ELECTRICAL CONDUCTIVITY AND STRUCTURAL DISORDER IN
Gd₂Ti₂O₇, -Gd₂Zr₂O₇, AND Y₂Ti₂O₇, -Y₂Zr₂O₇, SOLID SOLUTIONS

by

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of the Degree of Doctor of Philosophy

at the

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MAR 28 1988
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ABSTRACT

Two pyrochlore phase solid solutions, (Gd₂(Zr₆Ti₁₋ₓ)₂O₇, and
Y₂(Zr₆Ti₁₋ₓ)₂O₇), were investigated in order to clarify
the relationship between composition, structural disorder and
ionic conductivity in pyrochlore compounds. It was
established that (A⁺⁺)[B⁺⁺]₂O₇, (A=Gd,Y and B=Ti,Zr) pyrochlores
contain substantial intrinsic structural disorder especially
for the case of small A cations and large B cations. Disorder
occurs in pyrochlores when the superstructure ordering that
distinguishes pyrochlore structure from fluorite structure is
partially lost.

A defect chemical model was developed from electrical
conductivity and x-ray diffraction measurements. The basis of
the model is anion quasi-Frenkel defect dominated disorder
forming divalent mobile oxygen vacancies leading to
electrolytic conduction near stoichiometry and mixed
(i.e. both electronic and ionic) conduction under reducing
conditions.

An investigation of ionic and electronic transport in the
Gd₂(Zr₆Ti₁₋ₓ)₂O₇ system as a function of temperature,
atmosphere, dopant concentration and overall composition was
performed. The results were interpreted in light of the above
defect model and led to calculation of several defect chemical
parameters including the Frenkel constant, oxygen vacancy
mobility, energies of association, ionic motion, reduction and
thermal bandgap.

Polycrystalline specimens for electrical characterization
were prepared by the Pechini method of powder synthesis
followed by sintering at 1600 °C. The Pechini method produces
homogeneous, sinterable powders with well defined molar ratios
and allows considerable flexibility in the choice of
composition. A few single crystals, grown from a fluxed melt,
were also studied.

The contributions to the overall electrical impedance
from the bulk and grain boundaries of the polycrystalline
samples were successfully deconvoluted with complex impedance
spectroscopy. Bulk conductivity, bulk dielectric constant and
grain boundary resistance values were all derived from the
complex impedance measurements.

The individual ionic and electronic components of the
bulk conductivity were derived by fitting the bulk
conductivity vs. PO₄ data to the defect model using the
following equation:

\[ \log \sigma = \log \left[ A + B(PO_4^{1/4}) + C(PO_4^{3/4}) \right] \]

A is the ionic conductivity, B(PO₄⁻¹/₄) is the electronic
conductivity and C(PO₄⁻³/₄) is the hole conductivity. A, B and
C are independent of PO₄. The values of A, B and C were used
to calculate the extent of the electrolytic region as a
function of temperature, PO₄ and composition.

The anion Frenkel constant (Kᵥ) and oxygen vacancy
mobility (μᵥ) were calculated from doping experiments. The
value of Kᵥ for Gdₓ(Zrₒ.7Tiₒ.7)₂O₇, was calculated as
1.0x10⁹exp(-0.24±0.03eV/kT) cm⁻¹ and μᵥ was found to be
0.14exp(-0.78±0.02eV/kT) cm²V⁻¹s⁻¹ based on electrical
conductivity measurements on undoped, acceptor doped and donor
doped materials.

The structural disorder was quantified with cation (τᶜ)
and anion (τᵃ) order parameters. It was found that both order
parameters decrease as Zr is substituted for Ti in
Gdₓ(ZrₓTi₁₋ₓ)₂O₇. This increase in disorder was correlated
with the cation radius ratio and the ionic conductivity in
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Thesis Supervisor: Dr. Harry L. Tuller
Title: Professor of Ceramics and Electronic
Materials
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1 INTRODUCTION

1.1 Purpose of Research

Oxygen ion conduction has been intensively studied in many different laboratories over a period of decades and yet a detailed explanation of its dependence upon composition, structure, temperature and defect concentration is still lacking in most cases. The purpose of this thesis is to explore the relationships between composition, crystal structure and ionic conductivity in the relatively simple pyrochlore system. Knowledge of these relationships allows prediction of the composition and processing parameters required to obtain optimal anion conduction in this particular structure. Additionally, insight may be obtained into the general principles that underlie processes such as order-disorder transitions, fast ion conduction and defect associate formation that are fundamental to many ionic conducting systems.

The pyrochlore crystal structure system was chosen because it has several unusual attributes that simplify its use as an experimental model. First, certain pyrochlore compounds, such as Gd$_2$Zr$_2$O$_7$, are excellent oxygen ion conductors with conductivities that approach the values found in stabilized ZrO$_2$. Second, the pyrochlore structure accommodates a wide variety of substitutional impurities so
that many different solid solutions over a large concentration range are possible. Third, pyrochlore compounds are easy to characterize electrically since they have an almost ideal response to complex impedance spectroscopy. Finally, it is known that the ionic disorder present in certain pyrochlore solid solutions is a function of their composition and temperature.

The particular compositions Gd₂(ZrₓTi₁₋ₓ)₂O₇ and Y₂(ZrₓTi₁₋ₓ)₂O₇, were chosen because they exhibit large changes in conductivity with composition, include both pyrochlore and fluorite materials and, in the case of Y₂(ZrₓTi₁₋ₓ)₂O₇, are appropriate for structural studies by neutron diffraction. There is a considerable body of literature on Gd₂Zr₂O₇, but little previous research on any of the other compositions.

The experimental procedures for this thesis focus on measurement of bulk and grain boundary electrical resistances by complex impedance spectroscopy. The measurements are made on a variety of compositions, dopant concentrations, temperatures and oxygen partial pressures in order to determine the ionic and electronic conductivities and the defect chemical parameters and their composition dependences. These data are correlated with structural information obtained by x-ray diffraction and literature data on infrared and Raman spectroscopy and x-ray and neutron diffraction.

This thesis reports data using certain non-SI units such as centimeters, atmospheres and electron volts. Table 1.1 gives the conversion factors from these units to SI units.
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<tr>
<td>1 S/cm</td>
<td>100 S/m</td>
</tr>
<tr>
<td>1 atm</td>
<td>1.01 x 10^5 Pa</td>
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<tr>
<td>1 Å</td>
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<tr>
<td>1 cm²V⁻¹s⁻¹</td>
<td>10⁻⁴ m²V⁻¹s⁻¹</td>
</tr>
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<td>1 cm⁻³</td>
<td>10⁵ m⁻³</td>
</tr>
</tbody>
</table>
2 LITERATURE REVIEW

The literature review begins with a description of the pyrochlore structure and its crystal chemistry in order to clarify the relationship between this structure and the ionic mobility of its constituents. The next section briefly outlines the electrical properties of fluorite structure oxides in order to contrast them with pyrochlore compounds. The final sections consider the results of structural and electrical measurements of the titanate and zirconate pyrochlores made by previous authors.

2.1 Pyrochlore Structure

The pyrochlore structure has space group Fd3m, a cubic unit cell with a lattice constant of roughly 10 Å and general molecular formula of $A_xB_2O_6X$ where $A$ and $B$ are cations and $O$ and $X$ are anions. There are eight formula units per unit cell. A diagram of a portion of the pyrochlore structure projected onto the (100) plane is shown in Figure 2.1.

All the possible pyrochlore compositions must meet certain constraints of ionic charge and radii. The acceptable ionic charges include $(A^{3+})_2(B^{4+})O_7$, $(A^{2+})_2(B^{6+})O_7$, $(A^{+}A^{2+})(B^{5+})_2O_6F$, $(A'^{+})(B^{8+}B^{6+})O_6$ and various combinations of these[1]. The ionic radii constraints require a certain range of both cation radius ratio ($R_a/R_b$) and absolute cation radius values. The A cation can include most of the alkali, alkaline earth or
Figure 2.1 (100) Projection of a portion of one unit cell of the pyrochlore structure. Ionic radii are based on Gd₂Ti₂O₇ [2].
lanthanide elements and the B cation can be almost any transition element with the appropriate charge. Thus, the number of possible compositions is enormous.

2.1.1 PYROCHLORE AND FLUORITE STRUCTURES

The pyrochlore structure is a superstructure of the ideal defect fluorite structure (Fm3m) with exactly twice the lattice parameter. The ideal defect fluorite structure is adopted by materials such as yttria stabilized zirconia if the oxygen vacancies are assumed to occur completely at random on the oxygen sublattice and the yttrium dopant cations to occur at random on the cation sublattice. In reality, short range ordering occurs between the dopant cations and oxygen vacancies[3-5] so that stabilized ZrO$_2$ does not actually adopt the ideal defect fluorite structure. Other oxides, such as CeO$_2$ and ThO$_2$, form the fluorite phase without dopants[6] but, in that case, have very few vacancies and can not be considered as defect fluorite phase. Thus, there are no known materials that meet the requirements of ideal defect fluorite phase, i.e., a substantial oxygen vacancy concentration without defect ordering. Nevertheless, ideal defect fluorite serves as a good basis for understanding pyrochlore compounds. A projection of part of the fluorite structure onto its (100) plane is shown in Figure 2.2.

Pyrochlore and ideal defect fluorite differ in that pyrochlore has additional ordering on both the cation and anion sublattices and some of the oxygen ion positions are
Figure 2.2  (100) Projection of a portion of four unit cells of the fluorite structure. Ionic radii are based on CeO$_2$[2].
slightly distorted from their fluorite position. Oxygen vacancies occur at random throughout the anion sublattice in fluorite but are ordered onto particular sites in the pyrochlore structure. Table 2.1 shows the site occupation of ideal pyrochlore and ideal defect fluorite compounds. Throughout this thesis the site positions are based on the conventions that the pyrochlore unit cell origin is on the 16c site and that the fluorite sites can be described by their closest equivalent in the Fd3m space group.

<table>
<thead>
<tr>
<th>Table 2.1</th>
<th>Site Occupancies of A\textsubscript{x}B\textsubscript{y}O\textsubscript{z}X Compounds in Ideal Pyrochlore and Ideal Defect Fluorite Structures[7]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>Pyrochlore (Fd3m)</td>
</tr>
<tr>
<td>A</td>
<td>16c</td>
</tr>
<tr>
<td>B</td>
<td>16d</td>
</tr>
<tr>
<td>O</td>
<td>48f</td>
</tr>
<tr>
<td>X</td>
<td>8a</td>
</tr>
<tr>
<td>V\textsubscript{o}</td>
<td>8b</td>
</tr>
</tbody>
</table>

In (A\textsuperscript{3+})\textsubscript{2}(B\textsuperscript{4+})\textsubscript{2}O\textsubscript{6}, pyrochlore compounds[7] the A\textsuperscript{3+} cations have eight nearest neighbor oxygens forming a distorted cube with \(\bar{3}m\) symmetry. The smaller B\textsuperscript{4+} cations have only six nearest neighbor oxygen ions which form a distorted octahedron also with \(\bar{3}m\) symmetry. All the oxygen ions are surrounded by a tetrahedron of four cations but the 8a site has only A cations as its nearest neighbors while the 48f site has two A
and two B cations around it. The unoccupied 8b site is surrounded by four B cations as its nearest neighbors. If all the atoms are considered as hard spheres, then the 8b site has the largest space of any oxygen site in its nearest neighbor tetrahedron due to the small size of the B cations that surround it, but, it has the closest second nearest neighbors since the 48f anions move slightly inward towards the empty 8b site. Refer to Figure 2.1.

The second nearest neighbors of each oxygen site (i.e., other oxygen sites) are the logical sites for diffusion by oxygen vacancy hopping. Consideration of Figure 2.1 will show that the second nearest neighbors of the 8a and 8b sites are always 48f sites. Therefore, diffusion by interstitials on a continuous network of 8b sites or vacancy diffusion exclusively via 8a sites can be ruled out. The 48f sites, whose second nearest neighbors include 8a, 8b and other 48f sites, form the only oxygen sublattice with a continuous network of second nearest neighbors of the same type. Thus, the 48f sites are the most likely location for mobile oxygen vacancies.

The pyrochlore structure is often described[1] as a network of distorted corner shared octahedra made up of B cations and 48f oxygen ions with the implication that the A cations and 8a anions are not necessary for structural integrity. Indeed, certain pyrochlore compounds, such as \((K')(\text{Nb}^{5+}W^{6+})_0\), occur with partial occupancy of the 16c site and an empty 8a site[1,8,9]. However, the scant available
evidence[10] suggests that cation vacancies do not occur in 
\((A^{+})_{2}(B^{+})_{2}O\), pyrochlores. According to van Dijk et al[10], in 
compounds such as \(Nd_{0.44}Zr_{0.559}O_{1.7795}\) where one might expect both A 
site and anion vacancies, Zr partially substitutes for Nd on 
the A site so that the actual stoichiometry is 
\((Nd_{0.44}Zr_{0.059})(Zr_{0.500})O_{1.7795}\) which is equivalent to 
\((Nd_{0.882}Zr_{0.118})Zr_{2}O_{7.118}\). Thus, both cation sites are fully 
occupied and excess oxygen occurs as interstitials on the 8b 
sites.

A more complete description of the pyrochlore structure 
can be found in the review by Subramanian[1] or McCauley’s 
paper[7].

Structural disorder occurs easily in pyrochlore because 
the enthalpy difference between fluorite and pyrochlore is 
often rather small[11]. This disorder, which can be 
considered as a partial reversion of the pyrochlore structure 
back towards fluorite, may occur on a scale of either atoms or 
tens of nanometers[12,13]. For example, van Dijk et al[12] 
found a hybrid phase with ~50 nm. microdomains of pyrochlore 
in a fluorite matrix by TEM but entropy considerations suggest 
the possibility of disorder on an atomic scale. This study 
will treat the question of disorder using Kröger-Vink 
notation[14] for convenience while acknowledging the 
possibility of microdomains in compositions with substantial 
disorder.
2.1.2 PYROCHLOR PHASE STABILITY MAP

There is a wealth of data on the structure of \((A^{3+})_2(B^{4+})_2O_7\) compounds. These data can be used to construct a map of the pyrochlore stability field as a function of the radii of the \(A^{3+}\) and \(B^{4+}\) cations. Such a map is useful when planning experiments involving solid solutions with the pyrochlore structure because it allows one to easily visualize the compositions required to achieve solid solutions with constant radius of either cation or constant cation radius ratio. Figure 2.3 shows the pyrochlore stability field where the ionic radii are taken from Shannon and Prewitt's 1969 paper[2] and the radius of \(O^{2-}\) is assumed to be 1.38 Å when it is in 4-fold coordination. The cation radii are based on 8-fold coordination for the \(A^{3+}\) ions and 6-fold coordination for the \(B^{4+}\) ions.

The available literature data and the present study both suggest that quaternary compounds such as \(A_2(B^\prime,B^\prime\prime\prime)_2O_7\) will have the pyrochlore structure if the A cation radius \((R_a)\) and the average B cation radius \((R_s)\) are within the required limits. \(R_s\) is the composition weighted average B cation radius defined as: \(R_s=\alpha R_{a1}+(1-\alpha)R_{a2}\). Figure 2.3 shows horizontal lines corresponding to the locations of the \(Gd_2(Zr_xTi_{1-x})_2O_7\) and \(Y_2(Zr_xTi_{1-x})_2O_7\) solid solutions. Clearly, the former is entirely (although just barely) within the pyrochlore phase field while the latter will include both pyrochlore and fluorite compositions.
Figure 2.3  Pyrochlore stability field as a function of cation radii in $(A^{13+})_2(B^{4+})_2O_7$, compounds[15].
2.1.3 IONIC POSITIONS IN PYROCHLOR STRUCTURE

2.1.3.1 Cation Disorder

All real pyrochlore compounds must exhibit some disorder due to the entropy increase associated with defect formation. Those compounds where this disorder becomes significant are called defect pyrochlores as defined below. Recall that in the ideal pyrochlore structure the A cations occupy the 16c sites while the B cations are on the 16d sites but in the ideal defect fluorite structure the A and B cations are distributed at random on both cation sites. Defect pyrochlores are intermediate between the extremes of the ideal pyrochlore structure and the ideal defect fluorite structure having some A cations on the 16d sites and some B cations on the 16c sites. This disorder can be quantified with the cation order parameter ($\xi_c$), which we define as:

$$\xi_c = \frac{A_{16c} - A_{16c}(F)}{A_{16c}(P) - A_{16c}(F)} \quad [2.1]$$

where $A_{16c}$ is the actual A ion occupation of the 16c site and $A_{16c}(F)$ and $A_{16c}(P)$ are the A ion occupation of the 16c site in ideal defect fluorite and ideal pyrochlore respectively. Since, ideal defect fluorite is perfectly random and ideal pyrochlore is perfectly ordered:

$$A_{16c}(F) = \frac{1}{2} \quad [2.2]$$
\[ A_{16c}(P) = 1 \] [2.3]

Therefore,

\[ \xi_c = \frac{A_{16c} - \frac{1}{2}}{1 - \frac{1}{2}} = 2A_{16c} - 1 \] [2.4]

A cation order parameter (\( \xi_c \)) of one corresponds to ideal pyrochlore and \( \xi_c = 0 \) corresponds to ideal defect fluorite for the cation sublattices. A typical value of \( \xi_c \) determined by x-ray diffraction for Nd\(_2\)Zr\(_2\)O\(_7\), is 0.90-0.95[10]. Pyrochlore compounds with heavier lanthanides (Sm, Eu or Gd) and similar thermal histories have progressively lower \( \xi_c \) values[15]. Indeed, as shown in Figure 2.3, as the lanthanide becomes heavier (and therefore smaller) the structure can revert completely to defect fluorite.

The cation order parameter is a function of thermal history for compounds with compositions near the pyrochlore-fluorite phase boundary such as Sm\(_2\)Zr\(_2\)O\(_7\), and Gd\(_2\)Zr\(_2\)O\(_7\). Gd\(_2\)Zr\(_2\)O\(_7\), for example, changes from pyrochlore to fluorite when heated above 1550 °C[16,17]. The phase transition is sluggish due to the low mobility of cations in these structures so that the rate of quenching from temperatures above 1550 °C can influence the value of \( \xi_c \).

The value of \( \xi_c \) is also a function of composition in Ln\(_2\)B\(_2\)O\(_7\), (Ln is any lanthanide element or yttrium). High values of \( \xi_c \) occur in compounds with large cation radius ratios (\( R_a/R_s \)) such as La\(_2\)Zr\(_2\)O\(_7\)[1] or Sm\(_2\)Ti\(_3\)O\(_7\)[18] and low values of \( \xi_c \) occur when \( R_a/R_s \) decreases until the structure eventually
becomes defect fluorite as in \( \text{Tb}_2\text{Zr}_2\text{O}_7 \)[1] or \( \text{Er}_2\text{Zr}_2\text{O}_7 \)[1]. A fundamental starting assumption of this thesis, later proven, is that the same trend in \( \xi_c \) will also hold in quaternary compounds such as \( \text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7 \).

### 2.1.3.2 Anion Disorder

As mentioned previously, the ideal pyrochlore structure has oxygen ions on the 48f and 8a sites with the 8b sites systematically vacant. However, ideal defect fluorite with the same composition has the oxygen ions distributed at random on the fluorite sites that correspond to 48f, 8a and 8b in the pyrochlore space group. Real pyrochlore compounds (defect pyrochlore) are intermediate between the extremes of ideal pyrochlore and ideal defect fluorite having some oxygen vacancies on the 48f and 8a sites and some oxygen interstitial ions on the 8b sites. This disorder can be quantified with an anion order parameter \( \xi_n \) defined as:

\[
\xi_n = \frac{O_{48f} - O_{48f}(F)}{O_{48f}(P) - O_{48f}(F)} \tag{2.5}
\]

where \( O_{48f} \) is the actual oxygen occupation of the 48f sites and \( O_{48f}(F) \) and \( O_{48f}(P) \) are the oxygen occupation of the 48f sites in ideal defect fluorite and ideal pyrochlore respectively.

Strictly speaking, the 48f site in pyrochlore has no exact analogue in fluorite. However, the normal anion site in fluorite corresponds to the 48f site in pyrochlore if we disregard the anion positional parameter \( x_{48f} \) (see Section
2.1.3.3). Thus, $O_{48f}(F)$ is meant to be the fractional occupation of the normal anion site in ideal defect fluorite for the particular composition under consideration. Since ideal defect fluorite is considered to be entirely random, the value of $O_{48f}(F)$ is $7/8$ for (33% $A_2O_3$ - 67% $BO_2$). Therefore,

$$
\xi_A = \frac{O_{48f} - 7/8}{1 - 7/8} = 8(O_{48f} - 7/8)
$$

[2.6]

The definition of the anion order parameter is based on the assumption that the fractional occupancy of the 8a and 48f sites is always equal but this assumption is unlikely to be exactly true since the coordination of the two sites is different (two A and two B cations for 48f ions but four A cations for 8a ions). Lattice simulation calculations of the vacancy formation energies described by van Dijk et al[19] suggest that 48f vacancies are more stable than 8a vacancies. However, neutron diffraction measurements by the same research group[10] on stoichiometric $Nd_2Zr_2O_7$ provide weak evidence for a preponderance of 8a vacancies in this material. In view of the conflicting evidence, we have chosen the simplest assumption, i.e., equal fractional vacancy concentrations on the two anion sites. In any case, the assumption is not critical since none of the measurements in this thesis are very sensitive to the relative occupancies of the two oxygen sites (x-ray diffraction is not sufficiently precise to compensate for the low scattering factor of oxygen relative to the cations).
An anion order parameter of one corresponds to ideal pyrochlore structure and $\xi_a = 0$ corresponds to ideal defect fluorite for the anion sublattices. A typical value of $\xi_a$ determined by neutron diffraction for Nd$_2$Zr$_2$O$_7$ is 0.95[10]. Pyrochlore compounds with heavier lanthanides (Sm, Eu or Gd) and similar thermal histories have progressively lower $\xi_a$ values[20].

It is believed[21] that $\xi_a$ is a function of $\xi_c$ so that $\xi_a$ is influenced by the same factors as $\xi_c$. However, because the oxygen ions in pyrochlore compounds are always more mobile than the cations, $\xi_a$ will always be in equilibrium with the current value of $\xi_c$. One consequence of this assumption is that $\xi_a$ will be independent of temperature for conditions where the cation disorder is "frozen-in" by quenching. This assertion is essentially confirmed in this study by electrical conductivity measurements as a function of dopant concentration in Gd$_2$(Zr$_{0.5}$Ti$_{0.7}$)$_2$O$_7$.

2.1.3.3 Oxygen Positional Parameter ($X_{48f}$)

All the ions in the pyrochlore structure have their positions exactly fixed by symmetry except for the 48f oxygen ions. These oxygen ions have one variable position parameter usually designated as $X_{48f}$ which takes into account the amount that 48f anions move away from the center of their coordination tetrahedra toward the empty 8b sites. $X_{48f}$ can, in principle, have any value greater than 0.375 and less than
0.4375 while maintaining the $\bar{3}m$ symmetry of the cation sites but, in practice, it always exceeds 0.4[7].

The value of $X_{\text{4sf}}$ is a function of the radii of the cations. Nikiforov[22] has derived a formula that explicitly relates $X_{\text{4sf}}$ to $R_\alpha^{3+}$, $R_\text{s}^{4+}$ and $R_\text{O}^{2-}$ by assuming that the 48f oxygen ions move to maximize their distance from each other and that all the ions are hard spheres. In general, large cation radius ratios ($R_\alpha/R_\text{s}$) lead to large $X_{\text{4sf}}$ values and vice versa. The value of $X_{\text{4sf}}$ should decrease as Zr$^{4+}$ replaces the smaller Ti$^{4+}$ ion in Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$, for example.

Nikiforov’s formula[22] must be considered as only a qualitative indicator of the trend rather than a quantitative prediction of the value of $X_{\text{4sf}}$. Earlier attempts to use the formula for quantitative comparison with experimental measurements of $X_{\text{4sf}}$ have been flawed by questionable assumptions regarding the appropriate ionic radii[7]. Accordingly, this thesis will not treat $X_{\text{4sf}}$ in detail. None of the measurements in this thesis (i.e., x-ray diffraction experiments) are sufficiently precise to calculate the value of $X_{\text{4sf}}$ reliably.

2.2 Conductivity of Fluorite Structure Oxides

The general electrical properties of fluorite structure oxides such as stabilized ZrO$_2$ and CeO$_2$ will very briefly be described in order to provide a context for the later discussion on pyrochlores. This section describes the differences in electrical properties between fluorites and
pyrochlores and shows how they relate to the structural differences.

The fluorite structure oxides are the best known and most extensively studied examples of oxygen ion conductors. In general, they have the potential to be very good solid electrolytes with relatively high oxygen ion conductivities, reasonably low activation energies and wide electrolytic ranges in $\text{PO}_2$ space. However, because they must be acceptor doped to exhibit appreciable ionic conductivity, they suffer from defect association accompanied by reduced ionic conductivity and increased activation energy. Thus, the goal of achieving improved ionic conductivities in fluorite structure oxides is best approached through an analysis of the defect association process.

The existence of defect association in fluorites can be deduced from the relationship between ionic conductivity (or activation energy) and acceptor dopant concentration. For example, see Figure 2.4 which shows the effect of $\text{Y}_2\text{O}_3$ doping in $\text{CeO}_2$ at 181 °C[6]. Similar, although less dramatic, trends occur at higher temperatures and for other acceptor dopants and host materials. There is a maximum in the ionic conductivity and a minimum in the activation energy at an $\text{Y}_2\text{O}_3$ concentration of a few mole percent. At higher $\text{Y}_2\text{O}_3$ content the oxygen vacancies become associated with the acceptor dopant and their mobility is drastically reduced.

Kilner[4,5,23,24] has investigated the relationship between the association energy and dopant cation radius. He
Figure 2.4 The ionic conductivity and activation energy for Y$_2$O$_3$-CeO$_2$ at 181 °C[6]
reports that there is a minimum in the associate binding energy when the radii of the host and dopant ions are about the same. This result suggests that strain effects (in addition to the electrostatic attraction between vacancy and dopant) may contribute significantly to the association energy.

Pyrochlore structure compounds possess both advantages and disadvantages relative to fluorites for use as oxygen ion electrolytes. Pyrochlores, such as Gd₂Zr₂O₇, are intrinsic anion conductors with substantial ionic conductivities as pure materials where there is no possibility of dopant-vacancy association. Fluorites, on the other hand, are extrinsic conductors and there will always be a possibility of dopant-vacancy association leading to degraded electrical properties. Additionally, doped fluorites, unlike pyrochlores, are thermodynamically metastable and their conductivities can be reduced by prolonged annealing at elevated temperatures. On the other hand, Gd₂(ZrₓTi₁₋ₓ)₂O₇, pyrochlores with low Zr content have a limited electrolytic region and lower ionic conductivity than stabilized ZrO₂. This subject is more fully addressed in the Discussion section.
2.3 Lanthanide Zirconate Pyrochlores

2.3.1 STRUCTURAL STUDIES

Two types of structural studies on the lanthanide zirconate pyrochlores will be considered: diffraction and spectroscopic studies. The diffraction results include both x-ray diffraction and neutron diffraction data for quantitative information on ionic locations and order parameters. The spectroscopic studies, based on either infrared or Raman measurements, provide qualitative data for distinguishing between pyrochlore and fluorite or estimating order parameters. Electron diffraction results will also be considered briefly.

Numerous authors have used IR spectroscopy to study the lanthanide zirconate pyrochlores. The most systematic work, by Klee and Weitz[15], studied the IR spectra as a function of the rare earth element. They concluded, on the basis of both IR and x-ray data, that there is a gradual increase in the cation disorder as the lanthanide atomic number increases. Increasing atomic number corresponds to decreasing ionic radius for the lanthanide series. Pyrochlore compounds with lanthanides heavier than Gd form the fluorite structure rather than the pyrochlore structure. The trend in IR spectra can be seen in Figure 2.5 where the absorption peaks gradually become wider and more overlapped as the lanthanide atomic number increases. In the case of Er₂Zr₂O, the pyrochlore absorption
Figure 2.5  Infrared absorption spectra for several Ln₂Zr₂O₇ compounds[15].
peaks have completely disappeared. Generally wide, diffuse peaks occur in a disordered system and sharper, better defined peaks occur in well-ordered compounds.

Raman spectroscopy provides additional evidence for the trend in disorder in lanthanide zirconate pyrochlores. Deangelis et al[25] and Scheetz et al[20] have shown that the Raman spectrum of the pyrochlore structure depend only upon the anion positions and not the cations. This anion dependency of the Raman spectra is very useful since IR spectroscopy and x-ray diffraction are far more sensitive to cation positions than anion positions. Thus, a comparison of IR and Raman spectra for a series of compositions might provide direct evidence that \( f_a \) and \( f_c \) are correlated.

Scheetz and White[20] have measured the Raman spectra of several lanthanide zirconate pyrochlores. Some of their data are shown in Figure 2.6. Low atomic number lanthanide pyrochlores, such as Nd\(_2\)Zr\(_2\)O\(_7\), clearly show several peaks in Raman intensity. The two peaks in the Nd\(_2\)Zr\(_2\)O\(_7\) spectrum near 200 cm\(^{-1}\) are due to a second phase impurity present in their particular sample. As the lanthanide atomic number increases to Gd, the spectra become less sharp and the peaks become shorter and broader. This is clear evidence of disorder on the oxygen sublattice of Gd\(_2\)Zr\(_2\)O\(_7\), relative to Nd\(_2\)Zr\(_2\)O\(_7\).

Finally, Dy\(_2\)Zr\(_2\)O\(_7\) shows no evidence of pyrochlore ordering at all; it is simply defect fluorite. Y\(_2\)Zr\(_2\)O\(_7\), has also been assigned to the fluorite structure on the basis of its Raman spectrum[26].
Figure 2.6  Raman spectra for various Ln$_2$Zr$_2$O$_7$ compounds[20].
McCauley[26] has assigned the various absorption peaks in the pyrochlore Raman spectrum to particular atomic vibrations on the basis of their frequency shift with changes in composition and a factor-group analysis by Deangelis et al[25]. This peak assignment is useful in that it can be used to estimate the anion jump attempt frequency from Raman data. The third highest frequency peak is identified as an A cation and oxygen ion stretching mode[26] and will be used in this study as a measure of the anion jump attempt frequency. In Ln,Ti₂O₇, according to McCaffrey[27] it occurs at about 400 cm⁻¹ or 1.2x10¹⁵ Hz.

It is a major assumption of this thesis that \( \xi_c \) and \( \xi_n \) are functions of \( R_a/R_s \). The Raman data described above, suggesting that \( \xi_n \) decreases as \( (R_a/R_s) \) decreases, are consistent with the conclusions on \( \xi_c \) by Klee and Weitz[15] using IR spectroscopy and x-ray diffraction. This spectroscopic evidence and electrical measurements from the present work demonstrate that the order parameters and cation radius ratio are indeed correlated.

X-ray diffraction and neutron diffraction provide more quantitative data than the spectroscopic methods outlined above. Van Dijk et al[10,28] used neutron diffraction measurements to find the concentration of oxygen interstitials in Nd₂Zr₂O₇. Their data are useful to the present research on Gd₂Zr₂O₇, since their value for Nd₂Zr₂O₇ provides an upper limit on the oxygen order parameter in Gd₂Zr₂O₇. It is impossible to do neutron diffraction experiments on Gd₂Zr₂O₇, because of
the extremely high cross section for neutron absorption of gadolinium.

Van Dijk et al[10] and de Vries et al[28] found that their neutron diffraction data for oxygen positions in Nd₂Zr₂O₇, quenched from 1900 °C could be fit with the "imperfect pyrochlore model", oxygen ions in both the pyrochlore positions (8a and 48f) and the interstitial position (8b), or the "hybrid phase model", small domains of defect fluorite in a matrix of ideal pyrochlore. The alternative "perfect pyrochlore model" was rejected. However, the differences between the three models was rather small. Their conclusion is that Nd₂Zr₂O₇ has a relatively well ordered oxygen sublattice and they could not determine whether the few oxygen interstitials on the 8b sites occur at random throughout the pyrochlore host lattice or are confined to small domains of fluorite structure. In either case, the interstitials represent only about 5% of all the oxygen ions even after quenching from 1900 °C[28].

Transmission electron microscopy work by van Dijk et al[12] on Gd₂Zr₂O₇, and Michel et al[29] on Nd₂Zr₂O₇, and Gd₂Zr₂O₇, support the hybrid phase model for these compounds. Their results suggest 50-500 Å size domains of fluorite structure in a pyrochlore matrix. The larger fluorite domains occur in Gd₂Zr₂O₇, with its lower cation radius ratio.
2.3.2 ELECTRICAL STUDIES

The most extensive work on the electrical properties of the rare earth zirconate pyrochlores has been done by Burggraaf and his coworkers at Twente University in The Netherlands. They have investigated ionic and mixed conduction in large parts of the Gd₂O₃-ZrO₂[12,16,17,19,30], Nd₂O₃-ZrO₂[17,28] and Tb₂O₃-ZrO₂[31,32,33] phase diagrams. This section of the review will focus upon their results.

The work of van Dijk et al[17] in the Gd₂O₃-ZrO₂ system showed an interesting anomaly in the conductivity near the pyrochlore composition (50 mol% GdO₁.₅ or 33 mol% Gd₂O₃). There is an increase in the ionic conductivity of about a factor of five when the structure changes from fluorite to pyrochlore as shown in Figure 2.7.

The explanation for the conductivity anomaly becomes evident from an examination of Figures 2.8 and 2.9. Recall that, the conductivity of an ionic conductor (σᵢ) can be expressed as a function of its pre-exponential constant (σ₀) and activation energy (E⁺) as shown in equation [2.7]:

\[ \sigma_\text{i}T = \sigma_0 \exp(-E^+/kT) \]  \[ \text{(2.7)} \]

Clearly, the conductivity will decrease when σ₀ decreases but it will increase when E⁺ decreases. In Figure 2.8, the activation energy for ionic conduction is plotted as a function of GdO₁.₅ content. There is a minimum in the activation energy in the pyrochlore phase field. In Figure 2.9, the pre-exponential constant for ionic conduction also...
Figure 2.7  The ionic conductivity as a function of composition in the Gd$_2$O$_3$-ZrO$_2$ solid solution[17].
Figure 2.8 The activation energy for ionic conduction as a function of composition in the Gd$_2$O$_3$-ZrO$_2$ solid solution[17].
Figure 2.9  The pre-exponential constant for ionic conduction as a function of composition in the Gd$_2$O$_3$-ZrO$_2$ solid solution[17].
has a minimum in the pyrochlore phase field. The reduction in activation energy has more than compensated for the reduction in pre-exponential constant and so the conductivity has a maximum value.

The pre-exponential constant is proportional to the number of charge carriers in an unassociated system (see Equation [3.22]) so Figure 2.9 can be interpreted as a reduction in the number of oxygen vacancies due to increased ordering in pyrochlore relative to fluorite. The activation energy is, to a first approximation, inversely related to the carrier mobility. Thus, the increase in conductivity can be ascribed to the improved mobility of a smaller number of oxygen vacancies in pyrochlore relative to fluorite due to the presence of low energy pathways for oxygen migration in the ordered pyrochlore phase. Alternatively, one can view the oxygen vacancies in the fluorite phase as bound by an energy of association to immobile cation acceptor dopants (Gd$_{zc}^-$) and thus unable to migrate while in the pyrochlore structure the "acceptor dopants" are uncharged structural elements (Gd$_{ad}^+$). In either case, there is a significant effect of order upon the electrical properties of this material.

The fact that there are no discontinuities in the conductivity-composition curves in Figure 2.7 is consistent with TEM[12] and lattice constant[17] measurements suggesting that there is not an abrupt transition between the pyrochlore and fluorite single phase regions. Note that the lattice constants of the pyrochlore and fluorite phases differ by
exactly a factor of two; they form perfectly strain-free phase boundaries. There may also be a gradual increase in the order parameter of the pyrochlore phase as the composition approaches 50 mol% GdO₁.s.

An examination of the conductivity-composition curve for the Nd₂O₃-ZrO₂ system[17] reveals that it also has a conductivity anomaly at the pyrochlore composition. However, it is the opposite of the anomaly that occurs in Gd₂Zr₂O₇. In Figure 2.10, we see that Nd₂Zr₂O₇ represents a local minimum in the conductivity of the Nd₂O₃-ZrO₂ system. The explanation is found in a similar fashion to the method used for Gd₂O₃-ZrO₂. As shown in Figures 2.11 and 2.12, the activation energy and pre-exponential constant both have deep minima at the Nd₂Zr₂O₇ composition. However, in this case, the pre-exponential constant is so low (the vacancy concentration is so low) that the conductivity decreases rather than increasing as in Gd₂Zr₂O₇.

There must be a maximum in the ionic conductivity for an intermediate degree of ordering in the pyrochlore structure. Nd₂Zr₂O₇ is too well ordered to be a good oxygen ion conductor (\(\xi ≈ 1\)) and 33 mol% Gd₂O₃-67 mol% ZrO₂ is too poorly ordered (\(\xi ≈ 0\)) to be a good ionic conductor. Apparently, Gd₂Zr₂O₇ can be annealed to have a near optimum degree of disorder. One purpose of this thesis is to determine if Gd₂Zr₂O₇, in fact represents the ideal degree of disorder for maximizing the ionic conductivity or whether some other composition may be superior.
Figure 2.10 The ionic conductivity as a function of composition for the Nd$_2$O$_3$-ZrO$_2$ solid solution[17].
Figure 2.11  The activation energy for ionic conduction as a function of composition for the Nd$_2$O$_3$-ZrO$_2$ solid solution[17].
Figure 2.12  The pre-exponential constant for ionic conduction as a function of composition for the Nd$_2$O$_3$-ZrO$_2$ solid solution[17].
2.4 Lanthanide Titanate Pyrochlores

2.4.1 STRUCTURAL STUDIES

Several structural studies have been made on the lanthanide titanate pyrochlores using x-ray diffraction[15,34,35] and infrared[15,26] and Raman spectroscopy[20]. In general, these studies agree that all the lanthanide titanate compounds with stoichiometry Ln₂Ti₂O₇ have the pyrochlore structure if the lanthanide element has an ionic radius equal to or smaller than that of samarium (1.09 Å)[2]. Compounds based on the larger lanthanides (La, Ce, Pr and Nd) have non-cubic unit cells[15]. There is some evidence, as reported by Knop et al[15], that Sc₂Ti₂O₇ may have the defect fluorite structure rather than pyrochlore. Assuming that this is the case, then we know the full extent of the pyrochlore phase stability field for A₂Ti₂O₇.

Just as in the Ln₂Zr₂O₇ system, the order parameters for Ln₂Ti₂O₇ compounds can be qualitatively inferred from infrared or Raman spectroscopy. Figure 2.13 shows the IR absorption spectra for a series of Ln₂Ti₂O₇ compounds[15]. As the lanthanide ion becomes smaller, in going from Sm₂Ti₂O₇ to Er₂Ti₂O₇, the absorption peaks become wider and less distinct. The cation order parameter for the titanates follows the same trend of decreasing magnitude with decreasing cation radius ratio (Rₗ/Rₘ) as found earlier in the lanthanide zirconates.
Figure 2.13 The infrared absorption spectra for various Ln₂Ti₂O₇ compounds[15].
2.4.2 ELECTRICAL STUDIES

There are two significant studies of the electrical characteristics of \( \text{Y}_2\text{Ti}_2\text{O}_7 \). The first work, by Uematsu et al[36], includes high temperature electrical conductivity data as a function of \( \text{PO}_2 \) and temperature for a large part of the \( \text{Y}_2\text{O}_3-\text{TiO}_2 \) phase diagram. This review will initially focus upon their results for \( \text{Y}_2\text{Ti}_2\text{O}_7 \), as shown in Figure 2.14.

The data in Figure 2.14[36] must be interpreted with caution. Conductivity measurements in both the present study and as reported by van Dijk et al[31] on \( \text{Y}_2\text{Ti}_2\text{O}_7 \), show substantially lower conductivities and a higher activation energy than the results in Figure 2.14. It is possible that Uematsu et al[36] used samples that were contaminated with acceptor impurities or did not have the proper stoichiometry.

Despite its flaws, the \( \log \sigma \) vs. \( \log \text{PO}_2 \) data for \( \text{Y}_2\text{Ti}_2\text{O}_7 \), by Uematsu et al[36] are certainly worth considering. Their experimental value for the ionic conductivity of \( \text{Y}_2\text{Ti}_2\text{O}_7 \), is certainly valid—only its interpretation is open to question. The anomalously high conductivity value implies that a route exists to improved ionic conductivity, perhaps through acceptor doping to increase the oxygen vacancy concentration. This thesis will show that acceptor doping can indeed improve the ionic conductivity especially in well ordered pyrochlore compounds.

The second source of information on the electrical properties of \( \text{Y}_2\text{Ti}_2\text{O}_7 \), is a paper by Goldschmidt et al[37] examining the low temperature electronic conductivity and
Figure 2.14  The electrical conductivity of $Y_2Ti_2O_7$, as a function of the oxygen partial pressure[36].
thermopower of a single crystal specimen. The crystal was reduced in hydrogen and then quenched to room temperature. They found[37] that the electrons in Y₂Ti₂O₇ move as small polarons with an activation energy of 0.18 eV and a mobility of roughly $5 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 200 °C. This mobility value extrapolates to $3 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 1000 °C. If this low electronic mobility in Y₂Ti₂O₇ also applies to Gd₂(ZrₓTi₁₋ₓ)₂O, then we can expect an unusually wide electrolytic domain in those compounds.

2.5 Summary

We have developed several general conclusions from the literature survey. First, there is a correlation between the order parameters and cation radius ratio in pyrochlore compounds as shown by the spectroscopic data. Second, the pyrochlore structure is stable relative to fluorite only over a limited range of cation radius ratio as shown in Figure 2.3. Third, disorder on the anion sublattice may lead to improved conductivity due to an increase in carrier concentration but cation disorder appears to have the opposite effect by increasing the activation energy (reducing the mobility) of charge carriers as shown in Section 2.3.2. Fourth, the anion and cation order parameters are correlated. Some of these conclusions are based on sketchy or poor quality data but they form the basis for our initial understanding of pyrochlore compounds. The purpose of this thesis is to test these ideas by systematic experiments on the Gd₂(ZrₓTi₁₋ₓ)₂O, and
\(Y_2(Zr_{x}Ti_{1-x})_2O\), solid solutions. We will attempt to find correlations between the electrical properties of these solid solutions and \(\xi_c\), \(\xi_a\) and \(R_a/R_b\) and then fit the results into a comprehensive model for ionic conduction in rare earth transition element pyrochlores.

The literature review also uncovered some specific data for comparing \(Ln_2Ti_2O_7\) and \(Ln_2Zr_2O_7\). Some of these data are tabulated below in Table 2.2. Based on the admittedly sketchy evidence, the \(Ln_2Zr_2O_7\) compounds may be better ionic conductors and have lower activation energies than \(Ln_2Ti_2O_7\). Probably, the zirconates will have lower order parameters than the titanates based on their relative cation radius ratios and the correlation between \(\xi_c\), \(\xi_a\) and \(R_a/R_b\). These conclusions are consistent with the ideas in the above paragraph but clearly a complete and systematic study is required to provide more evidence.
<table>
<thead>
<tr>
<th>Property</th>
<th>Gd$_2$Ti$_2$O$_7$</th>
<th>Gd$_2$Zr$_2$O$_7$</th>
<th>Y$_2$Ti$_2$O$_7$</th>
<th>Y$_2$Zr$_2$O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a[1,34]</td>
<td>10.185</td>
<td>10.528</td>
<td>10.095</td>
<td>10.402 [Å]</td>
</tr>
<tr>
<td>R$_a$[2]</td>
<td>1.06</td>
<td>1.06</td>
<td>1.015</td>
<td>1.015 [Å]</td>
</tr>
<tr>
<td>R$_b$[2]</td>
<td>0.605</td>
<td>0.72</td>
<td>0.605</td>
<td>0.72 [Å]</td>
</tr>
<tr>
<td>R$_a$/R$_b$[2]</td>
<td>1.75</td>
<td>1.47</td>
<td>1.68</td>
<td>1.41</td>
</tr>
<tr>
<td>$\sigma_i$(700° C)[17,35]</td>
<td>?</td>
<td>$5 \times 10^{-3}$</td>
<td>$1 \times 10^{-4}$</td>
<td>? [S/cm]</td>
</tr>
<tr>
<td>E'[17,35]</td>
<td>?</td>
<td>0.88</td>
<td>0.94</td>
<td>? [eV]</td>
</tr>
<tr>
<td>$\sigma_o$[17,35]</td>
<td>?</td>
<td>$10^5$</td>
<td>$10^4$</td>
<td>? [S·cm$^{-1}$K]</td>
</tr>
<tr>
<td>$\varepsilon'$[19,33]</td>
<td>33</td>
<td>60</td>
<td>35</td>
<td>?</td>
</tr>
</tbody>
</table>
3 THEORY

The theory section first describes the relationship between electrical conductivity, defect concentration, defect mobility and the thermodynamic variables of temperature and oxygen activity. A defect chemical model is presented for these relationships in the case of oxygen ion conducting pyrochlore compounds.

The second part of the theory section describes complex impedance spectroscopy—the method of extracting bulk, grain boundary and electrode resistances and capacitances from AC electrical data. Complex impedance spectroscopy is used extensively in this research since its ability to distinguish between bulk and grain boundary effects allows the use of easily fabricated polycrystalline test specimens rather than single crystals.

Finally, we examine the basis for calculating the cation order parameter from x-ray diffraction patterns.

3.1 Defect Chemistry

This section starts with a derivation of the defect chemical model used in this study to calculate the individual ionic and electronic conductivities and other parameters of interest. Next, it applies the defect model to calculation of the enthalpies of ionic motion, reduction and the thermal bandgap followed by a derivation of the equation relating
dopant concentration, intrinsic anion disorder and ionic conductivity in Gd$_2$\((\text{Zr}, \text{Ti}_{1-x})_2\)O compounds. This section then concludes with a description of the relationship between the anion order parameter and the pre-exponential constant for ionic conduction.

3.1.1 DERIVATION OF DEFECT CHEMICAL MODEL

Electrical conductivity measurements are useful for making deductions about defect chemistry because they are rapid, accurate and can be made in-situ. However, they have one major inadequacy in that conductivity measurements can measure only the product of concentration and mobility of defects and not their individual values as shown in equation [3.1]:

\[
\sigma = nze\mu
\]  

where, \(\sigma\) = conductivity (S/cm) \(n\) = defect concentration (cm\(^{-3}\)) \(ze\) = defect charge (C) \(\mu\) = defect mobility (cm\(^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}\))

Calculating defect chemical parameters such as mass action constants requires knowledge of the defect concentrations. Fortunately, it is possible to determine the defect concentrations and mobilities when a verified defect model establishes a relationship between the unknown defect concentration and the known dopant concentration. Thus, the
experimental strategy for calculating the defect chemical parameters of a particular material often becomes a quest for conditions where a defect model can be specified and then applied to the conductivity data to determine the unknown parameters.

A reasonable defect chemical model for many oxides can be easily arrived at by consideration of the potential defect generation reactions and the constraints due to site, mass and charge balance. The model is simplified by eliminating reactions with excessive enthalpies of formation when there are other competing formation mechanisms. For example, in the case of fluorite or pyrochlore structure compounds, Schottky defects need not be considered since they make an insignificant contribution to the number of anion vacancies relative to the number generated by anion Frenkel defects. Eventually, the model will form a relationship between experimentally controllable quantities such as temperature, oxygen chemical potential and dopant concentration, measurable quantities such as electrical conductivity and unknown quantities such as defect concentrations and mobilities.

Several defect generation reactions can be neglected for the particular case of oxygen ion conducting pyrochlore structure compounds. For example, we assume that Schottky defects and cation Frenkel defects can be neglected due to their expected high formation enthalpies. We also neglect cation anti-site defects, although they undoubtedly occur, because they are self charge compensating and their
concentration is fixed by the very low mobility of cations in 
\((A^{3+})(B^{4+})_2O\), pyrochlores at the temperatures of interest.

Certain defect reactions must be included in the defect model. Anion Frenkel defects, for example, are included since it is known that the pyrochlore structure allows easy formation of anion interstitials and vacancies. Intrinsic electronic defect formation is also included because the bandgap energy of lanthanide titanate and zirconate pyrochlore compounds (3 to 5 eV) implies that a small but significant number of electron hole pairs will be formed at high temperatures. A reduction reaction is also considered since experience shows that these materials can be significantly reduced or oxidized.

Finally, the defect model is based on the following additional assumptions: the compound is pure except for intentionally added dopants, all defects have their maximum charge and the oxygen ions in the bulk are in chemical equilibrium with oxygen molecules in the gas phase. Since the last assumption above means that the oxygen fugacity and oxide ion activity are equivalent the symbol "PO₂" will be used interchangeably for either quantity. The dopants are either \(\text{Ca}^{2+}\) which substitutes for \(\text{Gd}^{3+}\) on the A-site or \(\text{Ta}^{5+}\) which substitutes for either \(\text{Ti}^{4+}\) or \(\text{Zr}^{4+}\) on the B-site.

The above assumptions lead to the following equations:

\[
\text{O}_o^{\cdot}\rightarrow \text{V}_o^{\cdot\cdot} + \text{O}_i^{\cdot\cdot}\]  \hspace{1cm} [3.2]

\[
\phi \rightarrow \text{e}^\cdot + \text{h}^\cdot\]  \hspace{1cm} [3.3]
\[ O_{o^*} \rightarrow V_{o} \cdot \cdot + \frac{1}{2} O_2 + 2e^- \]  

[3.4]

where, \( \phi \) represents the perfect lattice and equations [3.2] to [3.4] represent anion Frenkel defect generation, electron and hole generation and the reduction reaction, respectively.

These three pseudochemical reactions can be used to make mass-action relations as follows:

\[ K_{r} = [V_{o} \cdot \cdot ][O_{i} \cdot \cdot \cdot ] = K_{r_0}\exp(-E_r/kT) \]  

[3.5]

\[ K_{i} = n p = K_{i_0}\exp(-E_g/kT) \]  

[3.6]

\[ K_{r} = [V_{o} \cdot \cdot \cdot ]n^2(PO_2)^{1/2} = K_{r_0}\exp(-E_r/kT) \]  

[3.7]

where \( K_r \), \( K_i \) and \( K_r \) are the mass-action equilibrium constants for the anion Frenkel reaction, the intrinsic electron and hole generation reaction and the reduction reaction, respectively. The enthalpy changes for the various reactions are designated by E where \( E_r \) is the enthalpy of anion Frenkel pair formation, \( E_g \) is the thermal bandgap and \( E_r \) is the enthalpy of reduction. The entropy change associated with each reaction is incorporated into the appropriate pre-exponential constant.

The value of \( [O_{o^*}] \) is incorporated into \( K_r \) and \( K_r \) with the assumption that it is independent of temperature and the extent of reactions [3.5] and [3.7]. The further assumption is made that defects form ideal solutions in the crystal so that their activities can be replaced with fractional concentrations in the mass action relationships. Finally, in
accord with the usual convention, the fractional concentrations are replaced with volumetric concentrations. Therefore, the equilibrium constants will have dimensions of volume to the second or third power.

A fourth reaction, the electroneutrality relation (equation [3.8]), arises from considerations of charge balance. When equations [3.5] to [3.7] are combined with the electroneutrality relation,

\[ 2[V_0\cdot] + p + [Ta_n^+] = 2[O_i\cdot] + n + [Ca_{a}^\cdot] \]  

[3.8]

the result is four equations with four unknowns ([V_0\cdot], [O_i\cdot], n and p) and four experimental parameters ([Ta_n^+], [Ca_{a}^\cdot], T and PO_2).

The concentration of the four unknowns ([V_0\cdot], [O_i\cdot], n and p) can be displayed on a Brouwer plot[14] with log oxygen fugacity on the x-axis and log defect concentration on the y-axis. We have calculated three such plots using equations [3.5] to [3.8] and arbitrary values for the equilibrium constants and the four experimental parameters: [Ta_n^+], [Ca_{a}^\cdot], T and PO_2. Figure 3.1 shows these Brouwer plots for the case of a pure compound with \( K_r >> K_i \) and for two doped compounds. Note that the curves in Figure 3.1 have continuous first derivatives since they are calculated directly from equation [3.8] rather than several simplified approximations to the electroneutrality relation as in most other such plots.

The electroneutrality relation can be approximated by simplified expressions over limited regions of the Brouwer
Figure 3.1  Brouwer plots for (a) pure, (b) Ca\textsuperscript{2+} doped and (c) Ta\textsuperscript{5+} doped (A\textsuperscript{2+})\textsubscript{x}(B\textsuperscript{6+})\textsubscript{y}O\textsubscript{z}, compounds with K\textsubscript{f} >> K\textsubscript{i}.
diagram as shown in Figure 3.1. In the case of the pure compound, for example, there is a region at intermediate PO$_2$ where the majority defects are oxygen vacancies and interstitials. Note that all three Brouwer plots have regions where ionic defects predominate and have PO$_2$-independent concentrations.

Within each region of a Brouwer plot, where a simplified electroneutrality relation applies, the logarithm of the defect concentration is a linear function of log PO$_2$. Tables 3.1, 3.2 and 3.3 summarize the slopes of the log defect concentration vs. log PO$_2$ curves as calculated by the defect model for each of the three cases in Figure 3.1.

<table>
<thead>
<tr>
<th>Table 3.1 Power laws for defect concentration vs. PO$_2$ in a pure compound with K$_r$ $&gt;&gt;$ K$_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Defect</strong></td>
</tr>
<tr>
<td>n</td>
</tr>
<tr>
<td>p</td>
</tr>
<tr>
<td>V$_o$</td>
</tr>
<tr>
<td>O$_i$</td>
</tr>
</tbody>
</table>
Table 3.2 Power laws for defect concentrations vs. PO$_2$ in an acceptor doped compound with $K_r >> K_i$

<table>
<thead>
<tr>
<th>Defect</th>
<th>$n=2[V_o\cdot\cdot\cdot]$</th>
<th>$2[V_o\cdot\cdot\cdot]=[A']$</th>
<th>$p=[A']$</th>
<th>$p=2[O_i\cdot\cdot\cdot]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>$-1/6$</td>
<td>$-1/4$</td>
<td>$0$</td>
<td>$-1/6$</td>
</tr>
<tr>
<td>p</td>
<td>$+1/6$</td>
<td>$+1/4$</td>
<td>$0$</td>
<td>$+1/6$</td>
</tr>
<tr>
<td>$V_o\cdot\cdot\cdot$</td>
<td>$-1/6$</td>
<td>$0$</td>
<td>$-1/2$</td>
<td>$-1/6$</td>
</tr>
<tr>
<td>$O_i\cdot\cdot\cdot$</td>
<td>$+1/6$</td>
<td>$0$</td>
<td>$+1/2$</td>
<td>$+1/6$</td>
</tr>
</tbody>
</table>

Table 3.3 Power laws for defect concentrations vs. PO$_2$ for a donor doped compound with $K_r >> K_i$

<table>
<thead>
<tr>
<th>Defect</th>
<th>$n=2[V_o\cdot\cdot\cdot]$</th>
<th>$n=[D']$</th>
<th>$2[O_i\cdot\cdot\cdot]=[D']$</th>
<th>$p=2[O_i\cdot\cdot\cdot]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>$-1/6$</td>
<td>$0$</td>
<td>$-1/4$</td>
<td>$-1/6$</td>
</tr>
<tr>
<td>p</td>
<td>$+1/6$</td>
<td>$0$</td>
<td>$+1/4$</td>
<td>$+1/6$</td>
</tr>
<tr>
<td>$V_o\cdot\cdot\cdot$</td>
<td>$-1/6$</td>
<td>$-1/2$</td>
<td>$0$</td>
<td>$-1/6$</td>
</tr>
<tr>
<td>$O_i\cdot\cdot\cdot$</td>
<td>$+1/6$</td>
<td>$+1/2$</td>
<td>$0$</td>
<td>$+1/6$</td>
</tr>
</tbody>
</table>

The experimentally measurable quantity for evaluating defect models in this study is conductivity not defect concentration. The conductivities that correspond to the concentrations in Figure 3.1 are shown in Figure 3.2 along with their PO$_2$ dependencies. Figure 3.2 assumes that the mobilities of electrons and holes are equal and much larger
Figure 3.2 Theoretical plots of log conductivity as a function of log oxygen partial pressure for (a) pure, (b) Ca²⁺ doped and (c) Ta⁵⁺ doped \((A''')_2(B'')_2O\), compounds. See assumptions described in text.
than the mobility of any ionic species. Further, it is assumed that oxygen vacancies are much more mobile than oxygen interstitials. Although Figure 3.2a does not show a region with PO$_2$-independent conductivity such a region would develop if there was an increase in the concentration or mobility of vacancies relative to electrons.

The PO$_2$ dependence of conductivity can be very complex. However, no real material will exhibit all the different PO$_2$ dependencies since it is impossible to generate a wide enough variation in oxygen activity to distinguish all the possible conduction regimes without decomposing the material.

In light of the limited PO$_2$ range available in real experiments it can be difficult to distinguish between alternative defect models solely on the basis of conductivity measurements. The problem of distinguishing whether a PO$_2$ independent conductivity region with adjacent regions of mixed conductivity with PO$_2$ dependencies of $\frac{1}{2}$ represents a pure compound with $K_r \gg K_i$ or an acceptor doped compound is such a case. In general the solution to this type of problem is to perform a chemical analysis in search of acceptor impurities, intentionally dope the material or attempt to make deductions on the basis of the activation energy for conduction.

In the case of the compounds studied in this thesis, most of the log $\sigma$ vs. log PO$_2$ data are consistent with the assumption that ionic defects dominate the electroneutrality relation. This assumption corresponds to the regions: $[V_o^{\cdot\cdot}] = [O_i^{\cdot\cdot\cdot}]$ in the pure case, $2[V_o^{\cdot\cdot}] = [Ca_{oa}^{\cdot\cdot\cdot}]$ in the acceptor
doped case and \(2[O_{\cdot\cdot\cdot}]=[Ta_{\cdot\cdot\cdot}]\) in the donor doped case. All three cases should have a \(PO_2\)-independent region flanked by regions where the conductivity follows a \(PO_2^{-3/4}\) law as shown in Figure 3.2. Consequently, the data were fit to the following equation:

\[
\log \sigma = \log [A + B(PO_2)^{-3/4} + C(PO_2)^{-1/4}] \quad [3.9]
\]

where, \(A, B, C\) are independent of \(PO_2\) but are functions of temperature. \(A\) represents the ionic conductivity (\(\sigma_1\)) while \(B(PO_2)^{-3/4}\) is the electronic conductivity (\(\sigma_e\)) and \(C(PO_2)^{-1/4}\) is the hole conductivity (\(\sigma_h\)). Using a least squares fit of the experimental \(\log \sigma\) vs. \(\log PO_2\) data to this equation it is possible to distinguish the ionic and electronic conductivities and their temperature dependencies over most of the \(Gd_2(Zr_xTi_{1-x})_2O\), solid solution.

Figure 3.3 shows the result of fitting equation [3.9] (curved line) to the experimental data (filled circles) for \(Gd_2(Zr_{0.3}Ti_{0.69}Ta_{0.01})_2O_{7\cdot\cdot\cdot}\). It also shows the individual conductivity components, \(\sigma_1\), \(\sigma_e\) and \(\sigma_h\) (straight lines) that arise from fitting the data to equation 3.9. It can be seen, first, that the experimental data fit the defect model very closely and, second, that at low \(PO_2\) the conductivity is primarily electronic while at high \(PO_2\) it is a mixed conductor with significant amounts of both ionic and hole conduction.
Figure 3.3  Log conductivity versus log oxygen partial pressure for Gd$_2$(Zr$_x$Ti$_{1-x-y}$Ta$_y$)$_2$O$_7$ (x=0.30) (y=0.01) showing the least squares fit of equation [3.9] to the experimental data.
3.1.2 ENTHALPY CALCULATIONS

The values of A, B and C (the fitting parameters from equation [3.9]) are very valuable information. Knowing A as a function of temperature, for example, the ionic conductivity and its activation energy and pre-exponential constant are immediately known. The values of $E_a$ and $E_c$ are also useful since they provide information on the thermal bandgap and reduction energy as derived below.

Recall that the mass action relation for the reduction reaction can be written as:

$$K_r = [V_{o-} \cdot n^2(PO_2)^{1/2}] = K_{ro} \exp(-E_a/kT)$$  \[3.7\]

According to the defect model the n-type conductivity must obey:

$$\sigma_n = B(PO_2^{-1/4})$$  \[3.10\]

If it is assumed that the activation energy for $\sigma_n$ for a wide bandgap semiconductor such as Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ will be virtually entirely due to its thermally activated concentration (n) and that the electronic mobility even in the case of small polarons will be relatively temperature independent, then:

$$\sigma_n = B_0(PO_2^{-1/4})\exp(-E_a/kT)$$  \[3.11\]

In this case, and if the defect model applies (i.e., $[V_{o-}]$ is fixed by the electroneutrality relation), then equations
[3.1], [3.7], [3.10] and [3.11] yield the following at fixed PO₂:

\[
\frac{d(\ln K_r)}{d(1/kT)} = \frac{2d(1nn)}{d(1/kT)} = \frac{2d(1n\sigma_e)}{d(1/kT)} \approx -2E_a \approx -E_c \quad [3.12]
\]

Therefore, the enthalpy of reduction (Eₐ) can be determined very easily from the activation energy of the electronic conductivity parameter (Eₑ).

The thermal bandgap (Eₔ) can be calculated from Eₑ and Eₑ by starting with equation [3.6].

\[
K_i = np = K_{i0} \exp(-E_\text{q}/kT) \quad [3.6]
\]

It is known from the definition of the conductivity that:

\[
\sigma_e = ne\mu_e \quad [3.13]
\]

and

\[
\sigma_h = pe\mu_h \quad [3.14]
\]

therefore, using the same assumptions as for the case of the reduction enthalpy:

\[
\frac{d(\ln K_i)}{d(1/kT)} = \frac{d(1nn)}{d(1/kT)} \cdot \frac{d(1np)}{d(1/kT)} \approx \frac{d(1n\sigma_e)}{d(1/kT)} \cdot \frac{d(1n\sigma_h)}{d(1/kT)} = -E_\text{q} \quad [3.15]
\]

Now, the relationships between the conductivities, \( \sigma_e \) and \( \sigma_h \), and the fitting parameters, B and C, can be applied to calculate \( E_\text{q} \). When equations [3.11] and [3.16]

\[
\sigma_e \approx B(PO_2^{-1/4})\exp(-E_\text{q}/kT) \quad [3.11]
\]
\[ \sigma_n = C(\text{PO}_2^{'1/4}) = C_0(\text{PO}_2^{'1/4})\exp(-E_c/kT) \]  \[3.16\]

are substituted into equation [3.15] the result is:

\[ E_g = E_a + E_c \]  \[3.17\]

Thus, the thermal bandgap is simply the sum of the activation energies for two of the fitting parameters for the defect model. Note that it is not necessary to have experimental data at the conductivity minimum in order to apply equation [3.17].

3.1.3 \( K_r \) AND CARRIER MOBILITY CALCULATIONS

This section describes the derivation of the relationship between dopant concentration, ionic conductivity and the Frenkel constant. Using this relationship, it is possible to deconvolute the concentration and mobility of the charge carriers from the conductivity.

For ionic or mixed conducting compounds where intrinsic ionic disorder occurs by oxygen Frenkel defects and aliovalent dopants such as \( \text{Ca}^{2+} \) and \( \text{Ta}^{5+} \) are present in concentrations comparable to the intrinsic defect concentration, the electroneutrality condition becomes:

\[ 2[V_{o^{'2-}}] + [Ta^{+}] = 2[O_{i^{-'2}}] + [Ca_{n^{'2-}}] \]  \[3.18\]

When this equation is combined with the Frenkel mass action equation ([3.5]),

\[ [V_{o^{'2-}}][O_{i^{-'2}}] = K_r \]  \[3.5\]
a relationship between the oxygen vacancy concentration and dopant concentration can be derived:

\[
\log [V_o^{\cdot\cdot}] = \log \left\{ \frac{1}{2}(D+(D^2+16K_r)^{1/2}) \right\} \quad [3.19]
\]

where \( D=[Ca^{\cdot\cdot\cdot}]-[Ta^{\cdot\cdot\cdot}] \). Figure 3.4 shows a theoretical plot of \( \log \) concentration of oxygen defects vs. \( [Ca^{\cdot\cdot\cdot}]-[Ta^{\cdot\cdot\cdot}] \) based on equation [3.19] and assuming that \( K_r=10^{38} \) cm\(^{-6}\).

By introducing the definition of the ionic conductivity:

\[
\sigma_i = 2[V_o^{\cdot\cdot}]e\mu_v \quad [3.20]
\]

where \( \mu_v \) is the oxygen vacancy mobility, a relationship between the ionic conductivity and the alioivalent dopant concentration can be derived from equation [3.19], viz.

\[
\log \sigma_i = \log \left\{ \frac{1}{2}(D+(D^2+16K_r)^{1/2})e\mu_v \right\} \quad [3.21]
\]

Equation [3.21] assumes that, (a) doubly charged oxygen vacancies are the only mobile ionic species, (b) Ca and Ta are completely substituted on the A and B sites, respectively, (c) all the oxygen vacancies are equally mobile and (d) their mobility is independent of dopant concentration. These assumptions are more fully considered in Section 6.2.1.

Equation [3.21] is the route to calculating the Frenkel constant, oxygen vacancy mobility and oxygen vacancy concentration from a measurement of the ionic conductivity as a function of dopant concentration. In practice, the experimental data are fit to equation [3.21] using an iterative least squares minimization routine.
Figure 3.4  The concentration of anion defects as a function of the net acceptor concentration using equation [3.19].
3.1.4 ANION ORDER PARAMETER CALCULATIONS

The oxygen vacancy concentration and thus the anion order parameter can be calculated from the pre-exponential constant for ionic conductivity subject to a series of assumptions. This section describes and attempts to justify those assumptions.

For the case of an ionic conductor in a temperature range where the carriers are unassociated, the pre-exponential constant for ionic conduction can be shown to be:

\[
\sigma_o = \frac{4\alpha e^2a^2vN_o[V_{o\cdot\cdot}]\exp(S_o/k)}{k}
\]  

[3.22]

where,  
\(\alpha\) = geometrical factor = 1/3 (dimensionless)  
\(e\) = elementary charge = 1.6x10^{-19} C  
\(a_o\) = jump distance = 1/4 lattice constant  
\(v\) = attempt frequency = 1.2 x 10^{13} Hz  
\(N_o\) = oxygen 48f sites per unit volume (cm^{-3})  
\(V_{o\cdot\cdot}\) = fractional oxygen 48f site vacancy concentration (dimensionless)  
\(S_o\) = migration entropy (assumed to be zero)  
\(k\) = Boltzmann's constant = 1.38x10^{-23} J/K

Faktor[38] gives a derivation of equation [3.22] based on atomistic diffusion theory and the definition of conductivity. As used here, equation [3.22] incorporates the assumptions that oxygen vacancy motion occurs exclusively on the 48f sublattice but that vacancies occur with equal probability on
the 48f and 8a sites as described in Section 2.1.3.2. The attempt frequency was chosen based on Raman spectroscopy data as described in Section 2.3.1. The migration entropy was set to zero due to the lack of experimental evidence for a more appropriate value. Every variable in this equation is known, measurable or assumed except the vacancy concentration which, therefore, can be calculated.

Given the vacancy concentration it is straightforward to calculate the anion order parameter ($\xi_a$) from its definition:

$$\xi_a = 8(O_{48f} - 7/8) \quad [2.6]$$

The fractional 48f site occupancy ($O_{48f}$) is equal to one minus the fractional vacancy concentration ($V_{o''}$). The assumption that vacancies occur with equal likelihood on the 8a and 48f sites is implicit in this equation and is discussed in Section 2.1.3.2.

3.2 Complex Impedance

The principal experimental technique used in this research is complex impedance spectroscopy. This technique uses measurements of the frequency dependent electrical impedance to distinguish between electrical processes such as bulk, grain boundary or electrode impedances that have different characteristic time constants. In order to interpret experimental complex impedance data one must have a theoretical model for comparison.
The conventional electrical model for a polycrystalline ceramic material[39] consists of several parallel RC elements in series as shown in [3.23]. Each parallel RC element is related to a structural element such as the grain bulk or grain boundary impedance and has a characteristic time constant given by the product of its resistance and capacitance.

\[ C_b \quad R_b \quad C_{gb} \quad R_{gb} \quad C_e \quad R_e \]  

[3.23]

where,

- \( C_b \) = bulk capacitance (Farads)
- \( R_b \) = bulk resistance (\( \Omega \))
- \( C_{gb} \) = grain boundary capacitance (Farads)
- \( R_{gb} \) = grain boundary resistance (\( \Omega \))
- \( C_e \) = electrode capacitance (Farads)
- \( R_e \) = electrode resistance (\( \Omega \))

The complex impedance spectrum of a single parallel RC element is a semicircle that intersects the origin and has its center on the x-axis. We follow the convention that the sign of the imaginary impedance is reversed so that the semicircle is in the first rather than the fourth quadrant. The angular frequency at the maximum imaginary impedance value of the semicircle corresponds to the inverse of the time constant for that RC element. See the derivation below.
The impedance ($Z$) of the RC element in [3.24] is:

$$Z = \frac{1}{1/R + j(2\pi f)C}$$ \tag{3.25}

where, $Z$ = overall impedance (Ω)
R = resistance of resistive element (Ω)
$j = \text{square root of -}1$
$f = \text{frequency (Hz)}$
C = capacitance of capacitive element (Farads)

The total impedance can be separated into its real ($Z'$) and imaginary ($Z''$) parts:

$$Z = Z' + jZ''$$ \tag{3.26}

When equation [3.25] is multiplied by the complex conjugate of its denominator and then separated into its real and imaginary parts the result is:

$$Z' = \frac{1/R}{(1/R)^2 + (2\pi fC)^2}$$ \tag{3.27}

$$Z'' = \frac{2\pi fC}{(1/R)^2 + (2\pi fC)^2}$$ \tag{3.28}
When the frequency \((f)\) is eliminated from equations [3.27] and [3.28], the result is the equation for a circle with center at \((R/2, 0)\) and radius \(R/2\):

\[
(Z'')^2 + (Z'-R/2)^2 = R^2/4
\]  

[3.29]

We see that the complex impedance spectrum of a single RC element is indeed a circle.

The angular frequency \((2\pi f)\) at the peak of the semicircle can be calculated by substituting \(R/2\) for \(Z'\) in equation [3.27]. The result is:

\[
2\pi f = 1/RC
\]  

[3.30]

If the time constants are sufficiently different then several parallel RC elements in series will form several adjacent semicircles as shown in Figure 3.5. This figure represents experimental data as filled circles and the theoretical model as semicircular arcs. The values of the bulk and grain boundary resistance are labelled on the \(x\)-axis and the relation between the angular frequency at the peak of the first semicircle and its capacitive element is also shown. The reason that several parallel RC elements in series will form adjacent semicircles is best understood by considering that the imaginary impedance of a single parallel RC element is nonzero only at frequencies near the inverse of its time constant as is evident from equation [3.28]. At higher frequencies the capacitor is shorted out and the total impedance approaches zero while at lower frequencies the
Figure 3.5 A complex impedance plot for \( \text{Gd}_2\text{Zr}_2\text{O}_7 \) at 350 °C in oxygen showing the assignment of bulk and grain boundary resistances.
capacitor has a very high impedance and the total impedance is
due to the resistor in parallel. Therefore, if the time
constants are sufficiently different, a sweep in frequency
will form a semicircle from one RC element at a time and as
the frequency decreases each RC element will contribute an
impedance equal to its real resistance.

Given the model of parallel RC elements in series for the
electrical behavior of a polycrystalline ceramic, the
interpretation of a complex impedance plot is reduced to
assigning values to the parameters $R_n$, $C_n$, $R_{ab}$ etc. These
quantities can be determined easily and unambiguously from the
complex impedance plots of pyrochlore compounds because of the
small degree of overlap generally exhibited between adjacent
semicircles as shown in Figure 3.5.

3.3 Cation Order Parameter by X-Ray Diffraction

The cation order parameter ($f_c$) can be calculated from
powder x-ray diffraction data because different order
parameters mean different cation positions and the intensity
of each diffraction peak is a function of the cation and anion
positions as given by the structure factor. Certain peaks are
more sensitive to $f_c$ than others due to the detailed form of
the structure factor. A simplified view of the selection
rules for diffraction suggests that peaks with hkl values that
are all even occur in both the pyrochlore and fluorite
structure diffraction patterns with almost equal intensities
but peaks with all odd hkl values have zero intensity in
fluorite ($\xi_c=0$) and non-zero intensity in pyrochlore ($\xi_c=1$). Therefore, the ratio of the intensity of an all odd hkl peak to an all even hkl peak makes a convenient basis for calculating $\xi_c$.

Given a reliable mathematical relationship between the cation order parameter and the diffracted peak intensities we can calculate one from the other. For simplicity, we have chosen to use only two peaks rather than the entire diffraction pattern for order parameter calculations since the simple mathematical model described below works best over small increments of $2\theta$. The [331] and [400] peaks will be considered since they are relatively intense, and are very close in d-spacing. The mathematical relationship is described below.

The structure factor ($F_{hkl}$) can be written as[40]:

$$F_{hkl} = \sum f_n \exp[2\pi i (hx+ky+lz)] \quad [3.31]$$

where, $f_n$ = atomic scattering factor for atom n
$x$ = x coordinate of atom n
$y$ = y coordinate of atom n
$z$ = z coordinate of atom n

$x,y$ and $z$ are expressed as fractions of the lattice constant and the summation is over every atom in the unit cell.
Once the structure factor is known, the peak area (or intensity) of the powder diffraction peak can be calculated[40] from equation [3.32]:

\[ I_{hkl} = |F_{hkl}|^2 P_{hkl} (1 + \cos^2 \theta) / (\sin^2 \theta \cos \theta) \]  

[3.32]

where, \( I_{hkl} \) = integrated peak intensity of peak hkl

\( P_{hkl} \) = multiplicity factor for peak hkl

The formula for the peak area, equation [3.32], contains the assumption that the temperature factor \( \text{e}^{-2\mu} \) can be neglected although it is a weak function of \( \theta \) since it is difficult to calculate accurately. The error introduced by this assumption is very small due to the use of two closely spaced peaks[40].

The comparison of the experimental and theoretical peak intensity is complicated by two additional factors. First, the value of \( \xi_a \) has a slight influence upon the peak intensity which can not be accurately calculated since \( \xi_a \) is unknown. Fortunately, the size of the possible effect can be determined from consideration of the extreme cases where \( \xi_a \) is either zero or one. These calculations show that variations in \( \xi_a \) generally only change \( \xi_c \) by less than 10% due to the low scattering factor for \( O^2^- \) relative to the scattering factors of the cations. The case of \( Y_2Zr_2O_7 \), where the scattering due to cations almost exactly cancels out for all odd values of hkl even in the pyrochlore symmetry may be an exception to this rule. The effect of \( \xi_a \) is further minimized by setting \( \xi_a = \xi_c \).
for purposes of the structure factor calculation. The second complication is that low peak intensities can result in either unreasonably long integration times or unreasonably large statistical variations in the peak intensities. This problem can be substantially reduced with a high intensity x-ray source.

A computer program was written to calculate the peak intensities as a function of composition, \( \hat{c} \) and \( \hat{a} \), using the above equations. Since the composition is known a priori, and the ratio of the peak intensities is measured experimentally we are left with one relationship and two unknowns (\( \hat{c} \) and \( \hat{a} \)). This problem could be solved rigorously as in the usual structure determination by acquiring more peak intensity data. However, since the goal is simply to determine a semi-quantitative measure of the cation order parameter and since the peak intensities are relatively insensitive to \( \hat{a} \), the simplifying assumption that \( \hat{a} = \hat{c} \) has been made as described previously. Given this assumption, there is a direct relationship between \( \hat{c} \) and \( \frac{I_{331}}{I_{400}} \):

\[
\frac{I_{331}}{I_{400}} = \frac{|F_{331}|^2P_{331}(1+\cos^2\theta_{331})/(\sin^2\theta_{331}\cos\theta_{331})}{|F_{400}|^2P_{400}(1+\cos^2\theta_{400})/(\sin^2\theta_{400}\cos\theta_{400})}
\]

[3.33]

where, \( P_{hkl} \) is known, \( \theta_{hkl} \) is measurable and \( F_{hkl} \) is a function of known quantities and \( \hat{c} \).
4 EXPERIMENTAL METHODS

The experimental methods chapter is a brief description of the sample preparation procedure for conductivity and x-ray diffraction measurements, the single crystal growth process and some details of the actual measurements.

4.1 Sample Preparation

Sample preparation consisted of forming homogeneous oxide powders with the appropriate compositions and then sintering them into high density compacts. A few single crystal samples were also made by top seeded growth from a fluxed melt as described later.

4.1.1 POWDER PREPARATION

The powder preparation technique was a "liquid-mix" technique first developed by Pechini[41]. The Pechini process is used to form homogeneous, sinterable powders with precisely controlled compositions from a variety of elements. The composition control afforded by the Pechini process is essential when fabricating pyrochlore powders since it allows for a well-defined cation mole ratio. Furthermore, the homogeneity of a "liquid-mix" technique with near atomic scale mixing is preferable to calcining mechanical mixtures of oxide powders.
The Pechini method involves the dissolution of a metal compound in a citric acid-ethylene glycol mixture. Several such solutions are produced, assayed and mixed in the required proportions to produce the desired oxide compound. This step is followed by heating to condense the acid and alcohol groups which react via a dehydration reaction to form a crosslinked polyester:

\[
\text{citric acid} + \text{ethylene glycol} \rightarrow \text{water} + \text{polyester}
\]

The polymerized mass is further heated to drive off water and excess ethylene glycol and generate a hard crosslinked polymeric solid. The next steps are charring to partially burn off the organic material followed by comminution of the carbonized solid into powder. This powder is calcined at 700 °C to form the appropriate oxide although further heating may be required to generate the equilibrium phase. The details of the Pechini process as used in this study, including concentrations, temperatures and times, are described in Appendix A.

For the particular case of forming pyrochlore compounds, the following soluble metal compounds were used:

1. Gd,Y hydrated nitrates
2. Ti,Zr,Ta alkoxide
3. Ca carbonate

The rare earth compounds required a special procedure to remove their nitrate anions before dissolving in the ethylene glycol and citric acid mixture since Pechini\(^{[41]}\) states that
nitrates can cause precipitation of metal containing compounds during the polymerization stage. The nitrates were first dissolved in distilled water and then their metal hydroxides were precipitated with a concentrated ammonia solution. The suspension was filtered repeatedly and washed with isopropanol in order to remove the ammonium and nitrate ions and excess water. The hydroxide was then dissolved in the ethylene glycol and citric acid mixture.

The zirconium citrate solution was formed from Zr-n-propoxide, an inexpensive and readily available alkoxide. Due to its high reactivity, the alkoxide was first dissolved in isopropanol before being added to the ethylene glycol and citric acid. The combination of Zr-n-propoxide and ethylene glycol without excess isopropanol forms an insoluble polymer as ethylene glycol substitutes for the propoxide group.

The other compounds were dissolved directly in ethylene glycol and citric acid. Their volatile components, either alcohol or carbon dioxide, evaporated during polymerization.

The calcined powders were pressed into 2.5 gram pellets at 5000 psi in a 3/4" stainless steel die, cleaned with SiC polishing paper and paper tissues and then isopressed at 40000 psi. The die was cleaned between every pressing operation and lubricated with a saturated solution of stearic acid in isopropanol. The final green compacts had densities of only 50-60% due to the poor packing density of powder produced by the Pechini process.
One significant drawback of the Pechini powder preparation process is that it concentrates all the impurities from the organic precursors into the final oxide powder product. This study used high purity starting materials to minimize the resulting contamination. Nevertheless, it is necessary to perform a chemical analysis to check the impurity concentrations. Three powders were analyzed by Northern Analytical Laboratory Inc. [Amherst, New Hampshire] using spark source mass spectrographic (SSMS) analysis. They claim a precision of a factor of three and that SSMS is useful over a concentration range from 1000 ppm to a fraction of one part per million. The data are shown in Table 4.1 for all elements with reported concentrations exceeding 5 ppm by weight.
Table 4.1 Impurity content of Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$, powders as measured by spark source mass spectrographic analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Impurity concentration in ppmw</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gd$_2$(Zr$<em>x$Ti$</em>{1-x}$)$_2$O$_7$</td>
</tr>
<tr>
<td></td>
<td>(x=0.0)</td>
</tr>
<tr>
<td>Na</td>
<td>*</td>
</tr>
<tr>
<td>Mg</td>
<td>*</td>
</tr>
<tr>
<td>Al</td>
<td>55</td>
</tr>
<tr>
<td>Si</td>
<td>60</td>
</tr>
<tr>
<td>K</td>
<td>2</td>
</tr>
<tr>
<td>Ca</td>
<td>20</td>
</tr>
<tr>
<td>Sc</td>
<td>*</td>
</tr>
<tr>
<td>Ti</td>
<td>Major</td>
</tr>
<tr>
<td>Y</td>
<td>15</td>
</tr>
<tr>
<td>Zr</td>
<td>90</td>
</tr>
<tr>
<td>Gd</td>
<td>Major</td>
</tr>
<tr>
<td>Tb</td>
<td>20</td>
</tr>
<tr>
<td>Dy</td>
<td>6</td>
</tr>
<tr>
<td>Hf</td>
<td>70</td>
</tr>
</tbody>
</table>

* Interference

The data in Table 4.1 show that the alicialvalent impurity content is about 200 ppm in each sample that was studied. The total impurity load consists of rare earth elements,
ubiquitous impurities such as Si, Al, K and Ca and, most importantly, hafnium. Most of the impurity elements are in such low concentration that they will have a negligible effect on the properties of the intrinsically disordered pyrochlore system.

Hafnium, due to its unknown concentration, is a potential problem. It is probably a contaminant in the zirconium since the two elements are chemically very similar. Due to their chemical similarity, the presence of hafnium in zirconium is generally unimportant. It can be significant, however, when a composition is specified in moles but measured by weight. The different atomic weights of zirconium and hafnium can result in an overestimate of the moles of oxide in a particular weight of impure zirconium oxide if the oxide is assumed to be pure. The zirconium precursor used in this study, Zr-n-propoxide, contains an unknown concentration of hafnium.

4.1.2 SINTERING

The samples were fired in a furnace at $\sim 1600 \, ^\circ\text{C}$ for about 12 hours in air and then cooled in the furnace. The furnace used was a molybdenum wire heating element vertical tube furnace with $\text{H}_2$ gas flowing around the heating coil to protect the molybdenum from oxidation. The maximum heating rate was about 1000 $^\circ\text{C}$ per hour and the temperature stability was about $\pm 10 \, ^\circ\text{C}$ at 1600 $^\circ\text{C}$.

The isopressed pellets were sintered individually in air at $\sim 1600 \, ^\circ\text{C}$ for $\sim 12$ hours in an $\text{Al}_2\text{O}_3$ crucible with Pt foil
separating the pellet from the bottom of the crucible. A second smaller pellet was used to provide material for phase identification by powder x-ray diffraction. The fired pellets were cooled to near room temperature in the furnace. The pellets were creamy white and sometimes had a few brown spots. The spots are believed to be due to partial precipitation during the polymerization stage of powder preparation. However, elemental analysis of the spots by x-ray fluorescence showed that, within experimental error, they had the same composition as the bulk specimen. Samples with brown spots were generally not used for further experiments.

The sintered densities obtained in this study were 85-95% as measured by the Archimedes method. The densities were determined according to the ASTM standard method[42] except that the measurement precision was compromised by using small (~1 gram) sample sizes. Additionally, there are serious doubts about the accuracy of the density measurements due to their lack of correspondence with estimates of the porosity from SEM photographs. However, calculations of the sintered density from measurements of the weight and external dimensions of small rhombohedral specimens gave densities in excess of 90%.

Scanning electron micrographs of fractured surfaces of both the Gd_2(Zr_x Ti_{1-x})_2O, and Y_2(Zr_x Ti_{1-x})_2O, series suggest substantial porosity. See the SEM photos of Gd_2Ti_2O, in Figure 4.1. Apparently, the pores are primarily intergranular and thus further densification might be possible. The grain
size for this composition is roughly 10 μm but compositions with more Zr tend to have finer grains. Note that the grains are generally equiaxed. The reason for the low fired densities (perhaps 80%) seen in SEM photos is as yet unclear.

The fired pellets were polished with SiC paper to make the faces flat and coplanar. The pellets were then polished with 3 μm Al₂O₃ polishing grit. The surface preparation had no effect upon the measured bulk electrical properties during a comparison of the conductivities of specimens with electrodes on polished and as-fired surfaces.

After sintering some compositions were annealed at 1350 °C for two days to form the equilibrium phase. This annealing step was necessary because it is known that certain pyrochlore compounds, such as Gd₂Zr₂O₇, disorder to fluorite when heated above 1550 °C [16,17]. Therefore, annealing below the order-disorder transition temperature is necessary to restore the pyrochlore ordering. Measurements of the cation order parameter as a function of annealing time showed that two days was long enough to establish a steady state order parameter in Gd₂Zr₂O₇. All compounds with 60% or more zirconium were annealed although the sintered Gd₃(Zr₀.₆Ti₀.₄)₂O₇, and Y₂(Zr₀.₆Ti₀.₄)₂O₇ samples showed no change in cation order parameter after annealing.

4.1.3 SINGLE CRYSTALS

Single crystals of Gd₂Ti₂O₇ and (Gd₀.₉₉Eu₀.₀₁)₂Ti₂O₇ were grown in the Crystal Physics and Optical Electronics Laboratory from
a fluxed melt consisting of 1 part by mole Gd₂O₃, 3 parts TiO₂, 2 parts BaCO₃, and 2 parts B₂O₃. The oxide powders were mixed and placed in a small platinum crucible in a SiC globar heated furnace. After melting the powders and soaking at ~1500 °C for 80 hours to homogenize the melt, a rotating single crystal seed (50 rpm, (110) plane parallel to melt surface) was placed in contact with the top of the melt. A single crystal grew as the melt temperature was gradually lowered and the seed withdrawn. The growth temperature was ~1350 °C and was reduced by 0.3 °C/hour while withdrawing the seed at 0.1 mm/hour. The best crystals were a few cubic centimeters in volume with faceted faces.

A small piece of a single crystal of Y₂Ti₂O₇, grown in the same laboratory several years earlier by a similar technique, was also available for study.

4.2 Conductivity Measurements

Electrical conductivity measurements were made by several techniques. The vast majority of all the measurements were obtained via complex impedance spectroscopy using either the Hewlett Packard 4192a Low Frequency Impedance Analyzer (5 Hz to 13 MHz) or the Schlumberger Solartron 1250 Frequency Response Analyzer (10 mHz to 65 kHz). A few 2-probe DC measurements were made with either a Hewlett Packard 4140b Picoammeter/Programmable Voltage Source or a Keithley multimeter. A few of the earliest measurements were made with a homemade AC cross correlator device or a 4-probe DC
configuration. All the instruments gave comparable results when used within their operating limits as described below.

A major accomplishment of this study was the unambiguous and accurate identification of the impedances due to bulk effects and those attributable to the grain boundaries. In general, the interpretation of complex impedance plots is complicated by an insufficient frequency range for the measurement, depressed, distorted or overlapping semicircles and instrumental error. Those nonidealities have been minimized in this study by the use of state of the art equipment, appropriate choice of the experimental system and attention to the design of sample holders. In many cases, we were able to obtain high quality data such as is shown in Figure 4.2 for \( \text{Gd}_2(\text{Zr}_{0.6}\text{Ti}_{0.4})_2\text{O}_7 \) at 500 °C. This figure was produced by combining low frequency impedance data from the Solartron 1150 with high frequency data from the Hewlett Packard HP4192a. The design of the sample holder was chosen to minimize stray capacitance while the disk shape of the sample resulted in substantial sample capacitance. The bulk, grain boundary and electrode semicircles are clearly distinguishable and can be accurately determined. Figure 4.2 also shows the correspondence between different instruments. The maximum deviation in total impedance between the two instruments was less than 3%.

The sample holder for conductivity measurements was designed to make convenient, accurate, gas-tight impedance measurements on disk shaped samples. See Figure 4.3 for a
Figure 4.2 A complex impedance plot for $\text{Gd}_2(\text{Zr}_{0.6}\text{Ti}_{0.4})_2\text{O}_7$ (x=0.6) at 500 °C in air showing the bulk, grain boundary and electrode impedances.
Figure 4.3 The sample holder configuration for electrical conductivity measurements[43].
diagram of the sample holder configuration. The stray capacitance with this design is less than 0.5 pF. The sample temperature is monitored with a platinum/rhodium thermocouple located within 1 mm of the sample. Due to the close proximity of the thermocouple to the sample, the temperature distribution within the furnace is relatively unimportant. In certain cases, such as at high temperatures when the impedance of the disk was too low to produce good impedance plots, a bar shaped sample was used instead of the disk. In these cases, the sample capacitance is overwhelmed by stray capacitance and can not be measured. However, the sample resistance can still be accurately determined.

Figure 4.4 shows a comparison of data from three different samples of Gd₂Zr₂O₇, with different geometries and measurement techniques. The excellent correspondence between the various techniques has several implications. First, it shows that DC and AC measurements are equivalent at high temperatures where the grain boundary resistance can be neglected. Second, it shows the agreement between disk and bar shaped specimens. In this case, the geometric shape factors of the disk and bars differed by a ratio of more than 200 but their resistivities are almost identical. Finally, Figure 4.4 shows the reproducibility of the sample preparation and characterization technique over a period of more than two years. The slight differences between the conductivities of the bars and the disk can be ascribed to inaccuracies in the
Figure 4.4  An Arrhenius plot of the ionic conductivity of Gd$_2$Zr$_2$O$_7$, showing a comparison of different sample geometries and measurement techniques.
measurement of the sample geometric factors and differences in thermal history between the three specimens.

Electrical measurements were made as a function of temperature (200 °C - 1400 °C) and oxygen fugacity \((10^0 - 10^{-20} \text{ atm})\) using either oxygen/argon mixtures or carbon dioxide/carbon monoxide mixtures. The minimum temperature was limited by the sample impedance at low temperatures since our highest impedance instrument (the Solartron 1250) is inaccurate above about \(10^8 \Omega\). The oxygen fugacity was calculated from the thermodynamic values for the gas mixtures and periodically checked with a stabilized \(\text{ZrO}_2\) galvanic cell. The deviations between the \(\text{PO}_2\) calculated from the gas mixture ratio and the \(\text{PO}_2\) calculated from the \(\text{ZrO}_2\) cell voltage were less than one order of magnitude.

The Solartron 1250 was used with a simple buffer circuit to increase its effective input impedance from \(10^6\) ohms to a value in excess of \(10^9\) ohms. The design of the circuit, as suggested by Faktor[38], is shown in Figure 4.5.

4.3 X-Ray Diffraction Measurements

To a first approximation, the x-ray diffraction patterns of defect fluorite and pyrochlore differ only in that pyrochlore has a few additional weak superstructure reflections. The intensities of the superstructure x-ray reflections are roughly proportional to the difference in the x-ray scattering factors of the two cation site. Therefore, distinguishing between the two structures by x-ray diffraction
Figure 4.5 A circuit diagram for the buffer circuit used with the Solartron 1250 for conductivity measurements[38].
can be difficult when the cations have similar scattering factors as occurs in \( Y_2Zr_2O_7 \). In these cases, infrared or Raman spectroscopy may be superior methods for phase identification. However, when the scattering factors of the A and B cations are appreciably different the x-ray diffraction pattern can be used to deduce the structure and the cation order parameter.

In order to calculate the cation order parameter \( (\xi_c) \) one needs accurate measurements of peak areas. These measurements are most conveniently made by computer controlled equipment. In this research, a RU-300 Rigaku powder diffractometer was used with a Digital Equipment Corp. MicroVax host computer. The diffractometer has a rotating anode with a maximum electron beam power of 18 kW and produces a very high intensity incident x-ray beam. Due to the high power available it was possible to obtain good statistics on the intensities of diffracted beams. Additionally, the RU-300 collects and stores data digitally so that the peak area calculations can be made digitally rather than manually. Figure 4.6 shows the \{331\} and \{400\} peaks for Gd\(_2\)Ti\(_2\)O\(_7\).
Figure 4.6  An x-ray powder diffraction pattern of Gd$_2$Ti$_2$O$_7$, showing the (400) and (331) peaks.
The operating parameters for Figure 4.6 were as follows:

- X-ray tube voltage: 40 kV
- X-ray tube current: 200 mA
- X-ray tube power: 8 kW
- Divergence slit: 1.0 mm
- Scatter Slit: 1.0 mm
- Receiving Slit: 0.15 mm
- Scan rate: 1°20/minute
- Step width: 0.02°20

Peak areas were calculated by integrating the measured peak intensity over the whole peak and then subtracting the background counts. The background at the peak position was calculated by averaging the background at values of 2θ one degree higher and lower than the peak.

The lattice constant calculations were based on the locations of the \{10.6.2\} and \{884\} peaks from powder diffractometer diffraction patterns. These peaks were chosen because they occur at high angle where lattice constant measurements are most accurate and they have relatively high intensity in all compositions. The decision to use only two peaks was based on considerations of convenience and the required accuracy and precision of the measurements. It was possible to separate the $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks so that a total of four diffraction lines were available for analysis. Frequent checks on the calibration of the diffractometer alignment were made with an external polycrystalline silicon standard.
4.4 Optical Measurements

Optical transmission measurements were made on a single crystal of Gd₂Ti₂O₇, using a Perkin Elmer Lambda 9000 IR-visible-UV spectrophotometer. This instrument has a wavelength range of 300 to 1200 nanometers and is controlled by an IBM PC AT.
5 RESULTS

5.1 Results for Gd$_2$ (Zr$_x$Ti$_{1-x}$)$_2$O$_7$

The results for Gd$_2$ (Zr$_x$Ti$_{1-x}$)$_2$O$_7$ are broken into two sections: diffraction data and electrical data.

5.1.1 X-RAY DIFFRACTION

5.1.1.1 Lattice Constants

Measurements of the lattice constant of the Gd$_2$ (Zr$_x$Ti$_{1-x}$)$_2$O$_7$ solid solution were found to obey Vegard's Law, i.e. the lattice constant is linear as a function of composition across the solid solution. See Figure 5.1. The least-squares fit of the lattice constant data is given below:

\[ a = 10.19 + 0.3504 \, (x) \quad [5.1] \]

where, \( a \) is the lattice constant in Å and \( x \) is the Zr fraction as defined by Gd$_2$ (Zr$_x$Ti$_{1-x}$)$_2$O$_7$.

The implication of obedience to Vegard's Law is that this composition range indeed represents a solid solution. Formation of a second phase would show itself as a plateau in the lattice parameter vs. composition curve. The fact that this solid solution obeys Vegard's Law also gives confidence that the actual compositions correspond to their nominal
Figure 5.1  The lattice parameter as a function of composition for \( \text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7 \).
values since any discrepancy would appear as a deviation from the straight line.

All the peaks of the x-ray diffraction pattern could be indexed as pyrochlore, i.e., there was no evidence of a second phase. See Figure 5.2. Nineteen diffraction peaks were detectable in the 2θ range of 25-90° for Gd₂Ti₂O₇. Fewer peaks were found in the diffraction patterns for the other compositions since some of the peak intensities were reduced by the increasing average B cation scattering factor and increasing disorder as Zr replaced Ti.

5.1.1.2 Order Parameter

The cation order parameter (\(\xi_c\)) is calculated from the ratio of the areas of the \{331\} and \{400\} peaks from a powder x-ray diffraction pattern as described earlier in the theoretical and experimental methods sections. The data for the Gd₂(ZrₓTi₁₋ₓ)₂O₇ system are shown below in Table 5.1 and in Figure 5.3. The trend in cation order parameter with composition is consistent with our hypothesis that \(\xi_c\) is a function of \(R_a/R_s\).
Figure 5.2  X-ray powder diffraction pattern for Gd$_2$Ti$_2$O$_7$. 
Figure 5.3  The cation order parameter as a function of composition for Gd₂(ZrₓTi₁₋ₓ)₂O₇.
Table 5.1 Cation order parameter data for Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$

<table>
<thead>
<tr>
<th>Composition</th>
<th>Peak Area [331]</th>
<th>Peak Area [400]</th>
<th>Ratio [331]/[400]</th>
<th>$\xi_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd$_2$(Zr$<em>x$Ti$</em>{1-x}$)$_2$O$_7$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x=0.00</td>
<td>12250</td>
<td>16422</td>
<td>0.746</td>
<td>0.97</td>
</tr>
<tr>
<td>x=0.15</td>
<td>9607</td>
<td>13605</td>
<td>0.706</td>
<td>1.005</td>
</tr>
<tr>
<td>x=0.30</td>
<td>11466</td>
<td>23524</td>
<td>0.487</td>
<td>0.92</td>
</tr>
<tr>
<td>x=0.40</td>
<td>5840</td>
<td>13390</td>
<td>0.436</td>
<td>0.94</td>
</tr>
<tr>
<td>x=0.50</td>
<td>7942</td>
<td>21967</td>
<td>0.362</td>
<td>0.91</td>
</tr>
<tr>
<td>x=0.60</td>
<td>5762</td>
<td>18648</td>
<td>0.309</td>
<td>0.89</td>
</tr>
<tr>
<td>x=0.80</td>
<td>4186</td>
<td>21303</td>
<td>0.196</td>
<td>0.79</td>
</tr>
<tr>
<td>x=1.00</td>
<td>2462</td>
<td>22037</td>
<td>0.112</td>
<td>0.65</td>
</tr>
</tbody>
</table>

5.1.2 IONIC CONDUCTIVITY

In this section, the composition of the Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ solid solution is systematically varied and the resulting ionic disorder is indirectly measured with electrical conductivity measurements. Conclusions about the ionic disorder are drawn from an analysis of the trends in activation energy and pre-exponential constant for ionic conduction.

5.1.2.1 Isothermal Ionic Conductivity

The first problem is to determine the bulk ionic conductivity from a complex impedance measurement. In brief,
the procedure is to identify the bulk semicircle and calculate the bulk resistance and then knowing the shape of the conductivity sample one can calculate the total bulk conductivity. Measurements of this quantity as a function of PO₂ are then fit to the defect model (equation [3.9]) to determine the bulk ionic conductivity. The details are given below and in a paper by the author[44].

The bulk impedance portion of the complex impedance spectrum was unambiguously determined by comparison of the permittivity at high frequency with the known bulk capacitance. In Gd₃Zr₂O₇, for example, as shown previously in Figure 3.4, the dielectric constant at the peak of the first semicircle was calculated to be 47 in good agreement with the literature value of 60 [19]. Total bulk conductivities were calculated from the low frequency intercept of the complex impedance curve after eliminating the effects of grain boundary and electrode impedances.

The bulk electrical conductivity was measured as a function of temperature, PO₂ and composition. The temperature range was 600 to 1400 °C with 50 °C increments and the PO₂ range was 1 to 10⁻²⁰ atmospheres. The ionic conductivity at each temperature was determined by an iterative least-squares fit of the isothermal data as a function of PO₂ to equation [3.9].

\[
\log \sigma = \log[A + B(PO_2^{-1/4}) + C(PO_2^{3/4})] \quad [3.9]
\]
in which A represents the ionic component of the conductivity and the second and third terms are related to the electron and hole conductivities respectively.

Equation [3.9] is the general formula for the conductivity of an oxide compound when the electroneutrality condition is dominated by ionic defects and all the carrier mobilities are assumed to be PO₂ independent. A, B and C are constants.

Figures 5.4 to 5.11 show the log σ vs. log PO₂ data at a variety of temperatures for nominally pure Gd₂(ZrₓTi₁₋ₓ)₂O₇ along with the best fit of equation [3.9] to each isotherm. Many of the isotherms have been removed from the diagrams for clarity but the data were all used in all the calculations (with the exception noted below).

The defect model (lines) fits the experimental data (symbols) quite well for most samples. The principal exception is for low and moderate Zr content materials at high temperatures and reducing conditions. Under these conditions, the slope of the log σ vs. log PO₂ curve may be changing from -1/4 towards -1/6. Please refer back to Figure 3.2 which shows a transition in the slope of the theoretical log conductivity versus log PO₂ from -1/4 to -1/6 under reducing conditions. The data points used in the fits to equation [3.9] did not include the points with a deviation from the -1/4 slope.

The log σ vs log PO₂ data for the Gd₂(ZrₓTi₁₋ₓ)₂O, solid solution suggest several observations. It can be seen from
Figure 5.4 The log conductivity as a function of log oxygen partial pressure for Gd$_2$Ti$_2$O$_7$. 
Figure 5.5  The log conductivity as a function of log oxygen partial pressure for Gd$_2$(Zr$_{0.15}$Ti$_{0.85}$)$_2$O$_7$. 

\[ Gd_2(Zr_{x}Ti_{1-x})_2O_7 \quad (x=0.15) \]
Figure 5.6: The log conductivity as a function of log oxygen partial pressure for $\text{Gd}_2(\text{Zr}_{0.7}\text{Ti}_{0.3})_2\text{O}_7$. 
Figure 5.7  The log conductivity as a function of log oxygen partial pressure for Gd$_2$(Zr$_{0.4}$Ti$_{0.6}$)$_2$O$_7$. 
Figure 5.8  The log conductivity as a function of log oxygen partial pressure for Gd$_2$(Zr$_{0.5}$Ti$_{0.5}$)$_2$O$_7$.  

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Figure 5.9  The log conductivity as a function of log oxygen partial pressure for $\text{Gd}_2(\text{Zr}_{0.6}\text{Ti}_{0.4})_2\text{O}_7$.  

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Figure 5.10  The log conductivity as a function of log oxygen partial pressure for Gd$_2$(Zr$_{0.8}$Ti$_{0.2}$)$_2$O$_7$.  

Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$  ($x=0.80$)
Figure 5.11  The log conductivity as a function of log oxygen partial pressure for Gd$_2$Zr$_2$O$_7$. 
Figures 5.4 to 5.11 that the electrolytic domain (i.e., the region where the ionic transference number is very close to one) becomes wider at fixed temperature as the Zr content increases. The activation energies for ionic and electronic conduction are roughly independent of Zr content but the total conductivity and ionic conductivity both increase markedly with Zr content. These considerations and others are more fully considered in the Discussion section.

The bulk ionic conductivity for selected temperatures between 600 and 1100 °C is shown as a function of composition across the Gd₂(Zr₅Ti₁₋ₓ)₂O₇ solid solution in Figure 5.12. The dramatic increase in the conductivity as the Zr content increases is consistent with our expectations based on the argument that the order parameter decreases as the composition approaches Gd₂Zr₂O₇ and will be fully analyzed in the Discussion section. Also note that the maximum conductivity at 600 °C occurs for Gd₂(Zr₀.₈Ti₀.₂)₂O₇, not Gd₂Zr₂O₇.

The ionic conductivity could not be found for compositions with less than 30% Zr except at 600 °C because the log σ vs. log PO₂ curve did not include a large enough PO₂-independent region for accurate calculation of the ionic conductivity from a fit to equation [3.9] at higher temperatures. It is very difficult and time consuming to acquire conductivity data on these compositions due to their long equilibration times of up to several days per data point.

The log σ vs log PO₂ curves for a single crystal of Gd₅Ti₂O₁₀, are given in Appendix B. These data will not be
Figure 5.12  The ionic conductivity as a function of composition and temperature for Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$. 
analyzed except to state that they do not fit the defect model probably due to insufficient time to permit equilibration.

5.1.2.2 Activation Energy and Pre-Exponential Constant

The activation energy ($E'$) and pre-exponential constant ($\sigma_0$) for bulk ionic conduction were calculated from equation [5.2] for compositions with 30-100% Zr and temperatures of 600-1100 °C. The results are shown in Figures 5.13 and 5.14.

$$\sigma_T = \sigma_0 \exp(-E'/RT)$$  \hspace{1cm} [5.2]

Since the ionic conductivity was always calculated from equation [3.9], the following equalities apply. See Section 3.1.1 for more detail.

$$\sigma_i = A$$  \hspace{1cm} [5.3]

$$\sigma_0 = A_0$$  \hspace{1cm} [5.4]

$$E' = E_a$$  \hspace{1cm} [5.5]

At temperatures below 600 °C some of the high Zr content compositions showed a large increase in activation energy. This increase in activation energy was tentatively assigned to association between oxygen vacancies and cation anti-site defects. In this section, the reported conductivity data are only for temperatures above 600 °C where the Arrhenius plots fit one straight line. The low temperature conductivity data are described in another section.
Figure 5.13  The activation energy for ionic conduction as a function of composition for Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$. 
Figure 5.14  The pre-exponential constant for ionic conduction as a function of composition for $\text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7$.
5.1.2.3 Grain Boundary Conduction

Due to the high quality of the complex impedance spectroscopy data for disk shaped specimens it was possible, in certain circumstances, to obtain the grain boundary resistance. In this section, we report the grain boundary "conductivity"- the inverse of the product of the grain boundary resistance and the sample geometric factor.

The grain boundary conductivity was determined across most of the Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ solid solution and is shown for several temperatures in Figure 5.15. Interestingly, it has a similar composition dependence to the bulk conductivity. However, the activation energies are somewhat higher as shown in Figure 5.16. The interpretation of the grain boundary conductivity is complicated by our comparatively poor microstructure control.

The values of the activation energies are relatively reliable; the Arrhenius plots are quite straight and well correlated. See Figure 5.17 which gives the results for Gd$_2$(Zr$_{0.8}$Ti$_{0.2}$)$_2$O$_7$ as an example.

Reliable data could only be obtained at low temperatures since as the temperature increased the grain boundary semicircle in the complex impedance spectrum contracted relative to the bulk semicircle. At temperatures above about 600 °C, the grain boundary semicircle was badly overlapped with, and eventually disappeared into, the much larger bulk semicircle.
Figure 5.15  The grain boundary "conductivity" as a function of temperature and composition in $\text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7$. 
Figure 5.16 The activation energy for grain boundary conduction as a function of composition in $\text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7$. 

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Figure 5.17 An Arrhenius plot of the grain boundary "conductivity" of Gd$_2$(Zr$_{0.6}$Ti$_{0.4}$)$_2$O$_7$. 

Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$

(x=0.6)
It was not possible to determine the grain boundary conductivity of compositions with less than 30% Zr because they had no visible grain boundary impedance at any temperature. Apparently, the grain boundaries are not sufficiently blocking relative to the bulk in poorly conducting samples for a grain boundary impedance to be evident.

5.1.2.4 Doping Experiments

Aliovalent dopants are useful as experimental probes of the nature and concentration of mobile defects in ionic materials. In particular, when we replace Gd with Ca in Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$, we can expect an increase in the ionic conductivity if oxygen vacancies are the mobile species and are initially present in low enough concentration relative to the dopant level. The doping effect on conductivity is evident in Figure 3.2.

Several experiments were made with aliovalently doped specimens. The most extensive experiment, on Gd$_2$(Zr$_{0.3}$Ti$_{0.7}$)$_2$O$_7$, is described in the next section. In this section, we consider acceptor doped samples of the two end members: Gd$_2$Ti$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$. The results show that the conductivity of Gd$_2$Zr$_2$O$_7$ is insensitive to dopant content but that the conductivity of Gd$_2$Ti$_2$O$_7$ changes drastically with added impurities. These results are consistent with, and provide a significant verification of, our interpretation of the conductivity of nominally pure materials.
A comparison of the conductivity of Gd$_2$Zr$_2$O$_7$ and Gd$_{0.99}$Ca$_{0.01}$Zr$_2$O$_{7-s}$ shows that they have virtually the same conductivity. See Figure 5.18. Indeed, these two samples correspond as closely as the three samples of Gd$_2$Zr$_2$O$_7$, shown previously in Figure 4.4. The fact that doping has no effect on the conductivity is clear evidence of an intrinsic defect concentration that far exceeds the doping level. Thus we can consider Gd$_2$Zr$_2$O$_7$ to be an intrinsic oxygen ion conductor.

Doping experiments on Gd$_2$Ti$_2$O$_7$ tell a far different story. The nominally pure material has the lowest ionic conductivity of any compound studied in this thesis but with the substitution of calcium for one percent of the gadolinium there is a substantial increase in the ionic conductivity. Therefore, because purposeful acceptor doping is required to obtain substantial ionic conductivity in Gd$_2$Ti$_2$O$_7$, it can be considered as an extrinsic ionic conductor.

Figure 5.19 shows the PO$_2$ dependent conductivity measurements used to calculate the ionic conductivity for (Gd$_{0.99}$Ca$_{0.01}$)Ti$_2$O$_{7-s}$. It was not possible to obtain satisfactory data at 850 °C due to the substantial overlap between the bulk and grain boundary semicircles in the complex impedance plane and the frequency limitations of our equipment. This overlap also compromises the accuracy of the conductivity measurements made at other temperatures near 850 °C. Note also that the fit of the defect model (equation [3.9]) to the experimental data is relatively poor for this composition.
Figure 5.18  An Arrhenius plot of the conductivity of Gd$_2$Zr$_2$O$_7$ and (Gd$_{0.9}$Ca$_{0.1}$)$_2$Zr$_2$O$_{16}$.

Log $\sigma$ vs. $10^4/T$ (K$^{-1}$) for Gd$_2$Zr$_2$O$_7$ and Gd$_2$Zr$_2$O$_7 + 1\%$ Ca.
Figure 5.19  The log conductivity as a function of log oxygen partial pressure for $(\text{Gd}_{0.99}\text{Ca}_{0.01})\text{Ti}_2\text{O}_7$. 

\((\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7 \quad (x=0.01)\)
The ionic and electronic conductivity were separated in the usual manner using equation [3.9]. The ionic conductivity is several orders of magnitude higher for the doped specimen relative to the nominally pure Gd₃Ti₂O₇. Furthermore, an Arrhenius plot of the ionic conductivity, shown in Figure 5.20, gives an activation energy of only 0.52 eV. This activation energy is the lowest value ever found for ionic conductivity in a pyrochlore compound and suggests the possibility of producing a very good ionic conductor by doping Gd₃Ti₂O₇. However, at low temperatures (not shown in Figure 5.20), there is an increase in activation energy and the conductivity drops rapidly with temperature. Additionally, this result must be treated cautiously since it represents only a single sample. These data will be more fully discussed in the Discussion section.

5.1.3 DEFECT CHEMICAL PARAMETERS

Given a validated defect model it becomes possible to extract defect chemical parameters such as activation energies and the bandgap from conductivity measurements because these quantities do not require knowledge of the actual concentrations or mobilities of carriers. It is also possible to derive equilibrium constants such as the Frenkel constant from ionic doped doping experiments since such experiments fix the carrier concentration at a known value.

The general procedure is to use the log σ vs. log P{sub}O{sub}₂ data to calculate the ionic and electronic components of the
Figure 5.20 An Arrhenius plot of the ionic conductivity of $(\text{Gd}_{1-x}\text{Ca}_x)_2\text{Ti}_2\text{O}_7$ ($x=0.01$).
conductivity by fitting to equation [3.9]. The ionic conductivities as a function of aloivalent dopant concentration are then fit to equation [3.21],

$$\log \sigma_i = \log \{H(D+D^2+16K_0)\}^{1/2}\mu$$

[3.21]

to determine the concentration and mobility of the oxygen vacancies. The temperature dependence of the electron and hole conductivities is used to calculate the enthalpy of reduction and the thermal bandgap.

5.1.3.1 Frenkel Constant and Vacancy Mobility

In this section, we investigate the effect of aloivalent doping upon the anion disorder and electrical conductivity of Gd$_2$(Zr$_{0.3}$Ti$_{0.7}$)$_2$O$_7$ in order to quantitatively establish the amount of intrinsic anion disorder. These data were reported previously by the author[45]. This composition was chosen because it represents a case of intermediate intrinsic disorder where the oxygen Frenkel constant is large enough for intrinsic defects to overwhelm the impurities in undoped materials but still small enough for aloivalent doping at higher concentrations to affect the conductivity.

The log $\sigma$ vs log $P_{O_2}$ data for Gd$_2$(Zr$_{0.3}$Ti$_{0.7}$)$_2$O$_7$, Gd$_2$(Zr$_{0.3}$Ti$_{0.7}$)$_2$O$_7$, (Gd$_{0.99}$Ca$_{0.01}$)$_2$(Zr$_{0.3}$Ti$_{0.7}$)$_2$O$_7$, and (Gd$_{0.99}$Ca$_{0.01}$)$_2$(Zr$_{0.3}$Ti$_{0.7}$)$_2$O$_7$ are shown in Figures 5.21, 5.22, 5.23 and 5.24. The data were fit to equation [3.9] by an iterative least squares minimization technique. The lines
Figure 5.21  The log conductivity as a function of log oxygen partial pressure for \( \text{Gd}_2(\text{Zr}_{0.30}\text{Ti}_{0.69}\text{Ta}_{0.01})_2\text{O}_{7.75} \).
Figure 5.22 The log conductivity as a function of log oxygen partial pressure for Gd$_2$(Zr$_{0.3}$(Ti$_{0.7}$)$_{0.2}$)O$_7$. 

\[ \text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7 \quad (x=0.3) \]
Figure 5.23 The log conductivity as a function of log oxygen partial pressure for $(\text{Gd}_{0.95}\text{Ca}_{0.05})_2(\text{Zr}_{0.30}\text{Ti}_{0.70})_2\text{O}_7$.6.
Figure 5.24  The log conductivity as a function of log oxygen partial pressure for \((\text{Gd}_{0.99}\text{Ca}_{0.01})_2(\text{Zr}_{0.30}\text{Ti}_{0.70})_2\text{O}_{7.8}\).
connecting the data points in Figures 5.21 to 5.24 are the solutions to equation [3.9].

\[ \log \sigma = \log \{A + B(PO_2)^{-1/4} + C(PO_2)^{1/4}\} \quad [3.9] \]

For the four samples described above, the ionic conductivity was determined from the value of A in equation [3.9]. The ionic conductivity for one other calcium doped sample, \((Gd_{0.98}Ca_{0.02})_2(Zr_{0.3}Ti_{0.7})_2O_7\), was determined from the PO\(_2\)-independent region of each of its \(\log \sigma - \log PO_2\) isotherms since there were not enough data to justify fitting to equation [3.9].

The qualitative effect of alicovalent doping can be seen in Figure 5.25 which shows \(\log \sigma \cdot T\) vs \(1/T\) for all five samples in this experiment. The Ca doped samples have an enhanced ionic conductivity relative to the nominally pure material and the conductivity increases monotonically with dopant concentration. The Ta doped sample has a lower ionic conductivity than the nominally pure material since its vacancy concentration is suppressed by the donors.

A quantitative analysis of the conductivity as a function of the dopant concentration is possible in light of the simple model derived in Section 3.1.3 and shown in equation [3.21].

\[ \log \sigma_1 = \log \{1/2(D+(D^2+16K_e)^{1/2})e\mu_e\} \quad [3.21] \]

The ionic conductivity data for five different doping concentrations at seven temperatures between 800 and 1100 °C were fit by an iterative least-squares minimization method to
Figure 5.25  Arrhenius plots of the ionic conductivity for doped and nominally pure $\text{Gd}_2(\text{Zr}_{0.5}\text{Ti}_{0.5})_2\text{O}_7$. 
our model using equation [3.21]. This procedure generates values for the Frenkel constant and the oxygen vacancy mobility in addition to checking the validity of the theoretical model. Figure 5.26 shows a comparison of the experimental and theoretical data with half of the isotherms removed for clarity.

The calculated Frenkel constant was 1.0x10^{38} \exp(-0.24\pm0.03\text{eV}/kT) \text{ cm}^-6 and the oxygen mobility was 0.14\exp(-0.78\pm0.02\text{eV}/kT) \text{ cm}^2\cdot\text{V}^-1\cdot\text{s}^-1. Figure 5.27 shows Arrhenius plots for (a) the oxygen vacancy mobility and (b) the Frenkel constant. These data are analyzed in Section 6.2.1.

5.1.3.2 Reduction Energy and Thermal Bandgap

The relationship between the activation energy for n-type conduction (E_a) and the energy of reduction (E_r) was derived in the Theory section:

\[ E_r = 2E_a \]  

Therefore, we can immediately obtain the reduction energy, E_r, from E_a, the activation energy for one of the fitting parameters from our model for the PO_x dependence of total conductivity. The conductivities of the samples with greater than 60% Zr did not show enough PO_x dependence for calculation of E_a. Table 5.2 tabulates the results of the calculations for the reduction energy on the other compositions.
Figure 5.26  A plot of the least squares fit of equation [3.21] to experimental ionic conductivity versus net acceptor dopant concentration data.
Figure 5.27  Arrhenius plots of (a) the oxygen vacancy mobility and (b) the anion Frenkel constant for $\text{Gd}_2(\text{Zr}_{0.3}\text{Ti}_{0.7})_2\text{O}_7$. 
The thermal bandgap is easily obtained from the temperature dependence of parameters B and C as derived in the Theory section:

\[ E_g = E_s + E_c \]  \[3.17\]

These data are also included in Table 5.2. \( E_c \) could not be calculated for compositions with more than 50% or less than 30% Zr due to the lack of significant p-type conductivity. There is a general increase in \( E_r \) as a function of \( x \) in Gd\(_2\)(Zr\(_x\)Ti\(_{1-x}\))\(_2\)O\(_7\). It appears that \( E_g \) may also be increasing with Zr content but there is not enough data to be certain.
Table 5.2 The enthalpy of reduction and the thermal bandgap for Gd₂(ZrₓTi₁₋ₓ)₂O₇

<table>
<thead>
<tr>
<th>Composition</th>
<th>Eᵣ (eV)</th>
<th>Eₑ (eV)</th>
<th>E₉ (eV)</th>
<th>Eᵣ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZTO</td>
<td>2.4</td>
<td>-</td>
<td>-</td>
<td>4.8</td>
</tr>
<tr>
<td>GZTO + 1.0%Ca</td>
<td>2.4</td>
<td>-</td>
<td>-</td>
<td>4.8</td>
</tr>
<tr>
<td>GZT15</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
<td>5.2</td>
</tr>
<tr>
<td>GZT30</td>
<td>3.2</td>
<td>0.9</td>
<td>4.1</td>
<td>6.4</td>
</tr>
<tr>
<td>GZT30 + 0.5%Ca</td>
<td>3.0</td>
<td>1.3</td>
<td>4.3</td>
<td>6.0</td>
</tr>
<tr>
<td>GZT30 + 1.0%Ca</td>
<td>3.4</td>
<td>1.2</td>
<td>4.6</td>
<td>6.8</td>
</tr>
<tr>
<td>GZT30 + 1.0%Ta</td>
<td>2.9</td>
<td>1.0</td>
<td>3.9</td>
<td>5.8</td>
</tr>
<tr>
<td>GZT40</td>
<td>3.0</td>
<td>1.0</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>GZT50</td>
<td>3.6</td>
<td>0.8</td>
<td>4.4</td>
<td>7.2</td>
</tr>
<tr>
<td>GZT60</td>
<td>3.1</td>
<td>-</td>
<td>-</td>
<td>6.2</td>
</tr>
</tbody>
</table>

* Compositions are designated with the letters GZT followed by the percent Zr content, for example Gd₂(Zr₀.₅Ti₀.₇)₂O₇ is designated as GZT30.

5.1.3.3 Association Energy

For most of the Gd₂(ZrₓTi₁₋ₓ)₂O₇ solid solution, undoped materials show a break in the slope of their Arrhenius plots for ionic conduction at temperatures of about 600 °C as shown in Figure 5.28 for Gd₂(Zr₀.₅Ti₀.₅)₂O₇. The Arrhenius plots for the low temperature data are quite straight up to 600 °C and then as temperature increases there is an abrupt
Figure 5.28  An Arrhenius plot of the ionic conductivity of Gd$_2$(Zr$_{0.8}$Ti$_{0.2}$)$_2$O$_7$, showing a break in slope at 600 °C.
transition to a lower slope. As the Zr content and the anion disorder increases, the difference in slope becomes more dramatic.

Without a model for the nature of the associates, the association energy can not be determined from measurements of the activation energy. Therefore, since the exact nature of the associates is unknown, we will simply report the difference in activation energy between the high and low temperature conductivity data for each composition. For convenience, this difference will be described as an association energy ($E_{assoc}$).

Table 5.3 shows the ionic conductivity activation energy data and $E_{assoc}$ while Figure 5.29 shows $E_{assoc}$ vs. % Zr.

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>$E_{low}^*$</th>
<th>$E_{high}^*$</th>
<th>$E_{assoc}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd$<em>2$(Zr$</em>{0.3}$Ti$_{0.7}$)$_2$O$_7$</td>
<td>0.86</td>
<td>0.93</td>
<td>?</td>
</tr>
<tr>
<td>Gd$<em>2$(Zr$</em>{0.4}$Ti$_{0.6}$)$_2$O$_7$</td>
<td>0.82</td>
<td>0.78</td>
<td>0.04</td>
</tr>
<tr>
<td>Gd$<em>2$(Zr$</em>{0.5}$Ti$_{0.5}$)$_2$O$_7$</td>
<td>0.88</td>
<td>0.80</td>
<td>0.08</td>
</tr>
<tr>
<td>Gd$<em>2$(Zr$</em>{0.6}$Ti$_{0.4}$)$_2$O$_7$</td>
<td>0.88</td>
<td>0.75</td>
<td>0.13</td>
</tr>
<tr>
<td>Gd$<em>2$(Zr$</em>{0.8}$Ti$_{0.2}$)$_2$O$_7$</td>
<td>1.05</td>
<td>0.75</td>
<td>0.30</td>
</tr>
<tr>
<td>Gd$_2$Zr$_2$O$_7$</td>
<td>1.20</td>
<td>0.83</td>
<td>0.37</td>
</tr>
</tbody>
</table>

5.1.3.4 Dielectric Constant

The dielectric constant was calculated from the frequency of the maximum in the imaginary bulk impedance whenever an undistorted bulk semicircle was present. In many cases
Figure 5.29  A plot of the association energy as a function of composition in Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$.  

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however, particularly at high temperature, the bulk semicircle was not entirely within the usable frequency range of our impedance measurement equipment. In other cases, the sample was bar shaped which precludes accurate dielectric constant measurements due to the effect of stray capacitance upon the small capacitance of a bar. Thus, the dielectric constant data are only available for a small subset of the total data set.

The dielectric constant, $\varepsilon'$, is calculated from the bulk capacitance, $C_b$, using equation [5.6]:

$$\varepsilon' = \frac{C_b L}{\varepsilon_o A}$$  \hspace{1cm} [5.6]

$A$ is the sample cross sectional area and $L$ is its thickness.

For many compositions, including $\text{Gd}_2(\text{Zr}_{0.5}\text{Ti}_{0.7})_2\text{O}_7$, there is a slight negative temperature dependence to the dielectric constant; it decreases as temperature increases. For other compositions, such as $\text{Gd}_2\text{Zr}_2\text{O}_7$, the dielectric constant is independent of temperature. Figure 5.30 shows the dielectric constant as a function of inverse temperature for $\text{Gd}_2(\text{Zr}_{0.5}\text{Ti}_{0.7})_2\text{O}_7$. The apparent temperature dependence of the dielectric constant is probably an artifact of the wide variation in measuring frequencies, the slight frequency dependence of the dielectric constant and the slight deviation of the experimental complex impedance plots from ideal semicircles.
Figure 5.30  The dielectric constant as a function of inverse temperature for Gd$_2$(Zr$_{0.3}$Ti$_{0.7}$)$_2$O$_7$. 
The dielectric constant is also plotted as a function of composition in Figure 5.31. The data represent an average of the dielectric constant at a variety of temperatures. In general, the average varies from about 50 to 70 and is independent of composition. The data for Gd₂(Zr₀.₅Ti₀.₅)₂O₇ may be erroneous.

Measurements of the PO₂ dependence of the dielectric constant for Gd₂(Zr₀.₅Ti₀.₅)₂O₇ show that it is essentially PO₂-independent.

5.1.4 OPTICAL MEASUREMENTS

The optical transmittance of a single crystal of Gd₂Ti₂O₇ was measured as a function of wavelength from 300-860 nanometers with a Perkin Elmer Lambda 9 spectrometer controlled by an IBM PC AT. The raw data are shown in Figure 5.32. The rapid decrease in transmission as the wavelength approaches 330 nm appears to represent an optical bandgap of about 3.8 eV. However, this conclusion must be treated cautiously since the impurity concentration of the single crystal is unknown and a high impurity content could form optically absorbing defects with energies below the bandgap. Nevertheless, we can say that the bandgap is at least 3.8 eV.
Figure 5.31  The average dielectric constant as a function of composition in Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$.
Figure 5.32  The optical absorption as a function of wavelength for a Gd₂Ti₂O₇ single crystal.
5.2 \( Y_{2}Ti_{x}O_{7} - Y_{2}Zr_{x}O_{7} \)

5.2.1 X-RAY DIFFRACTION

5.2.1.1 Lattice Constants

The trend in lattice constants for \( Y_{2}(Zr_{x}Ti_{1-x})O_{7} \) is similar to the trend for \( Gd_{2}(Zr_{x}Ti_{1-x})O_{7} \), i.e., the lattice constants are proportional to the Zr fraction as shown in Figure 5.33. As in \( Gd_{2}(Zr_{x}Ti_{1-x})O_{7} \), the lattice constant vs. composition curve for \( Y_{2}(Zr_{x}Ti_{1-x})O_{7} \) obeys Vegard's law, as shown in equation [5.7], implying that \( Y_{2}(Zr_{x}Ti_{1-x})O_{7} \) is a true solid solution.

\[
a = 10.090 + 0.3229 \times [5.7]
\]

In equation [5.7], \( a \) is the lattice constant in units of Å and \( x \) is the Zr fraction as defined by \( Y_{2}(Zr_{x}Ti_{1-x})O_{7} \).

The magnitude of the lattice constant for a given value of the Zr content is slightly less for \( Y_{2}(Zr_{x}Ti_{1-x})O_{7} \) than for \( Gd_{2}(Zr_{x}Ti_{1-x})O_{7} \), due to the smaller size of the \( Y^{3+} \) ion (1.015 Å) [2] relative to \( Gd^{3+} \) (1.06 Å).

5.2.1.2 Cation Order Parameter

The cation order parameter of \( Y_{2}(Zr_{x}Ti_{1-x})O_{7} \), decreases monotonically with Zr content as shown in Figure 5.34. Recall
that the cation order parameter, $\xi$, is determined by an x-ray diffraction experiment comparing the areas of the [331] and
Figure 5.33  The lattice parameter of $Y_2(Zr, Ti_{1-x})_2O_7$ as a function of composition.
Figure 5.34  The cation order parameter of $Y_2(Zr_xTi_{1-x})_2O_7$, as a function of composition.
[400] peaks. This experiment is compromised at high Zr content in \( Y_2(Zr_{x}Ti_{1-x})_2O_7 \), because the scattering factors of Zr\(^{4+}\) and Y\(^{3+}\) are almost identical. Therefore, for \( Y_2(Zr_{0.8}Ti_{0.2})_2O_7 \) and \( Y_2Zr_2O_7 \), where no [331] peak was detected, we can only determine that the maximum order parameter was below the detection limit. The detection limit, in each case, corresponds to a \( \delta_c \) value of 0.20. The trend in \( \delta_c \) is consistent with our hypothesis that the order parameter is a function of \( R_a/R_s \).

5.2.2 ELECTRICAL CONDUCTIVITY

The electrical data on the \( Y_2(Zr_{x}Ti_{1-x})_2O_7 \) system are much less complete than for the \( Gd_2(Zr_{x}Ti_{1-x})_2O_7 \) system. As a result, it was not possible to determine most of the defect chemical parameters.

There was no attempt to fit the data to our defect model using equation [3.9] since the PO\(_2\) dependence of the conductivity was checked only on a few compositions. Therefore, we cannot always be certain about distinguishing between ionic and electronic conduction and simply report total conductivity. It is certain, however, that \( Y_2(Zr_{0.4}Ti_{0.6})_2O_7 \) is an electrolytic conductor in oxidizing atmospheres based on its PO\(_2\)-independent conductivity.

The trend in total conductivity in \( Y_2(Zr_{x}Ti_{1-x})_2O_7 \) is similar to that found for ionic conduction in \( Gd_2(Zr_{x}Ti_{1-x})_2O_7 \). There is a substantial increase in log \( \sigma \) with Zr content as shown in Figure 5.35.
Figure 5.35  The total conductivity of $Y_2(Zr_xTi_{1-x})_2O_7$, as a function of temperature and composition.
The similarity between the Gd₂(ZrₓTi[subscript 1−ₓ])₂O₇ and Y₂(ZrₓTi[subscript 1−ₓ])₂O₇ systems becomes further evident from an examination of the activation energy data in Figure 5.36. The activation energy is high for low Zr contents (0 ≤ x ≤ 0.2) but levels off to about 1.15 eV for compositions with intermediate Zr concentrations (0.3 ≤ x ≤ 0.6). This composition independent activation energy is reminiscent of the Gd₂(ZrₓTi[subscript 1−ₓ])₂O₇ system. At very high Zr contents, (0.8 ≤ x ≤ 1.0), the activation energy again increases slightly probably due to the loss of low energy transport pathways associated with the increase in cation disorder as also seen in Gd₂Zr₂O₇. Note that the activation energy at all compositions is substantially higher for Y₂(ZrₓTi[subscript 1−ₓ])₂O₇ than for Gd₂(ZrₓTi[subscript 1−ₓ])₂O₇.

The pre-exponential constant again shows similar behavior to the Gd₂(ZrₓTi[subscript 1−ₓ])₂O₇ system. See Figure 5.37. If we ignore the data for low Zr content (they probably represent primarily electronic conduction) then we see the same trend of increasing pre-exponential constant with Zr content. However, analysis of these data is complicated by uncertainty over their theoretical interpretation. Do they represent an associated or unassociated state? Is the conductivity ionic or electronic? In any case, the magnitude of the pre-exponential constant is much larger in Y₂(ZrₓTi[subscript 1−ₓ])₂O₇ than in Gd₂(ZrₓTi[subscript 1−ₓ])₂O₇.
Figure 5.36 The activation energy for total conduction as a function of composition for the $Y_2(Zr_xTi_{1-x})_2O_7$ system.
$Y_2(Zr_xTi_{1-x})_2O_7$

![Graph showing the relationship between $\log \sigma_0$ (S·cm$^{-1}$·K) and $x$ (Zr fraction) for the $Y_2(Zr_xTi_{1-x})_2O_7$ system.]

Figure 5.37  The pre-exponential constant for total conduction as a function of composition for the $Y_2(Zr_xTi_{1-x})_2O_7$ system.
6 DISCUSSION

6.1 Order Parameters

6.1.1 CATION ORDER PARAMETERS

The cation order parameter has been calculated as a function of composition throughout both the Gd\(_2\)(Zr\(_x\)Ti\(_{1-x}\))\(_2\)O\(_7\) and Y\(_2\)(Zr\(_x\)Ti\(_{1-x}\))\(_2\)O\(_7\) solid solutions. In general, \(\xi_c\) decreases as Zr replaces Ti in either solid solution. The Y\(_2\)(Zr\(_x\)Ti\(_{1-x}\))\(_2\)O\(_7\) solid solution has a lower \(\xi_c\) than Gd\(_2\)(Zr\(_x\)Ti\(_{1-x}\))\(_2\)O\(_7\) for the same composition. In this section, we consider the hypothesis that \(\xi_c\) is primarily a function of \(R_a/R_s\) and its implications for achieving optimal ionic conductivity in pyrochlores. First, however, we focus upon the potential problems with the \(\xi_c\) calculation.

The computer model that calculates \(\xi_c\) from the relative peak areas of the \{331\} and \{400\} peaks of an x-ray powder diffraction pattern seems to be accurate. It correctly generates \(\xi_c\) values very close to one for the titanate end members of each solid solution. However, in order to develop confidence in the \(\xi_c\) calculation, it would be useful to compare its results to data from neutron diffraction or infrared spectroscopy experiments. Unfortunately, neutron diffraction data do not yet exist for either solid solution and IR spectroscopy is only qualitative for \(\xi_c\) measurements.
Nevertheless, we can say that the available data, as shown in Figures 2.5 and 2.13, are at least consistent with our calculations. Clearly, neutron diffraction data would be very important for confirmation of our measurements of both $\xi_c$ and $\xi_A$.

If $R_n/R_s$ is the critical parameter for predicting $\xi_c$ then a plot of $\xi_c$ as a function of $R_n/R_s$ should form a single curve for both $Y_2(Zr_{x}Ti_{1-x})_2O_7$ and $Gd_2(Zr_{x}Ti_{1-x})_2O_7$. Such a plot has been made and is shown in Figure 6.1. The two solid solutions have almost the same $\xi_c$ vs. $R_n/R_s$ relationship providing strong evidence for the hypothesis.

It is known[19,23,31] that cation order in pyrochlore affects the anion conductivity by producing pathways through the crystal structure that facilitate anion motion. In an almost perfectly ordered pyrochlore, oxygen vacancies can move through a continuous set of 48f sites. The barrier between adjacent 48f sites consists of a triangular set of cations with either two A and one B cation or one A and two B cations. The effect of low $\xi_c$ on the anion mobility can be inferred from the relatively high activation energy for ionic conduction in partially disordered $Gd_2Zr_2O_7$, compared to the better ordered $Gd_2(Zr_{x}Ti_{1-x})_2O_7$, compounds with less Zr. This effect is also evident in the $Y_2(Zr_{x}Ti_{1-x})_2O_7$ system at high Zr content where the activation energy again increases as the cation order parameter decreases. These results along with the electrical conductivity data for $(Gd_{0.99}Ca_{0.01})_2Ti_2O_7$ suggest that the ideal cation order parameter for minimum
Figure 6.1  The cation order parameter for \( \text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7 \) and \( \text{Y}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7 \), as a function of the cation radius ratio \( (R_A/R_B) \).
activation energy and maximum anion mobility may be very close to one. This suggestion is compatible with earlier work by de Vries[28], Steele[24] and Faktor[21].

6.1.2 ANION ORDER PARAMETERS

The anion order parameter was calculated as a function of composition in Gd₂(ZrₓTi₁₋ₓ)₂O₅ from the pre-exponential constant for ionic conduction. The chain of reasoning leading to this calculation is described below.

The ionic conductivity shows a large increase in magnitude as a function of Zr content for x ≥ 0.4 in Gd₂(ZrₓTi₁₋ₓ)₂O₅. The data in Figure 5.14 show that the pre-exponential constant also increases substantially as the Zr content goes from 40% to 100%. At the same time, the activation energy for ionic conduction is almost independent of composition (E* = 0.80±0.05 eV) in this composition range. Thus the increase in ionic conductivity is primarily due to an increase in the pre-exponential constant which is a measure of the trend in carrier concentration.

The identity of the charge carriers can be confidently assigned to oxygen vacancies on the basis of theoretical considerations[19] and the aliovalent doping experiments described in Section 5.1.3.1. The presence of a substantial oxygen vacancy concentration due to intrinsic disorder in Gd₂(ZrₓTi₁₋ₓ)₂O₅ is confirmed by our quantitative measurement of the anion Frenkel constant in Gd₂(Zr₀.₃Ti₀.₇)₂O₅, (Kᵣ ≈ 10²⁸ cm⁻⁶ at 1000 °C) also described in Section 5.1.3.1.
Further confirmation comes from earlier conductivity\textsuperscript{[16,17,46-48]}, spectroscopic\textsuperscript{[1,15,20]} and neutron diffraction data\textsuperscript{[10]} obtained by other workers on similar pyrochlore systems and described in Sections 2.1.3.2, 2.3.1, 2.3.2 and 2.4.1.

Knowing that the charge carriers are vacancies and that the high temperature ionic conductivity represents essentially unassociated defect motion, the anion order parameter can be determined from the pre-exponential constant data for the Gd\textsubscript{x}(Zr\textsubscript{x}Ti\textsubscript{1-x})\textsubscript{2}O\textsubscript{2} system according to the method described in Section 3.1.4. Essentially, this consists of calculating the vacancy concentration from an atomistic model for the ionic conductivity using equation [3.22] and then using that value to find the order parameter from equation [2.6]. The values of the constants in equation [3.22] are given in section 3.1.4.

\[
\sigma_o = \frac{4\alpha e^2 a^2 vN_o[V_o\cdot\cdot\cdot]\exp(S_o/k)}{k} \tag{3.22}
\]

The results of the calculation using equation [3.22] are shown in Figures 6.2 and 6.3. It is important to emphasize that there is considerable uncertainty in the absolute value of the oxygen vacancy concentrations. Their relative values are probably valid but the absolute values depend upon an accurate value of the migration entropy. The order parameter is influenced to a lesser degree by this uncertainty especially when it is close to one.
Figure 6.2 The oxygen vacancy concentration as a function of composition in the Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ system.
Figure 6.3  The anion order parameter as a function of composition in the Gd₂(ZrₓTi₁₋ₓ)₂O₇ system.
The migration entropy can be found if the vacancy concentration in Gd₂(Zr₀.₅Ti₀.₅)₂O₃ is calculated from \( K_r \) and substituted into equation [3.22]. The fractional vacancy concentration in Gd₂(Zr₀.₅Ti₀.₅)₂O₃ is given by:

\[
[V_0^{\cdots}] = (K_r^{1/2})/N_o
\]

[6.1]

When this value (2.4 x 10⁻⁴) is substituted into equation [3.22] the quantity \( \exp(S_v/k) \) is found to be about seven.

There is rough agreement between the anion order parameter calculation and the quasi-Frenkel constant calculation. As shown above, these two entirely independent calculations differ by a factor of seven; when the uncertainties in the anion order parameter calculation are considered this level of agreement is acceptable.

It is apparent from Figures 6.3 and 5.3 that \( \xi_a \) and \( \xi_c \) have a similar composition dependence. This correspondence is gratifying since it is in accord with our predictions and the assumptions by Faktor[21] and Van Dijk et al[17] that the cation and anion disorder are linked. The similarity between \( \xi_a \) and \( \xi_c \) may be more than just coincidence- it may represent a cause and effect relationship. For example, it is possible that anion interstitials form only at sites where there is pre-existing cation disorder, i.e. an 8b anion site surrounded by one A cation and three B cations rather than the usual four B cations. This hypothesis would explain why the activation energy for anion quasi-Frenkel defect formation is so low; the cation sublattice is "frozen-in" by its low mobility and anion
interstitials form by moving into favorable 8b sites. As yet, there is no proof for this notion.

The anion order parameter data involve several key assumptions and can only be considered semi-quantitative, as mentioned previously. The assumption that vacancies occur with equal frequency on the 48f and 8a sites but are only mobile on the 48f sites is open to challenge, for example. Fortunately, this assumption has only a small effect on the final order parameter result. However, the value of the attempt frequency is also not entirely certain and will significantly affect the calculation. Most importantly, as discussed earlier, the migration entropy is unknown. Therefore, the δₐ data are meant primarily as a measure of the trend in anion disorder rather than as precise measurements. Neutron diffraction experiments have the potential to provide hard evidence for the value of the anion order parameter, at least in \( Y_{2(\text{Zr}_{x}\text{Ti}_{1-x})_2\text{O}_7} \).

The trends in δₐ and the ionic conductivity of the nominally pure materials demonstrate that \( \text{Gd}_2(\text{Zr}_{x}\text{Ti}_{1-x})_2\text{O}_7 \) is an extrinsic conductor at low Zr content but an intrinsic conductor at high Zr content. This fact is very well established since it is independently confirmed by both the quasi-Frenkel constant calculation on \( \text{Gd}_2(\text{Zr}_{0.3}\text{Ti}_{0.7})_2\text{O}_7 \) and the doping experiments on the two end members: \( \text{Gd}_2\text{Ti}_2\text{O}_7 \) and \( \text{Gd}_2\text{Zr}_2\text{O}_7 \). Furthermore, \( \text{Gd}_2(\text{Zr}_{x}\text{Ti}_{1-x})_2\text{O}_7 \), with \( x \geq 0.4 \) meets the criteria for an intrinsic fast ion conductor. It has a
large intrinsic concentration of mobile charge carriers and a relatively low activation energy of conduction.

The cause of the low ionic conductivity in the low Zr content compositions also becomes clear from this analysis; it is due to their low concentration of oxygen vacancies. Confirmation of this idea comes from the high ionic conductivity of the \((\text{Gd}_{0.99}\text{Ca}_{0.01})_2\text{Ti}_2\text{O}_{7.5}\) sample where the oxygen vacancy concentration was substantially increased by acceptor doping.

The anion order parameter data provide a possible explanation for the fact that \(\text{Gd}_2(\text{Zr}_{0.8}\text{Ti}_{0.2})_2\text{O}_7\), is more conductive at 600 °C than \(\text{Gd}_2\text{Zr}_2\text{O}_7\), as shown in Figure 5.12. The disorder in \(\text{Gd}_2\text{Zr}_2\text{O}_7\), may be so large that defect association has begun to reduce its ionic conductivity while \(\text{Gd}_2(\text{Zr}_{0.8}\text{Ti}_{0.2})_2\text{O}_7\) is closer to the optimum degree of disorder. This hypothesis is consistent with the data by van Dijk et al[17] described in Section 2.3.2 wherein they found that there is an optimum degree of disorder to maximize the ionic conductivity in pyrochlore compounds. This suggestion, that \(\text{Gd}_2\text{Zr}_2\text{O}_7\), exceeds the optimum degree of disorder, is also supported by the increase in activation energy for \(\text{Gd}_2\text{Zr}_2\text{O}_7\), relative to \(\text{Gd}_2(\text{Zr}_{0.8}\text{Ti}_{0.2})_2\text{O}_7\), shown in Figure 5.13.

The argument for an optimum degree of disorder also sheds light on the relative ionic conductivities of the \(\text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7\), and \(\text{Y}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7\), solid solutions. Comparison of Figures 5.12 and 5.35 show that, at the same Zr content, the \(\text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7\), system is more conductive. It
also has lower activation energies and lower pre-exponential constants. These facts all point towards increased disorder in Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ relative to Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$. The electrical characteristics of Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ with x ≥ 0.6 are consistent with the typical properties of fluorites[38,17] and, indeed, Figure 5.34 shows a very low cation order parameter for those compositions. Therefore, the leveling off of the conductivity in Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ as x approaches one is probably due to the opposing effects of increasing oxygen vacancy concentration and decreasing oxygen vacancy mobility due to either defect association or the loss of optimal transport pathways due to the cation disorder. Note that the pre-exponential constants for Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ are too high to fit the model described by equation (3.22), they undoubtedly represent defect association[49]. The difference in conductivity between Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ and Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ at high Zr content (a factor of two or three) may be an indicator of the effect of excessive disorder on the conductivity.

6.2 Defect chemical parameters

In this section, we discuss the calculation of several important defect chemical parameters including the Frenkel constant, oxygen vacancy mobility, enthalpy of reduction and several others. It is possible to obtain additional parameters including the electron mobility, electron concentration, their temperature dependencies and the mass-action equilibrium constants for reduction and
electron-hole pair generation, however, we have decided not to present these data since they would require making a correct analysis of the scant data obtained under reducing conditions and at high temperatures that exhibited a slope approaching $-1/6$ in $\log \sigma - \log PO_2$ space. Indeed, it is unclear whether the $\log \sigma - \log PO_2$ data can be correctly interpreted as having a $-1/6$ slope at all since linear regression shows that the slope decreases systematically with increasing temperature and reaches values of less than $-1/7$ at high temperature. Therefore, this thesis will focus upon only those parameters whose calculation is unambiguous and well supported by the data.

6.2.1 FRENKEL CONSTANT AND VACANCY MOBILITY

We have made the first determination of the anion quasi-Frenkel constant in a pyrochlore compound using electrical measurements on doped samples. In this section, we first consider sources of error in the calculation and then address the implications of the magnitude of the Frenkel product. The potential sources of error include erroneous assumptions in either the model for deriving the ionic conductivity or the model that relates the conductivity and doping concentration.

The conductivity of the nominally pure $Gd_2(Zr_{0.7}Ti_{0.3})_2O_7$ is consistent with either of two different defect chemical models: oxygen vacancies compensated by unintentional acceptor impurities or oxygen vacancies compensated by oxygen
interstitials. The use of relatively pure starting materials, leading to a total impurity content of about two hundred parts per million, and the crystal chemistry of the pyrochlore structure wherein anion disorder is already known to occur to a substantial degree suggests that intrinsic anion Frenkel defects should be predominant in undoped \( \text{Gd}_2(\text{Zr}_{0.3}\text{Ti}_{0.7})_2\text{O}_7 \).

The model leading to equation [3.17] also rests on several assumptions. The assumption that oxygen vacancies are by far the predominant mobile ionic species can be justified by the similarity between fluorite and pyrochlore structures and the observation that acceptors increase while donors decrease the ionic conductivity as shown in Figure 5.25. The assumption that the conductivity is in an essentially dissociated regime at temperatures above 800 °C is based on the observation that, at lower temperatures, the activation energy for ionic conduction of the acceptor doped materials increases from ~0.8 eV to 1.0-1.2 eV reflecting the onset of defect association as the temperature is reduced. Undoped \( \text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7 \) materials with \( x \geq 0.4 \) show the same trend, i.e. constant 0.8 eV activation energy at high temperatures increasing to 1.0-1.2 eV below 600 °C presumably due to association. Finally, the use of relatively low dopant concentrations and the correspondence between the theoretical model and the experimental data shown in Figure 5.26 supports the assumption of a dopant-independent ion mobility.

The data in Figure 5.26 show significant scatter probably due to difficulty controlling the cation mole ratio in ternary
compounds such as pyrochlores. This problem is exacerbated in the Gd₂(ZrₓTi₁₋ₓ)₂O₇ solid solution by the presence of two cations on the B site and the fact, as shown in Figure 5.12, that the ionic conductivity is very sensitive to Zr content for compositions near Gd₂(Zr₀.₃Ti₀.₇)₂O₇.

The calculated oxygen vacancy mobility is similar to the value of \( \mu_v = 0.42 \exp(-0.99eV/kT) \) cm²·V⁻¹·s⁻¹ calculated by Stratton et al[50] for 12% yttria stabilized ZrO₂ but shows a lower activation energy. At 1000 °C, Gd₂(Zr₀.₃Ti₀.₇)₂O₇ is calculated to have an oxygen vacancy mobility of 1.1x10⁻⁴ cm²·V⁻¹·s⁻¹ while the value for 12% Y₂O₃ stabilized ZrO₂ is 5.0x10⁻⁵ cm²·V⁻¹·s⁻¹. It is surprising that the mobility is only slightly higher in pyrochlore relative to defect fluorite in light of the superior pathway for oxygen vacancy migration believed to exist in ordered pyrochlores and the fact that Gd₂(Zr₀.₃Ti₀.₇)₂O₇ contains far fewer aliovalent impurities that can serve as sites for vacancy association. We conclude that cation order has only a small effect upon the anion mobility or, perhaps, is being compensated by some other factor.

It is instructive to calculate the oxygen vacancy mobility for Gd₂Ti₂O₇ using the data for (Gd₀.₉₉Ca₀.₀₁)₂Ti₂O₇₋₈ and assuming that the oxygen vacancy concentration is fixed by the Ca doping. In this case, the oxygen vacancy mobility is found to be 1.2 x 10⁻⁴ cm²/V·sec at 1000 °C in remarkably good agreement with the value for Gd₂(Zr₀.₃Ti₀.₇)₂O₇. This accord between the mobility values for Gd₂Ti₂O₇ and Gd₂(Zr₀.₃Ti₀.₇)₂O₇, in combination with the constant
activation energy found for compositions from Gd$_2$(Zr$_{0.4}$Ti$_{0.6}$)$_2$O$_7$ to Gd$_2$Zr$_2$O$_7$ is suggestive of a composition independent mobility across the entire Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ solid solution. However, one must consider this conclusion with great caution since the activation energy for conduction in (Gd$_{0.95}$Ca$_{0.05}$)$_2$Ti$_2$O$_7$ of 0.52 eV is inconsistent with the value of roughly 0.80 eV for the rest of the solid solution.

The calculated Frenkel constant is remarkably high for an oxide compound and has a very small temperature dependence of only 0.24 eV. Consider, for example, that the Frenkel constant for CeO$_2$ as reported by Tuller[51,52] is only about 6 x 10$^{-4}$ cm$^{-6}$ at 1000 °C and has an activation energy of about 4 eV. However, the unique characteristic of the pyrochlore structure whereby the 8b oxygen sites are considered as interstitial sites in pyrochlore but normally occupied sites in the fluorite substructure explains the anomalous Frenkel constant in Gd$_2$(Zr$_{0.3}$Ti$_{0.7}$)$_2$O$_7$. In pyrochlores, Frenkel disorder can be considered simply as partial reversion of the superstructure ordering back towards fluorite. Therefore, due to its high value, low temperature dependence and unusual structural origin we will refer to the anion disorder in pyrochlore as quasi-Frenkel disorder.

6.2.2 ENTHALPY OF REDUCTION

Measurements of the enthalpy of reduction and the thermal bandgap were made for the Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ solid solution. It was found that the reduction energy, E$_r$, increases with Zr
content in Gd₂(ZrₓTi₁₋ₓ)₂O₅, but the data are too scattered to permit any more specific conclusions. In this section, we analyze the sources of error in the measurements, compare the results to data from other material systems and consider the implications.

In the case of the reduction energy calculation the statistical uncertainty in the measurement is much smaller than the differences between different compositions but the actual accuracy of the measurement is unknown. The apparent scatter in the data is probably due to systematic errors in the determination of the electronic component of the conductivity for conditions of temperature, atmosphere and composition where the electronic transference number is small. Thus, the best data are for conditions with substantial electronic conductivity such as Gd₂Ti₂O₅ or Gd₂(Zr₀.₃Ti₀.₆₉Ta₀.₀₁)₂O₇.₈.

The Eᵣ calculation is based on the assumption that the activation energy for electronic conductivity is due essentially entirely to the temperature dependence of the concentration of electrons rather then their mobility. This assumption is confirmed by the measurement of the electronic mobility in Y₂Ti₂O₅, at low temperature by Goldschmidt et al[37]. They derived an activation energy of 0.13 to 0.18 eV for small polaron motion. This value is almost negligible with respect to the uncertainties in the measurement of the total electronic conductivity activation energy.
When we focus upon the more reliable data in Table 5.2, as described above, it becomes evident that $E_r$ increases substantially with Zr content. This conclusion is reasonable since titanates are generally easier to reduce than zirconates. The drop in $E_r$ for Gd$_2$(Zr$_{0.4}$Ti$_{0.6}$)$_2$O$_7$ is likely an error since the electronic conductivity was only a small proportion of the total conductivity in this case.

The enthalpy of reduction calculated in this study for Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ can be compared to data by Choi et al.[53] for $E_r$ in (Ba$_{0.05}$Sr$_{0.95}$)TiO$_3$. They find a value of about 500 kJ/mole (5.2 eV). This number is in reasonable accord with our value of 4.8 eV for Gd$_2$Ti$_2$O$_7$. Although, Gd$_2$Ti$_2$O$_7$ and SrTiO$_3$ have different structures, it is reasonable to compare their $E_r$ values since, in both cases, reduction forms electrons in the conduction band which is formed by titanium. Tuller et al.[51] report an $E_r$ of 4.96 to 5.2 eV in UO$_2$ doped CeO$_2$. Again, their results are similar to ours but in their case the conduction band is formed by cerium ions.

6.2.3 THERMAL AND OPTICAL BANDGAP

The calculations of the thermal bandgap require information on both the electron and hole conductivity which is somewhat difficult to obtain in Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ compounds due to their high ionic conductivity. Nevertheless, we have estimates of the bandgap for compositions with 30-50% Zr in Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$. These values can be compared to measurements in other titanates and zirconates.
The thermal bandgap as determined by electrical conductivity measurements can also be compared to the optical bandgap measured separately for Gd₂Ti₂O₇. However, we do not expect the two quantities to be identical since the thermal bandgap, in this case, is the energy for phonon stimulated electron-hole pair formation extrapolated to 0 K but the optical bandgap represents photon stimulated electron-hole pair formation at room temperature. However, after correction for the temperature difference, they should be fairly close. Goldschmidt[54] found the temperature dependence of the optical bandgap of Y₂Ti₂O₇ to be about -11 x 10⁻⁴ eV/K. In the absence of any other data, we will use this value to make the temperature correction between absolute zero and room temperature. Therefore, we expect the optical bandgap in Gd₂Ti₂O₇, at absolute zero to be about 4.1 eV in good agreement with our thermal bandgap data.

The bandgap is somewhat higher in titanate pyrochlores (4.1 eV) than in titanate perovskites[53] such as SrTiO₃ (3.2 eV). There are two possible explanations for this, both are based on the differences in crystal structure. First we note that the oxygen coordination of titanium is different in the two structures; in SrTiO₃, the Ti⁺⁺ ion is surrounded by a perfect octahedron of oxygen ions but in Gd₂Ti₂O₇, the octahedron is distorted. The second point is that the Ti-Ti distance is greater in the pyrochlore (about 4.4 Å versus about 3.9 Å in SrTiO₃. Both of these differences may lead to a difference in bandgap between the two structures.
6.2.4 ASSOCIATION ENERGY

The true association energy cannot be determined without an atomistic model for the association reaction. Therefore, we report only the difference between the low and high temperature activation energies. We have established on the basis of the doping experiments on Gd₂(Zr₀.₇Ti₀.₃)₂O₅ and Gd₂Zr₂O₇ that the high temperature activation energy for Gd₂(ZrₓTi₁₋ₓ)₂O₅ with x ≥ 0.3 is due almost exclusively to the temperature dependence of the "free" oxygen vacancy mobility. Further, if we assume that the activation energy for "free" vacancy motion is unchanged even at temperatures below 600 °C then the low temperature activation energy must be due to the sum of the temperature dependencies of the "free" vacancy mobility and "free" vacancy concentration. Therefore, the difference in activation energies calculated from high and low temperature experiments represents the temperature dependence of the concentration of "free" vacancies at low temperature.

Whether the vacancies become bound with cation anti-site defects, other oxygen vacancies or acceptor impurities is not known. However, it is known that the binding energy increases rapidly and monotonically with Zr content and thus cation and anion disorder. It is also known that the association energy is independent of the dopant content for Gd₂Zr₂O₇, but increases with acceptor dopant content for Gd₂(Zr₀.₇Ti₀.₃)₂O₅. There is evidence to support all three association mechanisms, therefore, more information is required before deciding upon their relative importance.
Can we better understand defect association in pyrochlores by making analogies with the better studied fluorite compounds? For example, in stabilized zirconia there is a clear increase in activation energy with acceptor dopant concentration as shown previously in Figure 2.4. This increase is generally interpreted as an association energy but the mechanism of association is controversial. Kilner[3,4] favors association between the dopant and oxygen vacancies primarily due to strain effects. He gives persuasive evidence for his viewpoint on the basis of comparison of the activation energies as a function of the dopant and host ionic radii. Yet, the literature on fluorites is of limited applicability to pyrochlore compounds due to the lower defect concentrations and lack of aliovalent dopants in the latter. Pyrochlore compounds, such as Gd₂Zr₂O₇, are intrinsic ionic conductors as opposed to fluorite structure oxides compounds which always require aliovalent doping to achieve reasonable ionic conductivity. We have to conclude that there is not enough available information to understand defect association in oxide pyrochlores. This unhappy situation may be improved by spectroscopic experiments on single crystals designed to deduce the symmetry of the low temperature associates.

6.2.5 DIELECTRIC CONSTANT

The permittivity measurements on Gd₂(ZrₓTi₁₋ₓ)₂O₇, in general, show no dependence on composition or PO₂. The data on Gd₂(Zr₀·₅₀Ti₀·₅₀)₂O₇, which form the single clear exception
to this assertion, are probably inaccurate. Furthermore, the apparent temperature dependence of \( \varepsilon' \) is an artifact as described below. The dielectric constant is calculated at the peak of the bulk semicircle but the frequency at the peak is a very strong function of temperature. Thus, even a very weak frequency dependence of the dielectric constant will appear as a temperature dependence. It is impossible to properly measure the true bulk dielectric constant as a function of temperature at fixed frequency due to the effect of other capacitive elements such as the grain boundaries at frequencies away from the peak in imaginary impedance. Therefore we conclude that, within the margin of error in our measurements, the dielectric constant is independent of temperature, \( \text{PO}_x \), and composition.

Our dielectric constant data agree well with the value of van Dijk et al[19] for \( \text{Gd}_2\text{Zr}_2\text{O}_7 \), of 60.

### 6.2.6 IONIC TRANSFERENCE NUMBER

Achieving a high ionic transference number in \( \text{Gd}_2(\text{Zr}_x\text{Ti}_{1-x})_2\text{O}_7 \), means maximizing the ionic conductivity (\( \sigma_i \)) while minimizing the electronic conductivities (\( \sigma_e \) and \( \sigma_h \)):

\[
t_i = \frac{\sigma_i}{\sigma_i + \sigma_e + \sigma_h}
\]

These goals are best accomplished by either acceptor doping or using a high Zr content. Either of these solutions can produce a \( t_i \) very close to one over the entire range of
experimentally accessible temperature and PO\textsubscript{2} (T ≤ 1400 °C and 10\textsuperscript{-20} ≤ PO\textsubscript{2} ≤ 10\textsuperscript{0} atm). Alternatively, it is possible to achieve a high t\textsubscript{i} simply by using low temperatures. For example, Gd\textsubscript{2}(Zr\textsubscript{0.3}Ti\textsubscript{0.7})\textsubscript{2}O\textsubscript{7} has a high t\textsubscript{i} at low temperature but a decreasing t\textsubscript{i} with increasing temperature as shown in Figure 6.4. Note that t\textsubscript{i} was calculated from equation [6.1] and the fitting parameters (A, B and C) from equation [3.9]. In Figure 6.4, it can be seen that t\textsubscript{i} is almost independent of temperature at high PO\textsubscript{2} because the ionic and hole conductivities have almost the same activation energies.
Figure 6.4 The ionic transference number as a function of oxygen partial pressure and temperature for $\text{Gd}_2(Zr_{0.7}Ti_{0.3})_2\text{O}_7$. 
Extensive electrical measurements were made on the Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$, pyrochlore solid solution as a function of temperature, oxygen partial pressure, composition and dopant content. The results were fit to a simple defect chemical model based on intrinsic anion Frenkel defects, mobile oxygen vacancies and mixed conduction due to electrons and holes. The model was used to obtain the individual ionic, electronic and hole conductivities as a function of the various experimental parameters. This information was then used to derive several quantities of interest including the energies of ionic motion and association, the anion order parameter, quasi-Frenkel constant, oxygen vacancy mobility, thermal bandgap and energy of reduction.

X-ray powder diffraction patterns were obtained on the Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$, solid solution and used to determine the cation order parameter as a function of Zr content. X-ray diffraction patterns for the Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$, system confirmed the cation order parameter results obtained for Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$.

The combined results of the electrical and x-ray measurements were used to form several major generalizations about the relationships between ionic disorder and conductivity in the pyrochlore structure.
(1) The $\text{Gd}_2(\text{Zr},\text{Ti}_{1-x})_2\text{O}$, system varies from an extrinsic ionic conductor at low Zr content where acceptor doping is required to produce substantial ionic conductivity to, at high Zr content, an intrinsic oxygen electrolyte whose conductivity is unaffected by acceptor doping.

(2) Disorder on the cation sublattice is relatively less important to the conductivity than anion disorder in that the former has only a small effect on the vacancy mobility but the latter can change the vacancy concentration and thus ionic conductivity by several orders of magnitude.

(3) To a first approximation, maximizing the ionic conductivity in the lanthanide titanate zirconate pyrochlore system is simply a question of maximizing the mobile oxygen vacancy concentration. This can be accomplished equally well either by extrinsically doping a relatively well ordered material or using a nominally pure but intrinsically disordered compound. A closer look shows that excessive disorder, such as in $\text{Gd}_2\text{Zr}_2\text{O}_7$, can reduce the conductivity slightly.

(4) The cation disorder is a monotonic function of the cation radius ratio. It may also be a weak function of the absolute cation radii.
Suggestions for further research include:

(1) Fabrication and electrical characterization of Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ with 0 \leq x \leq 0.4 and either acceptor or donor doping in order to extend the measurements of $K_T$ and $\mu_T$ on Gd$_2$(Zr$_{0.5}$Ti$_{0.5}$)$_2$O$_7$ to other compositions. This project would permit very firm conclusions about the trends in ionic disorder and oxygen vacancy mobility in the Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ system. It would also provide confirmation of the intriguing results with (Gd$_{0.95}$Ca$_{0.05}$)$_2$Ti$_2$O$_{7-\delta}$.

(2) A systematic structural study of the Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ and Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ systems using infrared and Raman spectroscopy and x-ray diffraction. This work could improve our ability to predict the pyrochlore compositions that will have the optimal disorder and ionic conductivity.

(3) The structural study in (2) can be supplemented with neutron diffraction data on the Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$ system. The quantitative data on atomic positions available from neutron diffraction suggest the possibility of comparison of experimental data with a theoretical analysis of the degree of disorder based on molecular dynamics or other computer calculations.
(4) A molecular dynamics calculation of the energy of migration as a function of cation radius ratio would be useful as a comparison to the experimental values.

(5) A study of the kinetics of cation ordering and disordering in Gd$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$, or Y$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$, with $x$ near one could be undertaken using in situ electrical measurements at 1200-1500 °C. This study could be supplemented with x-ray or neutron diffraction experiments on either quenched specimens or at high temperature.

(6) Calculation of the chemical diffusion coefficient obtained by electrical conductivity measurements on single crystals as a function of time after a step change in PO$_2$ might allow calculation of the oxygen diffusivity in mixed conductors such as Gd$_2$Ti$_2$O$_7$, where the ionic conductivity cannot be determined directly due to interference from the electronic conductivity.

(7) A test of the hypothesis that ionic disorder is exclusively a function of the cation radius ratio can be made by fabricating a series of quaternary pyrochlore compounds with constant radius ratio. A suitable series of compositions might be (Nd$_x$Gd$_{1-y}$)$_2$(Zr$_x$Ti$_{1-x}$)$_2$O$_7$, where $x$ and $y$ are chosen to keep the ratio of the weighted average radii constant. This technique can also be applied to develop solid solutions with constant lattice constants.

(8) The Pechini[41] powder preparation technique generates powder with a substantial impurity content because all the non-volatile impurities in the organic precursors
(primarily in the citric acid) are concentrated into the oxide powder. It would be useful to make materials with highly purified citric acid or via an entirely different powder fabrication route in order to test the effect of higher purity materials on the conclusions of this research.

(9) All pyrochlore compounds violate Pauling's rule for local electroneutrality[55]. Calculations of the local electrostatic environment at each occupied site in the pyrochlore site by a more sophisticated technique might provide insight into this violation, or, possibly help to explain the order-disorder phenomenon seen in pyrochlores.
APPENDIX A: POWDER PREPARATION

Gadolinium citrate

Dissolve 100 grams of hydrous Gd(NO$_3$)$_3$, in 300 ml of deionized water. Precipitate Gd(OH)$_3$ by adding NH$_4$OH until the pH is over 10. Filter the Gd(OH)$_3$, several times with deionized water to remove the ammonium nitrate and then with isopropanol to remove the water. Dissolve the Gd(OH)$_3$, in a mixture of 120 grams citric acid and 175 ml ethylene glycol. Heat to about 110 °C for several hours to ensure complete dissolution. Filter and then assay the solution. The raw materials came from the following sources:

- Gd(NO$_3$)$_3$, Research Chemicals
- Citric Acid, Fisher Scientific
- Ethylene Glycol, Mallinckrodt or Fisher
- Isopropanol, MCB Reagents

Titanium citrate

Dissolve 225 ml of titanium isopropoxide in 500 ml of ethylene glycol and then add 400 grams of citric acid while heating the mixture. Heat to about 110 °C for several hours to ensure complete dissolution. Filter and then assay the solution.
Titanium isopropoxide Du Pont

**Zirconium citrate**

Dissolve 40 grams of Zr-n-propoxide in 200 ml of isopropanol at room temperature. Wait five minutes. Add 160 grams of citric acid. Set hotplate to maximum power and heat mixture to 50 °C. Add 200 ml of ethylene glycol and heat to 100 °C as rapidly as possible while stirring continuously. Set temperature to about 110 °C for several hours to ensure complete dissolution. Filter and then assay the solution.

Zirconium-n-propoxide ALFA
Isopropanol MCB Reagents

**Dopants**

Calculate and weigh the correct amount of CaCO₃. Add it to the solution of metal citrates.

CaCO₃ Fisher Scientific

**Solution assay**

After the metal citrate solution is made it must be assayed to determine the exact concentration of the metal. The procedure is to weigh out a known quantity of solution in a porcelain or alumina container of known weight. The
solution is heated slowly to about 200 °C overnight to polymerize the solution and evaporate excess solvent. Next, the solution is heated to 800 °C overnight in a box furnace in a hood in order to produce the oxide phase. The container and the oxide powder are now weighed and the equivalent weight of metal oxide per unit weight of solution is determined.

Solution weighing

In order to produce a multicomponent oxide at least two citrate solutions (each containing one metallic element) must be mixed. Their correct proportions are calculated and then weighed out on a balance. Typical precision of the A:B ratio in $A_3B_2O$, is about 0.1%.

Solution mixing

The citrate solutions are often viscous and must be mixed for several hours to ensure a homogeneous solution.

Solution polymerization

After homogenization, a small amount of citrate solution is poured into a 150 mm diameter pyrex dish with a 2" stirring bar. About 50 vol% ethylene glycol is added to the dish. The mixture is slowly heated to 100 °C over the period of a day and then heated to about 120 °C over several more days. After this heat treatment the solution is very viscous and most of the ethylene glycol and water have evaporated off.
The polymer is slowly heated to roughly 170 °C over several more days until it is hard and tough and fully polymerized.

**Burning**

The polymer is heated to 250 °C for 2 hours and then 400 °C for 4 hours to completely carbonize the polymer. The result is a friable, gray powder.

**Crushing**

The carbonized material is comminuted into fine powder by placing in a small glass or plastic vial with a teflon coated stirring bar that is being agitated by a magnetic stirrer. After 12 hours the powder is very fine and uniform gray in appearance.

**Calcining**

The powder is spread in thin (1 mm) layers on alumina dishes and placed in a box furnace at 700 °C for two hours to calcine the powder. The furnace starts cold and is only at 700 °C for about one hour.
APPENDIX B: SINGLE CRYSTALS

Plots of log $\sigma$ vs. log $PO_2$ for the single crystals of Gd$_2$Ti$_2$O$_5$ and Y$_2$Ti$_2$O$_5$ are shown in Figures B.1 and B.2.

The results are markedly different from the sintered polycrystalline specimens with the same nominal composition. The differences may be due to poor equilibration of the single crystals during the conductivity measurements or differences in composition arising from the excess titanium and/or the flux used to grow the single crystals.

In the case of the Gd$_2$Ti$_2$O$_5$ crystal, the slope of the log $\sigma$ versus log $PO_2$ curve is close to $-1/6$. There is no obvious model to explain this behavior.
Figure B.1  The log conductivity as a function of log oxygen partial pressure for a single crystal of Gd$_2$Ti$_2$O$_7$. 
Figure B.2  The log conductivity as a function of log oxygen partial pressure for a single crystal of $Y_2Ti_2O_7$. 


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