sigma_i$ for the Sr and Mg doped samples saturate at a much lower dopant level. The corresponding activation energies for (Gd$_{0.95}$A$_{0.05}$)$_2$Ti$_2$O$_7$ (A=Mg,Ca,Sr) are given in figure 5.51. Also included are the activation energies for the (Gd$_{0.98}$A$_{0.02}$)$_2$Ti$_2$O$_7$ samples (i.e. 2.0 mole% dopant). Although both 2.0 and 5.0 mole% dopant samples show an increase in activation energy with increasing dopant-host mismatch, the magnitude change is much more dramatic in the 5.0 mole% samples. For example, an increase in $E_i$ of 0.2 - 0.4 eV is observed relative to Ca.
Figure 5.49 Ionic Conductivity for $(Gd_{0.98}A_{0.02})_2Ti_2O_7$ (A=Mg,Ca,Sr,K) as a function of normalized radius ratio ($r_A/r_{Gd}$).
<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>Log $\sigma_i$ 1000°C (S/cm)</th>
<th>$E_i$ (eV)</th>
<th>Log $\sigma_i^0$ (S/cm) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ x=0.02</td>
<td>-1.9</td>
<td>0.63</td>
<td>3.7</td>
</tr>
<tr>
<td>$(\text{Gd}_{1-x}\text{Sr}_x)_2\text{Ti}_2\text{O}_7$ x=0.02</td>
<td>-2.2</td>
<td>0.70</td>
<td>3.6</td>
</tr>
<tr>
<td>$(\text{Gd}_{1-x}\text{Mg}_x)_2\text{Ti}_2\text{O}_7$ x=0.02</td>
<td>-2.9</td>
<td>0.75</td>
<td>3.1</td>
</tr>
<tr>
<td>$(\text{Gd}_{1-x}\text{K}_x)_2\text{Ti}_2\text{O}_7$ x=0.02</td>
<td>-3.9</td>
<td>1.20</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 5.3  The ionic conductivity of $(\text{Gd}_{0.98}\text{A}_{0.02})_2\text{Ti}_2\text{O}_7$ ($\text{A}=$Mg,Ca,Sr,K) at 1000°C. Also given are the activation energies and pre-exponentials for ionic conduction.
Figure 5.50 Ionic Conductivity of \((\text{Gd}_{1-x}\text{A}_x)_2\text{Ti}_2\text{O}_7\) (A=Mg,Ca,Sr) as a function of x at 1000°C.
Figure 5.51 Ionic activation energy for \((Gd_{1-x}A_x)_{2}Ti_{2}O_{7}\) (A=Mg, Ca, Sr) as a function of normalized radius ratio \((r_A/r_{Gd})\).
5.1.4.4 Electronic Conduction

The n-type electronic conductivity as a function of $r_A/r_Gd$ is plotted in figure 5.52. In contrast to $\sigma_i$, $\sigma_e$ increases with increasing dopant-host size mismatch. The corresponding activation energies and pre-exponential are summarized in table 5.4.

5.1.5. ACCEPTOR-DOPED $Y_2Ti_2O_7$ AND $Sm_2Ti_2O_7$ PYROCHLORES

5.1.5.1 Phase Characterization

In this section on titanate pyrochlores, we examine results for two additional materials, $Y_2Ti_2O_7$ and $Sm_2Ti_2O_7$, to investigate the combined effects of doping and varying the host lattice size. The specific compositions under investigation were $(Y_{1-x}Ca_x)_{2}Ti_2O_7$ ($x=0.0$, $0.01$, $0.02$, $0.05$, and $0.10$), $(Sm_{1-x}Ca_x)_{2}Ti_2O_7$ ($x=0.01$, and $0.10$), $(Sm_{1-x}Mg_x)_{2}Ti_2O_7$ ($x=0.10$) and $(Sm_{1-x}Sr_x)_{2}Ti_2O_7$ ($x=0.10$). For each composition, a single phase diffraction pattern was obtained.

5.1.5.2 Partial-Pressure Dependence of Conductivity

Figures 5.53 - 5.59 give the partial pressure dependence of conductivity for Ca doped $Y_2Ti_2O_7$ and $Sm_2Ti_2O_7$ compositions. Several features worth noting are the concentration dependence and increase in $PO_2$-independent
Figure 5.52 Electronic Conductivity for (Gd_{0.98}A_{0.02})_2Ti_2O_7 (A=Mg, Ca, Sr) at 1 atm as a function of normalized radius ratio (r_A/r_{Gd}).
<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>Log $\sigma_e$</th>
<th>$E_e$</th>
<th>Log $\sigma_e^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{(Gd}_{1-x}\text{Ca}_x\text{)}_2\text{Ti}_2\text{O}_7$</td>
<td>-6.3</td>
<td>2.69</td>
<td>4.3</td>
</tr>
<tr>
<td>$x=0.02$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{(Gd}_{1-x}\text{Sr}_x\text{)}_2\text{Ti}_2\text{O}_7$</td>
<td>-6.22</td>
<td>2.71</td>
<td>4.6</td>
</tr>
<tr>
<td>$x=0.02$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{(Gd}_{1-x}\text{Mg}_x\text{)}_2\text{Ti}_2\text{O}_7$</td>
<td>-6.0</td>
<td>2.55</td>
<td>4.7</td>
</tr>
<tr>
<td>$x=0.02$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{(Gd}_{1-x}\text{K}_x\text{)}_2\text{Ti}_2\text{O}_7$</td>
<td>-5.9</td>
<td>2.60</td>
<td>4.82</td>
</tr>
<tr>
<td>$x=0.02$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4 The n-type electronic conductivity of $(\text{Gd}_{0.98}\text{A}_{0.02})_2\text{Ti}_2\text{O}_7$ $(\text{A}=\text{Mg,Ca,Sr,K})$ at $1000^\circ\text{C}$ and 1 atm. Also given are the activation energies and pre-exponentials for n-type conduction.
Figure 5.53  Log conductivity as a function of log oxygen partial pressure for $Y_2Ti_2O_7$. 
Figure 5.54  Log conductivity as a function of log oxygen partial pressure for 
$(Y_{0.99}Ca_{0.01})_2Ti_2O_7$ with $x=0.01$. 
Figure 5.55 Log conductivity as a function of log oxygen partial pressure for $(Y_{1-x}Ca_x)_{2}Ti_2O_7$ with $x=0.02$. 
Figure 5.56 Log conductivity as a function of log oxygen partial pressure for \((Y_{1-x}Ca_x)_2Ti_2O_7\) with \(x=0.05\).
Figure 5.57 Log conductivity as a function of log oxygen partial pressure for \((Y_{1-x}Ca_x)_2Ti_2O_7\) with \(x=0.10\).
Figure 5.58 Log conductivity as a function of log oxygen partial pressure for \((\text{Sm}_{0.99}\text{Ca}_{0.01})_2\text{Ti}_2\text{O}_7\) with \(x=0.01\).
Figure 5.59 Log conductivity as a function of log oxygen partial pressure for \((\text{Sm}\text{,Ca})_2\text{Ti}_2\text{O}_7\) with \(x=0.10\).
conductivity with increasing Ca. Similar to Ca doped Gd$_2$Ti$_2$O$_7$, the electrolytic regime widens as the Ca concentration increases. For the Sr and Mg doped Sm$_2$Ti$_2$O$_7$ samples, however, figures 5.60 and 5.61 show n-type behavior is observed.

5.1.5.3 Oxygen Ion Conduction

The ionic conductivity as a function of temperature for Ca doped Y$_2$Ti$_2$O$_7$ is plotted in figure 5.62. Similar to Ca doped Gd$_2$Ti$_2$O$_7$, $\sigma_i$ increases with decreasing temperature and increasing Ca concentration. Table 5.5 summarizes the activation energies and pre-exponentials for these samples. Although $E_i$ initially drops with increasing Ca, as is the case for GT, we note the magnitude of the drop is much more extensive in YT (i.e. $E_i$ drops over 1.0 eV between $x=0.0$ and 0.02). An explanation for the large drop is yet clear. However, we again point out that cation stoichiometry could be influencing these results. For example, a slightly Ti rich composition, results in a donor doped material with an extra formation term associated with the activation energy (i.e. equation 3.34).

To compare the effects of Ca doping in $A_2$Ti$_2$O$_7$ ($A=Y,Gd,Sm$) pyrochlores, figure 5.63 plots the combined effects of a variable A-site host ion and dopant concentration on $\sigma_i$. In each case, an initial sharp rise in $\sigma_i$ is observed, followed by a tendency to saturate at higher doping levels. For a given dopant level, $\sigma_i$ is highest for the (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$ solid solution.

Figure 5.64 gives the temperature dependence of $\sigma_i$ for (Sm$_{0.9}$R$_{0.1}$)$_2$Ti$_2$O$_7$ with (R=Sr,Ca,Mg) being a divalent "A" site dopant of various size. In the temperature range of 800 - 1100 °C, the highest ionic conductivity is found for the intermediate size Ca dopant.
Figure 5.60 Log conductivity as a function of log oxygen partial pressure for (Sm$_{1-x}$Sr$_x$)$_2$Ti$_2$O$_7$ with x=0.10.
Figure 5.61 Log conductivity as a function of log oxygen partial pressure for (Sm$_{1-x}$Mg$_x$)$_2$Ti$_2$O$_7$ with x=0.10.
Figure 5.62 The temperature dependence of ionic conductivity for $(Y_{1-x}Ca_x)_2Ti_2O_7$ between 1100 - 800°C.
<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>Log $\sigma_i$</th>
<th>$E_i$</th>
<th>Log $\sigma_i^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(Y_{1-x}Ca_x)_{2}Ti_2O_7$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x=0.00$</td>
<td>-4.88</td>
<td>2.53</td>
<td>7.1</td>
</tr>
<tr>
<td>$(Y_{1-x}Ca_x)_{2}Ti_2O_7$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x=0.01$</td>
<td>-4.65</td>
<td>1.94</td>
<td>6.7</td>
</tr>
<tr>
<td>$(Y_{1-x}Ca_x)_{2}Ti_2O_7$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$x=0.02$</td>
<td>-3.52</td>
<td>1.0</td>
<td>3.66</td>
</tr>
<tr>
<td>$(Y_{1-x}Ca_x)_{2}Ti_2O_7$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x=0.05$</td>
<td>-2.4</td>
<td>0.88</td>
<td>4.31</td>
</tr>
<tr>
<td>$(Y_{1-x}Ca_x)_{2}Ti_2O_7$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x=0.10$</td>
<td>-2.0</td>
<td>0.97</td>
<td>5.07</td>
</tr>
</tbody>
</table>

Table 5.5 The ionic conductivity of $(Y_{1-x}Ca_x)_{2}Ti_2O_7$ as a function of $x$ at 1000°C. Also given are the ionic activation energies and pre-exponentials.
Figure 5.63 Ionic Conductivity of \( (A_{1-x}Ca_x)_2Ti_2O_7 \) (A=Y,Gd,Sm) as a function of \( x \).
Figure 5.64. The temperature dependence of ionic conductivity for \((\text{Sm}_{0.9}\text{A}_{0.1})_{2}\text{Ti}_2\text{O}_7\) (A=Mg,Ca,Sr) between 1100 and 800°C.
5.1.5.4 Electronic Conductivity and Domain Boundary

In figure 5.65 we plot $\sigma_e$ for $(Y_{1-x}Ca_x)_2Ti_2O_7$ as function of temperature in two different oxygen atmospheres ($10^{-15}$ and $10^{-20}$ atm). In each case, the electronic conductivity is shown to decrease as the temperature decreases and the Ca concentration increases.

The effects of dopant size on $\sigma_e$ for $(Sm_{0.9}R_{0.1})_2Ti_2O_7$ (R= Sr, Ca, and Mg) is shown in figure 5.66. At a temperature 1000°C, $\sigma_e$ is largest for the dopants with the poorest dopant-host size match. The dopants Mg and Sr are shown to have an electronic conductivity approximately one order of magnitude higher than that of Ca doped Sm$_2$Ti$_2$O$_7$. A similar effect is observed for the domain boundary position. Figure 5.67 shows $P_n$ for the Ca doped sample to be 10 orders of magnitude lower than for the Mg or Sr doped compositions.

5.2 ACCEPTOR DOPED ZIRCONATE PYROCHLORES

5.2.1 Gd$_2$(Zr$_{0.25}$Ti$_{0.75}$)O$_7$

5.2.1.1. Ca doping

Until now, our doping studies have been limited to titanate based materials. In this section, we continue earlier work of Moon et al. [6,18, 55] on the doping of zirconate - titanate solid solutions of Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ (GZT). In particular we examine the effects of Ca doping in a partially disordered oxygen ion conductor Gd$_2$(Zr$_{0.25}$Ti$_{0.75}$)$_2$O$_7$. 
Figure 5.65 The temperature dependence of electronic conductivity for (Y_{1-x}Ca_x)_2Ti_2O_7 at 10^{-15} and 10^{-20} atm.
Figure 5.66 The electronic conductivity for $(Sm_{0.90}A_{0.10})_2Ti_2O_7$ (A=Mg,Ca,Sr) at 1 atm as a function of normalized radius ratio ($r_A/r_{Sm}$).
Figure 5.67 The electrolytic domain boundary position, $P_n$, as a function of normalized radius ratio $r_A/r_{Sm}$ in $(Sm_{0.9}A_{0.1})_2Ti_2O_7$ (A=Mg, Ca, Sr).
Figure 5.68 shows the electrical conductivity of undoped Gd$_2$(Zr$_{0.25}$Ti$_{0.75}$)$_2$O$_7$ plotted as a function of PO$_2$. Similar to the titanate based materials, the data points were fit to equation 3.19. Even under the most reducing conditions, excellent agreement with the defect model is observed. The partial pressure dependence is shown to consist of three distinct regimes; n-type conduction at low PO$_2$, PO$_2$-independent conductivity at intermediate PO$_2$, and p-type conduction at high PO$_2$.

The total conductivity of (Gd$_{1-x}$Ca$_x$)$_2$(Zr$_{0.25}$Ti$_{0.75}$)O$_7$ with x=0.005, and 0.01 is next shown in figures 5.69 and 5.70. As Ca is added to the composition, several features are worth noting. First, while the undoped specimen exhibits a reasonably high ionic conductivity (e.g. 10$^{-4}$ S/cm at 950°C), $\sigma_{ionic}$ is increased by approximately a factor of 20 by the addition of 0.5% calcium followed by an approximate further doubling upon the addition of 1.0% calcium. Secondly, the data shows that the electrolytic domain widens as the Ca content increases. At 950°C, the PO$_2$ independent conductivity is found to extend over 20 orders of magnitude for both x=0.005 and x=0.01.

Table 5.6 summarizes the values of the fitting parameters A, B, and C obtained from equation 3.19. These parameters are only presented here. We refer our analysis to the discussion part of the thesis (section 6.1.3.2).

5.2.2 (La$_{1-x}$A$_x$)$_2$Zr$_2$O$_7$ (A=Ca,Sr)

5.2.2.1 Partial Pressure Dependence of Conductivity

We next investigate La$_2$Zr$_2$O$_7$. The compositions studied included La$_2$Zr$_2$O$_7$, (La$_{1-x}$Sr$_x$)$_2$Zr$_2$O$_7$ (x=0.01 and 0.10) and (La$_{0.90}$Ca$_{0.10}$)$_2$Zr$_2$O$_7$.  

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Figure 5.68 Log conductivity as a function of log oxygen partial pressure for Gd$_2$(Ti$_{0.75}$Zr$_{0.25}$)$_2$O$_7$. 
Figure 5.69 Log conductivity as a function of log oxygen partial pressure for \((\text{Gd}_{1-x}\text{Ca}_x)_2(\text{Ti}_{0.75}\text{Zr}_{0.25})_2\text{O}_7\) with \(x=0.005\).
Figure 5.70  Log conductivity as a function of log oxygen partial pressure for 
(Gd$_{1-x}$Ca$_x$)$_2$(Ti$_{0.75}$Zr$_{0.25}$)$_2$O$_7$ with $x=0.01$. 
<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>A(T) (eV, (S/cm)K)</th>
<th>B(T) (eV, (S/cm)K)</th>
<th>C(T) (eV, (S/cm)K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Gd}_{1-x}\text{Ca}<em>x)</em>{2}(\text{Zr}<em>y\text{Ti}</em>{1-y})_2\text{O}_7$</td>
<td>$E_A=0.96$</td>
<td>$E_B=2.96$</td>
<td>$E_C=2.96$</td>
</tr>
<tr>
<td>$x=0.00$ $y=0.25$</td>
<td>$\sigma^0=1023$</td>
<td>$\sigma^0=1.38\times10^5$</td>
<td>$\sigma^0=2.14$</td>
</tr>
<tr>
<td>$(\text{Gd}_{1-x}\text{Ca}<em>x)</em>{2}(\text{Zr}<em>y\text{Ti}</em>{1-y})_2\text{O}_7$</td>
<td>$E_A=0.74$</td>
<td>$E_B=3.14$</td>
<td>$E_C=1.28$</td>
</tr>
<tr>
<td>$x=0.005$ $y=0.25$</td>
<td>$\sigma^0=1862$</td>
<td>$\sigma^0=3.89\times10^5$</td>
<td>$\sigma^0=1.40$</td>
</tr>
<tr>
<td>$(\text{Gd}_{1-x}\text{Ca}<em>x)</em>{2}(\text{Zr}<em>y\text{Ti}</em>{1-y})_2\text{O}_7$</td>
<td>$E_A=0.76$</td>
<td>$E_B=2.63$</td>
<td>$E_C=0.79$</td>
</tr>
<tr>
<td>$x=0.01$ $y=0.25$</td>
<td>$\sigma^0=3890$</td>
<td>$\sigma^0=5.75\times10^3$</td>
<td>$\sigma^0=1.27$</td>
</tr>
</tbody>
</table>

Table 5.6 The fitting parameters A, B, and C in equation 3.19 for Ca doped Gd$_2$(Ti$_{0.75}$Zr$_{0.25}$)$_2$O$_7$. 

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Figure 5.71 gives the Arrhenius temperature dependence of $\sigma_i$ for $\text{La}_2\text{Zr}_2\text{O}_7$ measured in oxygen. (Measurements at lower PO$_2$'s were unobtainable due to an increasing sample resistance). When Sr$^{2+}$ and Ca$^{2+}$ are added to the composition we note several changes. Figures 5.72 - 5.74 show the log $\sigma$ vs log PO$_2$ curves for $(\text{La}_{1-x}\text{Sr}_x)\text{Zr}_2\text{O}_7$ (x=0.01 and 0.10) and $(\text{La}_{0.9}\text{Ca}_{0.1})\text{Zr}_2\text{O}_7$. Similar to other acceptor doped materials the magnitude and size of the PO$_2$-independent regime increases with increasing acceptor concentration.

5.2.2.2 Oxygen ion conduction

Figure 5.75 shows the Arrhenius temperature-dependence of ionic conductivity for $(\text{La}_{1-x}\text{A}_x)\text{Zr}_2\text{O}_7$ (A=Ca,Sr) in the temperatures range of 800-1100°C. A concentration-dependent conductivity is shown, with the Ca doped sample giving the highest $\sigma_i$. Also noted is the linear behavior.

The extracted activation energies and pre-exponential constants are summarized in table 5.7. In contrast to the titanates, the samples with the highest acceptor dopant concentrations, $(\text{La}_{0.9}\text{A}_{0.1})\text{Zr}_2\text{O}_7$ (A=Sr,Ca), are shown to exhibit the highest ionic activation energy. However the pre exponential constant are also noted to be higher in these samples relative to $(\text{La}_{0.9}\text{Sr}_{0.1})\text{Zr}_2\text{O}_7$. 

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Figure 5.71 Temperature dependence of conductivity for $\text{La}_2\text{Zr}_2\text{O}_7$ in oxygen between 1100 and 800°C.

Activation Energy = 1.31 eV
Figure 5.72 Log conductivity as a function of log oxygen partial pressure for $(\text{La}_{0.90}\text{Sr}_{0.01})_2\text{Zr}_2\text{O}_7$ with $x=0.01$. 
Figure 5.73 Log conductivity as a function of log oxygen partial pressure for $(La_{1-x}Sr_x)_2Ti_2O_7$ with $x=0.10$. 
Figure 5.74 Log conductivity as a function of log oxygen partial pressure for \((\text{La}_{0.90}\text{Ca}_{0.1})_2\text{Zr}_2\text{O}_7\) with \(x=0.10\).
Figure 5.75  The temperature dependence of ionic conductivity for 
\((La_{1-x}A_x)_{2}Ti_2O_7\) \((A=\text{Sr, Ca})\) between 1100 and 800°C.
<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>Log $\sigma_i$ (1000°C) (S/cm)</th>
<th>$E_i$ (eV)</th>
<th>Log $\sigma_i^\circ$ (S/cm) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{La}_{1-x}\text{Sr}_x)\text{Zr}_2\text{O}_7$ $x=0.01$</td>
<td>-4.6</td>
<td>1.10</td>
<td>2.0</td>
</tr>
<tr>
<td>$(\text{La}_{1-x}\text{Sr}_x)\text{Zr}_2\text{O}_7$ $x=0.10$</td>
<td>-4.2</td>
<td>1.30</td>
<td>3.5</td>
</tr>
<tr>
<td>$(\text{La}_{1-x}\text{Ca}_x)\text{Zr}_2\text{O}_7$ $x=0.10$</td>
<td>-3.5</td>
<td>1.25</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Table 5.7 The ionic conductivity for $(\text{La}_{1-x}\text{A}_x)\text{Ti}_2\text{O}_7$ (A=Sr,Ca) as a function of $x$ at 1000°C. Also given are the ionic activation energies and pre-exponentials.
5.3 Short Circuit Current Results

5.3.1 PARTIAL-PRESSURE AND TEMPERATURE DEPENDENCE

The mixed ionic-electronic conducting specimen under investigation was (Gd\textsubscript{0.9975}Ca\textsubscript{0.0025})\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} whose electrical conductivity was presented earlier in figure 5.10. To test the accuracy of the short-circuit current technique, as described in section 3.3, measurements were performed as functions of both temperature and PO\textsubscript{2}.

Figures 5.76 - 5.78 show the short circuit voltage, $V_{SC}$, obtained in microvolts measured across a 100 Ω series resistor versus the initial open circuit voltage $V_{OC}$. For the temperatures of 700°C, 800°C, and 950°C, a linear relationship is observed which is in excellent agreement with the linear relation of equation 3.45 (i.e. $R = V_{th}/I_{SC}$ with $V_{OC}$ taken as $=V_{th}$ and $I_{SC}=V_{SC}/100$ Ω).

The temperature dependence of the ionic conductivity as obtained from ac impedance is compared with that obtained by the short circuit current method in figure 5.79. While the values determined by the two methods are nearly equal at 950°C, they diverge with decreasing temperature. The upper curve is characterized by an activation energy of 0.9eV while the lower curve follows an activation energy of 1.2 eV.

In figure 5.80, we compare the short circuit current results with "bulk" ac impedance data as a function of PO\textsubscript{2}. For the short circuit measurements, the data points represent an average PO\textsubscript{2} (e.g., the 10\textsuperscript{-1} atm data point represents a gradient between PO\textsubscript{2} = 0.0 and 10\textsuperscript{-2} atm while the 10\textsuperscript{-13} atm data point represents a gradient between 10\textsuperscript{-15} and 10\textsuperscript{-11} atm). As the PO\textsubscript{2} is lowered, the short circuit current data points appear to follow the total conductivity

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(i.e. \( \sigma_i + \sigma_e \)) rather than the ionic conductivity \( \sigma_i \). An explanation for this result is not yet clear. However, we note large leaks in the gas tight seal were observed at low PO\(_2\)'s. Accordingly, the assumption of \( V_{oc} = V_{th} \) would no longer be valid.
Figure 5.76. Short circuit and open circuit voltages, $(V_{sc}, V_{oc})$ for $(\text{Gd}_{0.9975}\text{Ca}_{0.0025})_2\text{Ti}_2\text{O}_7$ at 950°C.
Figure 5.77 Short circuit and open circuit voltages, $(V_{sc}, V_{oc})$ for $(Gd_{0.9975}Ca_{0.0025})_2Ti_2O_7$ at 800°C.
Figure 5.78 Short circuit and open circuit voltages, \( (V_{sc}, V_{oc}) \) for \((Gd_{0.9975}Ca_{0.0025})_2Ti_2O_7\) at 700°C.
Figure 5.79 Temperature dependence of ionic conduction for \((\text{Gd}_{0.9975}\text{Ca}_{0.0025})_2\text{Ti}_2\text{O}_7\). Both “bulk” ac impedance and short circuit current data are shown between 1100 and 700°C.
Figure 5.80 Log conductivity as a function of log oxygen partial pressure for (Gd$_{0.9975}$Ca$_{0.0025}$)$_2$Ti$_2$O$_7$ at 950°C. The solid dots in the figure represent ac impedance data while the open circles are conductivity data extracted from the short circuit current method.
6 DISCUSSION

The discussion section is broken into two parts: (1) the effects of extrinsic doping on crystallographic disorder and oxygen ion transport and (2) applications of titanate and zirconate pyrochlore compounds.

6.1 Extrinsic Doping, Order, and Oxygen Ion Transport

Our discussion on rare earth titanate/zirconate pyrochlore compounds begins by first reiterating the significance of this work. As outlined in the literature review, zirconia and titania based pyrochlore oxides are both of technological and scientific interest. Scientifically, a number of systematic studies have been performed involving oxygen ion transport and the relative role of order. In most of these studies, however, investigations have been limited to disorder in pyrochlores where "intrinsic" crystallographic disorder controls the transport mechanism.

In this thesis, a primary objective has been to investigate the order/disorder phenomena in highly "ordered" materials (e.g., Gd$_2$Ti$_2$O$_7$). Specifically, a series of systematic doping experiments has been used to evaluate the relative role of aliovalent acceptor dopants on carrier generation, migration and association. With this in mind, the first part of our discussion will focus on oxygen ion transport in highly ordered titanate and zirconate pyrochlores. Specific topics include (1) concentration dependent conductivity, (2) effects of lattice strain on oxygen ion transport and (3) intrinsic versus extrinsic conduction.
6.1.1 CONCENTRATION DEPENDENT CONDUCTIVITY

In figure 5.16 we showed that the ionic conductivity of \((\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\) (1000°C) can be increased by over 2 1/2 orders of magnitude by doping with highly soluble impurities. With similar results for \((\text{Y}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\) and \((\text{Sm}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\) (i.e., figure 5.63), we conclude that the introduction of aliovalent acceptor impurities such as \(\text{Ca}^{2+}\) results in charge compensating oxygen vacancies as predicted by equation 3.25:

\[
[V_0^{\cdot\cdot}] = [A']/2
\]  

(3.25)

However, the conductivity behavior for \((\text{A}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\) (\(\text{A}=\text{Gd,Sm,Y}\)) is quite distinct from the linear dependence predicted by equation 3.25 or from the defect-impurity association model presented in section 2.3.3. In that section, we noted that for a dopant with an effective charge of one, equation 2.12 predicts that both the pre-exponential and activation energy remain concentration independent.

Examination of the conductivity parameters for \((\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\) in figure 5.17 shows neither to be true. Both \(\sigma^0\) and \(E_i\) are concentration dependent with the activation energy showing a substantial drop from 0.94 eV to 0.63 eV in the composition range of 0 to 2 mole% Ca. Although \(\sigma^0\) also increases in this same composition range, we find that the increase in ionic conductivity with Ca doping, (up to 2.0 mole%) is primarily driven by the decrease in \(E_i\) (e.g., 90% of the change at 1000°C is due to the exponential dependence of \(E_i\) in equation 2.9).
Like (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$, Y doped CeO$_2$ shows a concentration
dependent conductivity and corresponding initial drop in activation energy. A
common denominator in both systems is that one defect is created for every two
acceptor dopants (i.e. $\beta$=1/2). In Y-doped CeO$_2$, Wang et al. [43] proposed an
explanation based on electrostatic interactions, a key parameter effecting the
migration pathway for ion transport. Since the two systems appear to be quite
similar, we examine this model more closely.

In Wang et al’s electrostatic defect-impurity association model, the
compositional dependence of conductivity for Y-doped CeO$_2$ is attributed to
coulombic interaction between the free defect ($Y'$$_{Ce}$) and the defect-vacancy
associate ($Y'$$_{Ce}$-V$_0$$^-$). The authors suggest that the decrease in activation
energy results from a favorable transport path created between the
uncompensated $Y'$$_{Ce}$ sites and the ($Y'$$_{Ce}$-V$_0$$^-$) complex. To demonstrate this
point, we give two schematic potential energy versus distance curves in figure
6.1 showing the interaction of a bound defect in a crystal lattice. For low levels
of impurity concentrations the upper curve shows that the defects are isolated
with no overlap between their potential wells. In this case a deep barrier to ion
transport exists. As the defect concentration increases, the second schematic
diagram shows that the overlap of the potential wells increases with the net
result of lowering the energy barrier for ion transport.

With one vacancy created for every two Ca'Gd impurities in
(Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$, the electrostatic interaction model appears to be valid in our
system as well. However several distinctions between the two systems should be
made. First, while CeO$_2$ is a binary compound, Gd$_2$Ti$_2$O$_7$ is ternary with two
distinct cation sublattices. The electrostatic interactions, in the latter system, are
likely more complex. In particular, we note the difference in migration path. A
number of theoretical studies on conduction in pyrochlore oxides [24,52] have
Figure 6.1 Schematic of an impurity-defect electrostatic interaction. The model was obtained from reference [43].
demonstrated that the primary transport mechanism in pyrochlores involves the oxygen 48f sublattice. Since the 48f ion is surrounded by two "A" cations and two "B" cations, the coulombic interaction of the smaller "B" site ion on the (Ca'Gd - V0'-) complex may play a role as well.

A second point to be made is that the electrostatic interaction model described above is valid in (Gd1-xCa2)2Ti2O7 only up to the solubility limit of 7.0 mole% Ca. Any comparison of Ei versus [A'] at high dopant concentration is therefore misleading. To highlight this point, figure 5.17 shows that the activation energy for (Gd1-xCa2)2Ti2O7 has a broad minimum between 2 and 15 mole% [A'] while Y doped CeO2 (figure 2.11) shows a sharp minimum in the Ei versus [A'] curve with a dramatic increase in the energy barrier at high doping levels. This increases in Ei was explained by Wang et al. [43] as due to the creation of deep traps for vacancies at sufficiently high levels of acceptor concentrations.

To clarify the apparent differences between the two systems, we compare our results to those of Wang et al. by plotting the activation energy as a function of vacancy fraction rather than composition. Figure 6.2 shows that for vacancy fractions up to 1.0%, both (Gd1-xCa2)2Ti2O7 and Y-doped CeO2 exhibit a sharp drop in Ei between 0.0 and 0.05 [V0'-]% followed by a broad minimum between 0.05 - 1.0%. Only for [V0'-]%>1.0%, do the two systems differ. In the pyrochlore, however, this region corresponds to a two phase mixture as represented by the circled points in the figure. It is possible that the occurrence of a second phase prevents us from observing the expected increase in Ei for (Gd1-xCa2)2Ti2O7.

Finally, it is of interest to compare the activation energy minimum for (Gd1-xCa2)2Ti2O7 (0.63 eV) versus that of Y doped CeO2 (0.77 eV). Although Ei appears to be lower for the pyrochlore, we point out that a direct comparison of the two is difficult since Ei represents a combination of migration and
Figure 6.2 The ionic activation energy versus oxygen vacancy fraction for $(\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7$. The circled points represent data points after the solubility limit of 7.0 mole% Ca. Also shown is the data for solid solutions of CeO$_2$ + Y$_2$O$_3$ obtained from reference [43].
association energies. In Y doped CeO$_2$, Nowick et al. [33] established a migration energy of 0.61 eV similar in magnitude to the minimum value of 0.63 eV found in (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$. However the 0.63 eV obtained in our material may only reflect an upper limit to $E_m$ with the true value somewhat lower. Further studies including dielectric and anelastic relaxation are needed to examine these features in more detail. Not only will these techniques confirm the existence of associates, but also the degree and type of interaction involved.

6.1.2 EFFECTS OF LATTICE STRAIN ON OXYGEN ION TRANSPORT

Until now, our analysis has primarily involved the effects of electrostatic interactions on ion transport. Since the A$_2$Ti$_2$O$_7$ pyrochlores accommodate a wide variety of "A" site ions and dopants, a logical extension is to examine the effects of strain. Two types of strain are considered. The first, a localized strain involves the effects of dopants (size and site location) on defect association, $E_A$. In the second, we examine the effects of strain on the migration energy $E_m$ with the substitution of variable "A" site ions.

6.1.2.1 Defect Association and Variable dopant size

In section 2.3.3.3 we presented conductivity data for Ce(Mf)O$_{2-x}$ showing the effects of dopant size on the oxygen ion transport [47]. In these studies, the authors established that both conductivity and association enthalpy vary with the size mismatch between dopant and host. As shown in figure 2.13, the lowest
association energy is found when the size difference between dopant and host is minimized.

Looking at the ionic conductivity values for \((\text{Gd}_{1-x}\text{A}_x)_2\text{Ti}_2\text{O}_7\) with a fixed dopant concentration but variable dopant size (figure 5.4), a well defined maximum in \(\sigma_i\) vs. normalized radius ratio \((r_{\text{dopant}}/r_{\text{host}})\) is observed. Amongst the dopants \(\text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}\) and \(\text{K}^{2+}\), \(\text{Ca}^{2+}\) the dopant with closest dopant-host size match, has the highest conductivity. Given the similarity in our results and those obtained for the trivalent doped fluorites, we evoke an argument similar to the one proposed by Kilner and Brook [47]. In their work, the authors conclude that the elastic strain energy is an important component of the dopant-vacancy association energy. This term is minimized when there is a small size mismatch between dopant and host. For the \(\text{A}_2\text{Ti}_2\text{O}_7\) pyrochlores a similar situation seems apparent. A number of theoretical studies [24,52] have established that a preferential diffusion path exists in "ordered" pyrochlores with the strain energy a dominant part of the total activation energy. Since \(\text{Gd}_2\text{Ti}_2\text{O}_7\) is one such ordered pyrochlore, we expect that any change in dopant-host size match would result in a corresponding large change in strain energy in the lattice.

It is of interest to compare our activation energies directly to those of trivalent doped fluorites. In table 5.3, we give activation energies for \((\text{Gd}_{0.98}\text{A}_{0.02})_2\text{Ti}_2\text{O}_7\) (A=\(\text{Mg}, \text{Ca}, \text{Sr}, \text{K}\)) with \(\text{Ca}^{2+}\) having the lowest value of \(E_i=0.63\) eV. Taking this value as the migration energy \(E_m\), (i.e. an estimate given the fact that this value represents the minimum obtained in \((\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\)), we obtain association energies for \(\text{Mg}, \text{Sr},\) and \(\text{K}\) using equations 2.11 and 2.12. These values are: \(E_A=0.12\) for \(\text{Mg}\), \(E_A=0.07\) for \(\text{Sr}\) and \(E_A=0.57\) eV for \(\text{K}\). In figure 6.3, we plot these values versus normalized radius ratio. Also included are the 1.0 mole% acceptor dopants in \(\text{CeO}_2\) from figure
Figure 6.3 Association energy versus normalized radius ratio ($r_{dopant}/r_{host}$) for (Gd$_{0.98}$A$_{0.02}$)$_2$Ti$_2$O$_7$ (A=Mg,Ca,Sr,K) and Ce$_{0.98}$A$_{0.02}$O$_2$ (A=La,Gd,Y,Sc). The data for Ce$_{1-x}$A$_x$O$_2$ was obtained from reference [45]. In both cases a migration energy of 0.6 eV is used.
2.15. Comparing the values at a fixed radius ratio, the association effect is shown to be much weaker for the pyrochlore oxides for $r_{\text{dopant}}/r_{\text{host}}$ ratios of less than unity.

For dopant levels higher that 2.0 mole%, pyrochlore compounds show a much larger association energy. For example, if we again assume an $E_m$ of 0.63 eV for $(\text{Gd}_{0.95}\text{A}_{0.05})_2\text{Ti}_2\text{O}_7$, one derives apparent association energies of 0.25 eV and 0.4 eV for Mg and Sr respectively using the data of figure 5.50. These higher values however, may simply reflect a solubility limit for the dopants. In $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ the solubility limit was found at 7.0 mole%. Due to the difference in dopant-host size, Sr and Mg dopants are expected to have even lower solubilities. Confirmation for this argument comes from the diffraction data for the 5.0 mole% Sr doped sample which shows several extra peaks. The simulated solution energy calculations of Wilde and Catlow [52] are in further agreement with this result. Figure 2.18 for example shows that Ca$^{2+}$, the dopant with the best size match to Gd$^{3+}$, has the lowest solution energy. A difference of over 1.0 eV is noted for the dopants Mg$^{2+}$ and K$^{1+}$.

Finally, we note that for dopants such as Mg$^{2+}$, the ability to substitute at least partially on the "B" site may also play a role in the high activation energy. Under these circumstances, our formulation would lead to "A"-site deficiency, which could be a source of the large $E_f$.

6.1.2.2 Defect Association and "A" vs "B" Site Doping

A second type of localized association involves "A" site versus "B" site doping. As mentioned in the previous section, a number of theoretical studies have established that the primary transport mechanism in pyrochlores occurs
through the creation of oxygen vacancies on the 48f sublattice. The migration path therefore consists of successive 48f-48f type jumps between two "A" cations and two "B" cations. With Al and Ca dopants substituting on different atomic sites, the local environment surrounding the 48f ion is expected to change. Correspondingly, this would create a difference in localized strain.

Our data in figure 5.43 suggests that this is indeed the case. For the "B" site Al doped samples, the ionic activation energy is shown to be slightly higher than that for an equivalent amount of "A" site dopant (e.g., the activation energy for the 1 mole% Al - 1 mole% Ca sample is 0.12 eV higher than that for 2.0 mole% Ca).

In explanation, we again refer to the general conclusions of Kilner et al. [47]:

i. The pair binding energy depends upon dopant ion size displaying a minimum when \( r_{\text{dopant}} = r_{\text{host}} \).

ii. The dependence upon size is much greater for ions smaller than the host than those larger than the host cation.

It is the second of these two observation which appears to be consistent with our results. Although the size difference for both Ca and Al substitutions are relatively small (e.g., 0.06 Å for Ca\( ^{\text{Gd}} \) and 0.1 Å for Al\( ^{\text{Ti}} \), we note that Ca\( ^{2+} \) is a slightly larger ion the Gd\( ^{3+} \) while Al\( ^{3+} \) is slightly smaller than Ti\( ^{4+} \). Thus, the higher activation energy and lower conductivity found in the co-doped samples (figure 5.41) may simply reflect a stronger strain energy contribution connected with Al doping.
6.1.2.3 Defect migration and Variable Host Lattice Size

Given the flexibility of the $A_2Ti_2O_7$ host in accommodating a variety of "A" site ions and dopants, we now explore the effects of lattice strain on defect migration. We state a simple hypothesis; all else being equal, the larger the host lattice parameter (i.e. open structure) the higher the ion mobility due to reduced strain contributions to the migration energy. The higher ionic conduction of $(Gd_{0.1-x}Ca_x)2Ti_2O_7$ relative to $(Y_{1-x}Ca_x)2Ti_2O_7$ in figure 5.63 is consistent with this hypothesis. In apparent contradiction to this, however, we find in figure 5.63 that $Sm^{3+}$ which has the largest "A" site host radius $(r=1.09\text{Å})$ has the lowest conductivity.

An explanation of these results may be related to the fact that $Sm_2Ti_2O_7$ lies close to the pyrochlore phase boundary. Knop et al. [30] has observed that when the cation radius ratio $(R_A/R_B)$ becomes $>1.80$, the cubic pyrochlore phase is no longer stable. For rare-earth ions larger than Sm (e.g., $R_{Nd} = 1.12\text{Å}$), a distorted cubic pyrochlore phase is observed. Since $Ca^{2+}$ has an ionic radius of $1.12\text{Å}$ in 8-fold coordination, it also may promote crystal lattice distortion when dissolved in the $Sm_2Ti_2O_7$. This lowered symmetry is expected to produce an enhanced degree of order on the oxygen sublattice thereby immobilizing at least a subset of oxygen defects. Further structural conformation is needed to verify this result.
6.1.3 INTRINSIC VS EXTRINSIC TRANSPORT

6.1.3.1 \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\) versus \(\text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})\text{O}_7\)

Oxygen ion conduction in pyrochlore oxides changes markedly as a function of order. Generally speaking, for "intrinsic" oxygen ion conducting pyrochlores, the degree of order is a function of the \(R_A/R_B\) radius ratio, the temperature treatment of the material, and deviation from pyrochlore stoichiometry. Variations in any of these parameters results in a change in carrier concentration and mobility.

In the previous section, we demonstrated that carrier formation, migration and association may be manipulated in another way, namely by extrinsic doping. In this section we make several general comparisons between disorder induced intrinsically to that induced extrinsically.

Figure 6.4 shows the trend in ionic conductivity as a function of disorder or oxygen vacancy fraction in the host lattice. The first curve (circles) represents data points for the extrinsic Ca doped \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\). In this case the vacancy fraction was calculated from equation 3.21 assuming the defect concentration was fixed by the acceptor dopants. The second curve (squares) gives the vacancy fraction for the intrinsic oxygen ion conductor \(\text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})\text{O}_7\) (GZT). In this case, \([V_o\cdot\cdot]\) at each value of \(x\) was calculated from the pre-exponential constant of ionic conduction obtained from electrical measurements and the atomistic model of equation 3.33. The variables used in the model included those used by Heremens [27] with \(\nu_o=1.2 \times 10^{13} \text{ Hz}\), \(\exp(S_{\text{Ti}}/k)=7.0\) and the vacancies assumed to occupy only the 48f sublattice.

At first glance, the two curves seem to indicate that ionic conductivity is independent of how disorder is created. That is for a fixed vacancy
Figure 6.4 The ionic conductivity versus oxygen vacancy fraction for \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\). The circled points represent data points after the solubility limit of 7.0 mole\% Ca. Also shown is the data for \(\text{Gd}_2(\text{Ti}_{1-y}\text{Zr}_y)\text{O}_7\) as a function of \(y\) from reference [18].
concentration, \( \sigma_i \) is equivalent whether the disorder is induced extrinsically or intrinsically. These results, however, must be taken with caution. In calculating the values for \([V_0^-]\) we note several approximations. In the atomistic model (equation 3.33), the vacancy fraction is a function of two unknown quantities: the jump attempt frequency \( v_o \) and migration entropy \( S_m \). In our case, the values of \( v_o = 1.2 \times 10^{13} \text{ Hz} \) and \( \exp(S_m/k) = 7.0 \) were used. Changing either of these quantities results in a shift in the log \( \sigma_i \) versus \([V_0^-]\) curve. For example if \( \exp(S_m/k) \) is taken as zero (e.g. the value used by Moon [18]), the intrinsic curve is shifted downward with respect to the extrinsic case.

Secondly, we note that the data is compared only at a fixed temperature of 1000°C. In figure 6.5 we plot the ionic activation energy versus vacancy fraction. For a fixed vacancy fraction, the activation energy is shown to be lower for the extrinsic case. From an atomistic point of view, this results is somewhat surprising since the mobility is expected to increase with the larger lattice parameter (i.e. increasing Zr). A partial explanation, however, may result from examining the degree of order in the two systems. As noted earlier [24], oxygen ion transport in pyrochlores changes markedly as a function of order. A preferential diffusion path is suggested to exist in the ordered material (e.g., \((\text{Gd}_1-x\text{Ca}_x)_2\text{Ti}_2\text{O}_7\)) with the strain energy contribution reduced.

6.1.3.2 Extrinsic Doping In \( \text{Gd}_2(\text{Zr}_{0.25}\text{Ti}_{0.75})_2\text{O}_7 \) (GZT25)

The dramatic change in carrier concentration for \( \text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7 \) and \((\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\) shown in figures 6.4 implies that the free vacancy concentration for ion transport is a function of order. However the results presented above were only approximations with several unknown parameters
Figure 6.5 The ionic activation energy constant versus oxygen vacancy fraction for \((\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7\). The circled points represent data points after the solubility limit of 7.0 mole% Ca. Also shown is the data for \(\text{Gd}_2(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_7\) as a function of \(y\) from reference [18].
used in the calculations. We now try to quantify the trend of increasing carrier concentration with increasing disorder using dopants in the intrinsic oxygen ion conductor Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ (GZT).

In section 2.1.2 we presented the earlier work of Moon et al. [18] on pyrochlore solid solutions of Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ (GZT). In these studies, GZT was found to be a mixed ionic-electronic conductor in which the ionic component of conductivity increased orders of magnitude with increasing "x". The large increase was attributed primarily to an increase in intrinsic anion disorder, or the creation of oxygen vacancy-interstitial pairs. For the composition Gd$_2$(Zr$_{0.30}$Ti$_{0.70}$)$_2$O$_7$ (x=0.3) an effective Frenkel constant given by:

$$K_F(T) = 1.0 \times 10^{39} \exp[-0.24+0.03eV)/kT]cm^{-6}$$

was derived by examining the effects of dopants on the ionic conduction. Based on the findings of an increase in the pre-exponential term of ionic conduction along with x-ray determined structural disorder, it was suggested that the effective frenkel energy must decrease with increasing x, becoming negligibly small at values of x close to one. To confirm this result, we now examine the frenkel activation energy of a slightly more "ordered" pyrochlore Gd$_2$(Zr$_{0.25}$Ti$_{0.75}$)$_2$O$_7$ (GZT25).

The analysis starts by first confirming that GZT25 is an intrinsic oxygen ion conductor. In figure 6.6 we compare the pre-exponential term of ionic conduction to that of the other GZT compositions. The Log $\sigma^0$ vs "x" data for Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ was obtained from the study by Moon [18] while $\sigma^0$ for GZT25 was obtained from the a "A" fitting parameter in table 5.6. When $\sigma^0$ for GZT25 is plotted on this curve, excellent agreement with a linear extrapolation for the oxygen vacancy fraction is observed. Assuming the atomistic model of
Figure 6.6 The ionic pre-exponential constant and oxygen vacancy fraction as a function of $y$ in Gd$_2$(Ti$_{1-y}$Zr$_y$)$_2$O$_7$ from reference [18]. Included in the figure are the results for Gd$_2$(Ti$_{0.75}$Zr$_{0.25}$)$_2$O$_7$. 
equation 3.33, an intrinsic mobile oxygen vacancy fraction of \(2 \times 10^{-4}\) is calculated, a factor of 25 lower than the smaller of the two doping densities (e.g., 0.5% Ca).

With the data in figure 5.68 reflecting intrinsic oxygen ion disorder alone, we can apply equations 3.34 to the conductivity parameters. Table 5.6 shows an ionic activation energy for the undoped material of 0.96 eV. Correspondingly:

\[
E_{\text{ion}} = 0.96 \text{ eV} = E_F/2 + E_{\text{mig}}
\]  

(3.34)

For the doped case, table 5.6 shows an activation energy of 0.74 eV is obtained. (We use the data for \(y=0.005\) since this sample shows less scatter than the data for \(y=0.01\)). Accordingly, equation 3.27 shows this value to be the migration energy \(E_{\text{mig}}\). Substituting 0.74 eV into equation 3.34 one derives a value of 0.44 eV for the frenkel activation energy. This value of 0.44 eV, compared to 0.24 eV for GZT \(x=.3\) is consistent with the trend of increasing intrinsic structural disorder with increasing Zr in Gd\(_2\)(Ti\(_{1-x}\)Zr\(_x\))\(_2\)O\(_7\) (GZT) solid solutions.

6.1.3.3 Extrinsic Doping In \((La_{1-x}A_x)Zr_2O_7\) (A=Sr,Ca)

This section examines the effects of dopants in an ordered zirconate, La\(_2\)Zr\(_2\)O\(_7\), comparing these results to those obtained in other intrinsic zirconate based materials.

In the literature review, section 2.3.2.4, we presented conductivity data for several zirconia based pyrochlore compounds. Table 2.3 showed a general trend of decreasing ionic activation energy and pre-exponential constant with
increasing \( r_A/r_B \) radius ratio. The trend was found valid up to a \( r_A/r_B=1.51 \) or \( \text{Sm}_2\text{Zr}_2\text{O}_7 \). For the next composition \( \text{Nd}_2\text{Zr}_2\text{O}_7 \) the pre-exponential continued to decrease but the activation energy increased. For the doped materials, dopants had little or no effects on the conductivity parameters for \( r_A/r_B<1.51 \). However for \( r_A/r_B>1.51 \) (e.g., \((\text{Nd}_{1-x}\text{Ca}_x)\text{Zr}_2\text{O}_7\)) dopants were shown to have a pronounced effect on the conductivity.

Examination of conductivity parameters for \((\text{La}_{1-x}\text{A}_x)\text{Zr}_2\text{O}_7 \) \((\text{A}=\text{Sr},\text{Ca})\) in table 5.7, reveals a similar pattern to \((\text{Nd}_{1-x}\text{Ca}_x)\text{Zr}_2\text{O}_7\). In this case acceptor doping results in an increase in carrier concentration and activation energy. However the increase in \( \sigma_0 \) outweighs the increase in \( E_1 \) with the net result being an increase in \( \sigma_1 \).

In discussing the above results, we first explore the role of order on the carrier concentration, \( \sigma_0 \). For pyrochlore compounds such as \( \text{Nd}_2\text{Zr}_2\text{O}_7 \), and \( \text{La}_2\text{Zr}_2\text{O}_7 \), a larger "A" site ion results in ordering of the "A" and "B" site cations and a lower intrinsic carrier concentration \( \sigma_0 \). Further, since the number of free vacancies is reduced on ordering, it is logical to assume that dopants would have a larger effect on the carrier concentration in ordered materials rather than in disordered materials.

Our results for \((\text{La}_{1-x}\text{A}_x)\text{Zr}_2\text{O}_7 \) \((\text{A}=\text{Sr})\) appear to be consistent with this trend. If we compare \( \sigma_0 \) of \( \text{La}_2\text{Zr}_2\text{O}_7 \) with 1.0\% Sr to \( \text{Gd}_2\text{Zr}_2\text{O}_7 \) (tables 2.2 and 5.7) the pre-exponential is several orders of magnitude lower. Even the 10 mole\% Sr doped sample has a lower \( \sigma_0 \) than \( \text{Gd}_2\text{Zr}_2\text{O}_7 \). We conclude therefore that although doping increases the carrier concentration in ordered zirconates the increase in \( \sigma_0 \) is still not as great as that induced intrinsically in \( \text{Gd}_2\text{Zr}_2\text{O}_7 \).

Caution, however, is noted in comparison of the activation energies. \( E_1 \) is shown to be over 1.0 eV in \((\text{La}_{1-x}\text{A}_x)\text{Zr}_2\text{O}_7 \) \((\text{A}=\text{Sr},\text{Ca})\) much larger than the values for the \( \text{A}_2\text{Zr}_2\text{O}_7 \) \((\text{A}=\text{Gd}, \text{Sm}, \text{Nd})\) pyrochlores presented in table 2.2.
Although this results may reflect a optimum lattice size (e.g., "A" site ion) for ionic transport, we point out that the effects of defect association and solubility are yet resolved. Further work on other "order" zirconate materials is needed to confirm this result.

6.2 APPLICATIONS OF TITANATE-ZIRCONATE PYROCHLORES

In the second part of our discussion we generalize to address several technological issues. In particular, we evaluate the rare earth titanate/zirconate pyrochlores as oxygen ion conducting electrolyte materials and their ability to provide essential information on modeling and measuring MIEC.

6.2.1 TRENDS IN $\sigma_i$, $P_n$, $P_p$

We first examine trends in $\sigma_i$, $P_n$, and $P_p$, three parameters essential to electrolyte performance.

In the theory section of this thesis (table 3.1), we summarized expressions for $\sigma_i$, $P_n$, $P_p$, and $P_p/P_n$ under the limiting cases of (a) intrinsic frenkel disorder (b) unassociated acceptor doping and (c) associated acceptor doping. We start with the factors influencing $\sigma_i$. Column #1 in table 3.1 shows that optimum values of $\sigma_i$ are obtained for high oxygen vacancy densities coupled with high oxygen mobilities. For intrinsic disorder, this cindition is satisfied when $K_F$ is large as possible. For extrinsic disorder, however, the acceptor density $[A']$ needs to be high, and the association energy low, as this lowers the fraction of mobile ions.
For the pyrochlore oxides GT, ST and GZT we find these trends to be valid. Figures 5.49 and 5.64 demonstrate that $\sigma_1$ is optimized by selecting highly soluble dopants with a good size match to the host. The correlation between the carrier concentration and frenkel activation energy in GZT (e.g., $\sigma^0$ increases as $E_F$ decreases) demonstrates the influence of $K_F$ on $\sigma_1$.

The magnitude of $\sigma_1$ also may be varied by systematic changes in lattice parameter. For example, the ionic mobility of large ions such as oxygen are influenced more by strain than electrostatic considerations. One tends to select compositions with larger lattice parameters, all else being equal for optimum $\sigma_1$. This is demonstrated in figure 6.7. The figure compares the 1000°C isotherms of log $\sigma$ versus log PO$_2$ for the host A-site ions Y and Gd, i.e.

(A$_{0.98}$Ca$_{0.02}$)$_2$Ti$_2$O$_7$ (A=Y, Gd,). In each case, the PO$_2$ independent ionic conductivity is seen to dominate over the electronic conductivity at high PO$_2$'s. Both the magnitude and extent of the PO$_2$-independent conductivity of (Gd$_{0.98}$Ca$_{0.02}$)$_2$Ti$_2$O$_7$ are, however, considerably greater than that of (Y$_{0.98}$Ca$_{0.02}$)$_2$Ti$_2$O$_7$. This results in a much stronger increase in MIEC with decreasing PO$_2$ in the (Y$_{0.98}$Ca$_{0.02}$)$_2$Ti$_2$O$_7$ relative to (Gd$_{0.98}$Ca$_{0.02}$)$_2$Ti$_2$O$_7$.

The applicable working range of an electrolyte material may be described by its electrolytic domain boundary position $P_n$ (i.e., for our particular case, the PO$_2$ for which $\sigma_1 = \sigma_e$). This boundary separates the range of temperatures and PO$_2$'s above which predominantly electrolytic behavior is present and below which reflects largely semiconducting behavior. Column #2 in table 3.1 shows that the same parameters which influence $\sigma_1$ are evident in $P_n$ along with two additional parameters $K_F$ and $\mu_e$.

To demonstrate the effects of temperature and composition on $P_n$ we refer to figure 5.26. In this figure we plot the domain boundary position as a function of temperature for (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$. As the temperature is lowered,
Figure 6.7 Log conductivity as a function of log oxygen partial pressure for (Gd_{0.98}Ca_{0.02})_2Ti_2O_7 and (Y_{0.98}Ca_{0.02})_2Ti_2O_7 at 1000°C.
the boundary position is shown to shift to lower PO$_2$'s. P$_n$ drops ~20 orders of magnitude at 1000°C as x increases from 0 to 0.10. Figure 5.27 shows that this decrease is qualitatively consistent with the predictions of Table 3.1 (i.e. a slope of -6.4 compared to the predicted value of -6).

The effects of K$_r$ and $\mu_e$ on P$_n$ are represented by Al doping. We have observed that increasing the acceptor content results in a decrease in $\sigma_e$. For the Al dopants we can partially attribute this decrease to a decrease in both K$_r$ and $\mu_e$ induced by the dilution of Ti with Al. Al removes the readily reducible species as well as narrowing the Ti derived 3d-like conduction band.

Lastly, we examine the figure of merit P$_p$/P$_n$, a measure of the domain width, which is maximized under conditions for which the ion/electron-hole carrier density and mobility ratios are optimized. Notice that, while K$_r$ does not influence the domain width, it does determine its position in PO$_2$ space. In fuel cell or sensor applications, we wish P$_p$ and P$_n$ to include within their bounds, the most oxidizing and reducing gases likely to be utilized. Figure 5.38 demonstrates this point showing that the working range for both P$_n$ and P$_p$ may be varied by changing the Al concentration.

6.2.2 SHORT CIRCUIT CURRENT TECHNIQUE

In the theoretical part of this thesis (section 3.3), a novel short circuit current method was described for measuring ionic conductivity in a mixed ionic - electronic conductor (MIEC). The method, as proposed by I. Riess [64], involves eliminating the driving force for electrons by shorting the electrical potential
across them. Since the validity of this technique had not yet been confirmed, our initial study involved a series of experiments to test its accuracy.

In figure 5.79 we compared the ionic conductivity data of \((\text{Gd}_{0.9975}\text{Ca}_{0.0025})_2\text{Ti}_2\text{O}_7 (\text{GT .25}\%\text{Ca})\) obtained from the short circuit current method to that of ac "bulk" impedance. Although the two values are shown to be nearly equal at 950°C, as the temperature is lowered, the values diverge. The short circuit current data gives a lower conductivity and a higher activation energy of 1.2 eV.

The question arises as to the source of this discrepancy. Examination of equation 3.44 may provide the answer. In this equation, the total measured ionic current was taken as:

\[
I_{\text{SC}} = \frac{V_{\text{th}}}{(R_i + R_{i,C})}, \quad V = 0
\]  

(3.44)

where \(R_i\) is the ionic resistance, \(R_{i,C}\) the ionic contact resistance, and \(V_{\text{th}}\) the theoretical Nernst voltage. Since the short circuit current method, as applied here, is a two probe technique, the bulk resistance, \(R_i\), cannot be isolated from the contact resistance \(R_{i,C}\). Presumably, the difference between the two methods represents the \(R_{i,C}\) contribution. Unfortunately, the complex impedance spectra for this particular sample in the \(\text{PO}_2\)-gradient cell were insufficiently clear to enable isolation of the contact resistance.

Another reason why the values could deviate is gas leakage around the sample. For large leaks, the approximation of \(V_{\text{OC}} = V_{\text{th}}\) is no longer valid. In our case leakage was usually observed \(\text{PO}_2\) gradients larger than four orders of magnitude.

To confirm the accuracy of the short circuit current technique therefore, future experiments are recommended on similar specimens with gas leakage.
problems minimized. The test configuration should also be such as to eliminate contact resistance or specifically under a four-probe type configuration where the voltage probes block the flow of electrons.
7 CONCLUSIONS

Pyrochlore solid solutions of \((\text{Gd}_{1-x}\text{A}_x)\text{Ti}_{1-y}\text{B}_y\text{O}_7\), (GT), 
\((\text{Y}_{1-x}\text{A}_x)\text{Ti}_2\text{O}_7\), (YT), 
\((\text{Sm}_{1-x}\text{A}_x)\text{Ti}_2\text{O}_7\), (ST), and 
\((\text{La}_{1-x}\text{A}_x)\text{Zr}_2\text{O}_7\), (LZ), 
have been prepared in order to examine the combined effects of structural 
disorder (extrinsically and/or intrinsically induced) and composition on the 
electrical properties of rare-earth pyrochlore compounds. A variety of "A" site 
(Ca, Sr, Mg, K), and "B" site (Al) acceptor dopants were incorporated 
substitutionally into the host \(\text{A}_2\text{B}_2\text{O}_7\) lattice. The following observations have 
been made:

1. Both the magnitude and type of conduction (ionic and/or electronic) were 
found to be influenced by dopant size, effective charge, site location ("A" or "B"
cation sublattice) and net dopant density.

2. The highest ionic conductivity was found in the gadolinium system (GT) with 
an "A" site (Ca) dopant. For the composition \((\text{Gd}_{0.9}\text{Ca}_{0.1})\text{Ti}_2\text{O}_7\), a maximum 
in \(\sigma_i\) of \(5\times10^{-2}\) S/cm at 1000°C was obtained, within a factor of two of stabilized 
zirconia (YSZ). This represents the highest ionic conductivity reported to date for 
a titanate based material.

3. For the "A" site Ca doped titanates (GT, YT, ST), a concentration dependent 
ionic conductivity was observed. In each system, the maximum conductivity 
corresponded to a minimum in activation energy. In \((\text{Gd}_{1-x}\text{Ca}_x)\text{Ti}_2\text{O}_7\) for 
example, the activation decreased from 0.94 eV to 0.63 eV as the conductivity 
increased 2 1/2 orders of magnitude for \(x\) between 0.0 and 0.1. These results 
are qualitatively similar to those reported in yttria-doped ceria in which the 
decrease in activation energy is attributed to the creation of favorable transport 
paths between the uncompensated \(Y'_\text{Ce}\) sites and the \((Y'_\text{Ce} - V_{O^{\cdot\cdot}})\) complexes.
4. The increase in $\sigma_i$ and decrease in $E_i$ was evident for "B" site Al doping as well (e.g. Al$^{\text{III}}$). In this case, however, the trend was valid only up to a doping level of $y=0.01$ in $\text{Gd}_2(\text{Ti}_1-y\text{Al}_y)_2\text{Ti}_2\text{O}_7$. At higher dopant levels, $\sigma_i$ dropped sharply as the solubility limit was exceeded. X-ray diffraction lattice parameter measurements confirmed the solubility limit for Al doping in $\text{Gd}_2(\text{Ti}_1-y\text{Al}_y)_2\text{Ti}_2\text{O}_7$ to be $y \leq 0.01$

5. The effects of dopant-host size mismatch were examined using the dopants Mg($r=0.89$ Å), Ca($r=1.12$ Å), and Sr($r=1.25$ Å). In ST and GT, a well defined maximum in $\sigma_i$ vs. normalized radius ratio ($r_{\text{dopant}}/r_{\text{host}}$) was obtained with the highest ionic conductivity found for the smallest dopant-host size mismatch. These results are consistent with theoretical and experimental studies of acceptor doped fluorites which show a minimum strain energy contribution as the dopant ionic radii approaches that of the host.

6. Electronic conduction in the titanate based materials showed an opposite dependence with acceptor doping. For the "A" site dopants Ca, Sr and Mg, n-type conductivity decreased with increasing dopant concentration and dopant-host size match.

7. The flexibility of the $A_2\text{Ti}_2\text{O}_7$ ($A=Y$, Gd, Sm) host in accommodating substitutions of "A" site ions and dopants has been used to explore combined effects of doping and variable host lattice size on the conductivity parameters. The higher conductivity in $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$, relative to $(\text{Y}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$, is consistent with reduced strain energy contributions to the migration energy for the crystal with the larger lattice parameter. In apparent contradiction to this observation, $(\text{Sm}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$, the largest "A" site host ion, has the lowest
conductivity. This may result from the fact that Sm$_2$Ti$_2$O$_7$ lies close to the pyrochlore-monoclinic phase boundary. Since Ca$^{2+}$ has a slightly larger ionic radius than Sm$^{3+}$ (1.12 Å vs 1.09 Å), it is expected to promote crystallographic distortion when substituted into the Sm$_2$Ti$_2$O$_7$ lattice.

8. Key thermodynamic and kinetic parameters were extracted from the conductivity measurements using a defect chemical model. Values for Frenkel formation ($E_F$), migration ($E_m$), association ($E_A$), reduction ($E_r$) and band gap ($E_g$) were obtained for several acceptor doped materials. In Ca doped (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$, an ionic activation energy of 0.63 ± 0.05 eV was found for the composition range of x=0.02 - 0.15. Assuming a migration energy of 0.6 eV in (Gd$_{0.98}$A$_{0.02}$)$_2$Ti$_2$O$_7$ (A=Ca, Sr, Mg), association energies of 0.03 eV, 0.12 eV, and 0.07 are obtained for the dopants Ca, Mg, and Sr respectively. The intrinsic frenkel activation energy ($E_F$) was obtained for the pyrochlore composition (Gd$_{1-x}$Ca$_x$)$_2$(Ti$_{0.75}$Zr$_{0.25}$)$_2$O$_7$ (GZT x=0.25). Its value of 0.44 eV, compared to 0.24 eV for GZT x=0.3 was consistent with the trend of an increase in intrinsic structural disorder with increasing Zr in Gd$_2$(Ti$_{1-x}$Zr$_x$)$_2$O$_7$ (GZT) solid solutions.

9. In contrast to the acceptor doped titanates, the ionic activation energy of zirconia-based La$_{1-x}$AxZr$_2$O$_7$ (A=Ca,Sr) increased with increasing acceptor concentration. However the increase in pre-exponential factor outweighed the increase in activation energy resulting in significantly higher ionic conductivities for the doped material.

10. The "short circuit current" method of measuring ionic conduction in a mixed ionic - electronic conductor (MIEC) has been applied experimentally for the first time. Ca doped (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$, was the material selected since its ionic and
electronic conductivities could be isolated independently by examination of the
PO$_2$-dependence of the total conductivity. A PO$_2$-independent ionic conductivity
characterized by an activation energy of 1.2eV was obtained by the short circuit
current method, somewhat lower in magnitude and higher in activation energy
(by 0.3eV) than values obtained by complex impedance. This difference was
attributed to the contact resistance associated with a 2-probe configuration of
measurement.
8 Future Work

1. An electrostatic defect-impurity association model has been used to explain the concentration dependent conductivity defect association found in Ca doped (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$. Further studies including dielectric and anelastic relaxation are required to confirm this hypothesis. Not only will these techniques confirm the existence of associates, but also the degree and type of interaction involved.

2. The impedance spectra at low temperatures for (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$. often show depressed semicircles. These results were taken as the influence of grain boundary conduction. Further work is needed to verify these effects including measurement on single crystals of (Gd$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$.

3. The conductivity behavior of an "A" site (Ca) versus "B" site (Al) dopant were found to be similar. In both cases, the ionic conductivity increased with increasing acceptor concentration. However for the "B" site dopant, the trend was valid only up to the solubility limit of ≤1.0 mole% Al. To confirm this trend, a "B" site dopant is needed with a higher solid solubility.

4. In acceptor-doped titanate pyrochlores, the highest ionic conductivity was found for the dopant with the best size match to the host. An increase in ionic activation energy was found to accompany the dopants with a larger mismatch. This increase was attributed to association and/or solubility. To confirm a solubility limit, further structural studies are required. For dopants such as Mg$^{2+}$, the ability to substitute at least partially on the "B" site may also play a role. Under these circumstances, our formulation would lead to "A"-site...
deficiency, which could also be a source for the high activation energy. Neutron
diffraction experiments are recommended to confirm this hypothesis.

5. For a fixed oxygen vacancy concentration (1000°C), the ionic conductivity in
GT, an extrinsic, ordered pyrochlore, was found equivalent to GZ, an intrinsic
disorder pyrochlore. The exact nature of this results needs further examination.
In particular, continued theoretical and experimental studies are need to
investigate the migration mechanism and the role of dopants on lattice strain and
electrostatic interactions in extrinsic doped pyrochlores.

6. Acceptor doping in La$_2$Zr$_2$O$_7$ resulted in an increase in ionic conductivity with
the ionic activation energy increasing with acceptor concentration.. Caution
however is noted in this results. Since only two dopant concentrations were
investigated, the effects of solubility, and defect association on the activation
energy needs to be further studied.

7. A simple hypothesis stated in this thesis was that the larger the host
lattice (i.e. open structure) the higher the ion mobility due to reduced strain
contributions to the migration energy. In apparent contradiction to this
observation, (Sm$_{1-x}$Ca$_x$)$_2$Ti$_2$O$_7$, the largest "A" site host ion investigated,
had the lowest conductivity. This may result from the fact that Sm$_2$Ti$_2$O$_7$
lies close to the pyrochlore phase boundary with Ca additions resulting in
crystallographic distortion. Neutron diffraction experiments are suggested to
verify this hypothesis.

8. The "short circuit current" method was used to measure ionic conduction in a
MIEC. The somewhat lower ionic conductivity and higher activation energy was
attributed to the contact resistance associated with a 2-probe configuration. Future experiments are needed to confirm this conclusion. In particular, experiments should be performed on similar MIEC specimens under a four-probe type configuration which block the minority carriers (i.e. electrons).

9. Zirconium and titanium based pyrochlore oxides are of technological interest as ionic conducting electrolyte's and MIEC electrode materials. In this thesis a novel idea for a SOFC was proposed which consists of alternating layers of ionic and mixed ionic - electronic conducting pyrochlore compounds. Such a "composite" structure could take advantage of single phase structure. The electrical and mechanical properties of this "composite" and its flexibility of controlling either ionic or MIEC needs to be evaluated.
BIBLIOGRAPHY


