Atomistic Simulation Studies of Oxygen Ion
Conducting Metal Oxides for Fuel Cell Applications

by

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ABSTRACT

This thesis describes the application of computer simulation techniques to the detailed study of the defect chemistry and ion transport properties of oxygen ion conducting metal oxides. Attention is focused on two materials: stabilised zirconia (ZrO$_2$), a conventional solid electrolyte with important applications within solid oxide fuel cells, and perovskite-structured LaGaO$_3$, a promising new oxygen ion conductor. First, a wide-variety of low-valent metal ions are substituted into zirconia, and the energetics of solution investigated. Favourable dopants (on energetic grounds) have been calculated which include CaO, Y$_2$O$_3$ and Gd$_2$O$_3$, in agreement with observation. Dopant-vacancy clusters are also examined, and the results reveal significant relaxation around dopant ions. These simulations are extended to examining the topical area of Nb/Y co-doping. Oxygen ion diffusion in yttria-stabilised zirconia is studied by application of Molecular Dynamics (MD) techniques; our results support models in which diffusion is mediated by oxygen vacancies, with calculated diffusion coefficients and activation energies in accord with tracer diffusion studies. The results from the first reported computational study of the LaGaO$_3$-based oxygen ion conductor are then presented. We consider a range of cation dopant substitutions with oxygen vacancy compensation. Favourable acceptor-dopants are predicted to be Sr at La and Mg at Ga, in agreement with conductivity studies. The pathway for oxygen vacancy migration is found to be along the GaO$_6$ octahedron edge with a curved trajectory. Hole formation from an oxidation process is calculated to be relatively unfavourable, which is compatible with experimental findings that show predominantly ionic conduction in doped LaGaO$_3$. Furthermore, consideration of water incorporation suggests that proton conduction will not be significant in this material. Finally, shell model MD is used to examine oxygen transport in doped LaGaO$_3$ with varying concentrations of Sr and Mg dopants. Oxygen diffusion coefficients are calculated over a wide temperature range, with useful information on the atomistic mechanism for oxygen ion migration illustrated in the form of trajectory plots.
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# Chapter 1

## Introduction

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Chapter 1: Introduction

1.1 Background

A number of historic events have occurred over the last three decades which have influenced views of industrialised societies concerning the need for energy conservation and lower emissions of pollutants. In the 1970s the oil crisis led to wide-spread fuel shortages and a sharp increase in petroleum prices. It was at this time that analysts began to view oil reserves as a finite, irreplaceable resource. This opinion has been further strengthened by the loss in confidence in the long-term viability of nuclear energy replacing conventional power stations. The last 15 years has seen the steady increase in the general concern with environmental damage, in particular the depletion of the ozone layer and the “greenhouse effect” due to excess CO$_2$ emissions. A major consequence of these events has been new government legislation instructing, for example, automotive manufacturers to design and build more fuel efficient and less polluting vehicles [1,2].

In an attempt to address some of the issues mentioned above, electroceramics have become materials of considerable scientific interest and technological importance. Advances in these materials have led to the development of a range of efficient, “environmentally-friendly” devices for industry and consumers alike. The electrical conductivities of various solid-state materials cover one of the broadest range of any observable physical property, from the essentially infinite conductivity of superconductors to the near zero conductivity of the best insulators. Electroceramics are represented across this entire spectrum; some having electronic conductivities close to that of metals, while others having ionic conductivities equivalent to the most highly conducting aqueous solutions [3].
Fast oxygen ion conductors constitute an important class of electroceramic and are of commercial interest for a number of electrochemical applications, including oxygen sensors, oxygen pumps and solid oxide fuel cells (SOFC) [4-8]. One of the most topical areas of research over the last few years has been in the field of environmentally-friendly SOFCs, in which the electrolyte material is most commonly based on fast oxygen ion conductors [9]. Some of the more common solid electrolytes used in SOFC configurations, and other electrochemical devices, are based on the fluorite-structured oxides such as doped ceria [10,91] and stabilised zirconia [91]. However, these fuel cells operate at high temperatures, typically above 1000°C [9]. It is generally believed that if the operating temperature could be reduced to around 800°C this would be a significant technical advance. The perovskite-structured family of materials have provided some interesting candidates for use as solid electrolytes in possible low-temperature SOFCs as discussed below. Figure 1.1 depicts a comparison of ionic conductivities between some common oxygen ion conductors, which shows that at higher temperatures the fluorite-structured oxides exhibit superior conductivities.

Figure 1.1 - Comparison of the conductivity of various oxygen ion conductors [157]
1.2 Applications of Oxygen Ion Conductors

1.2.1 Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFC) are of great technological and environmental interest because of their efficient conversion of chemical energy into electrical energy and heat, with a very low output of pollutants [11,12]. Another major advantage with SOFCs is the elimination of rotating machinery (a source of frictional loss) and the release from the thermodynamic limitations of the Carnot cycle. Through the use of SOFCs in stationary power stations and electrical vehicles atmospheric pollution could be lowered [13]. Indeed, they have been dubbed by some as "an environmental solution in the making" [14].

A SOFC consists of three main components [9]: an anode, a cathode and a solid electrolyte (Figure 1.2). The interconnect (separator) is also an indispensable component used to connect individual cells and separate the reactant gases, and is usually based on the perovskite \( \text{LaCrO}_3 \) [15]. The oxidation and reduction reactions that occur within an oxygen ion conducting fuel cell are summarised in Figure 1.3. The stability and compatibility as well as performance are important factors when considering the most suitable materials for SOFC components.

The electrolyte is the principal component of the SOFC and should exhibit high oxide (or proton) conductivity, low electronic conductivity, and have high chemical and crystallographic stabilities under the operation and fabrication condition [9,16]. The fuel for SOFCs is either \( \text{H}_2 \), CO or \( \text{CH}_4 \), and therefore, the oxygen potential difference in which the electrolyte is placed has to be wide. Zirconia based electrolytes, in particular yttria-stabilised (YSZ), have been used in solid electrolyte fuel cells from as early as 1937 [17], and satisfy the above criteria for the electrolyte.
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Figure 1.2 - Schematic of a planar SOFC [18]

![Diagram of a planar solid oxide fuel cell (SOFC)](image)

Figure 1.3 - Schematic diagram of reactions within a SOFC [9]

<table>
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<th>Component</th>
<th>Reaction</th>
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<tr>
<td><strong>Anode</strong></td>
<td>[2H_2 \rightarrow 4H^+ + 4e^-]</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>[O^2-]</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td>[O_2 + 4e^- \rightarrow 2O^{2-}]</td>
</tr>
</tbody>
</table>

Overall: \[O_2 + 2H_2 \rightarrow 2H_2O\]
However, stabilised zirconia only shows appreciable oxygen ion conductivity at elevated temperatures, typically above 900°C [9]. Recently, high oxygen ion conductivity has been discovered in the LaGaO$_3$ perovskite material which exhibits high ionic conductivity at significantly lower temperatures than electrolytes based on zirconia [157-162].

On the cathode (air electrode) side, oxygen molecules are ionised and incorporated in the electrolyte. Therefore the cathode material should have catalytic activity in order to dissociate oxygen molecules, high electronic conductivity, high chemical stability in air under the fabrication and operating conditions, and compatibility with the electrolyte material. The most common material used in SOFC configurations is Sr doped LaMnO$_3$ [19,20]. However, a change in the morphology of the cathode layer with time and interfacial reaction between the cathode and electrolyte during operation have limited the life of SOFCs and need to be minimised.

The anode usually consists of a metal due to the highly reducing nature of the fuel gas. At the 1000°C operating temperature of YSZ-based SOFCs, suitable metals are limited to Ni, Co, Ru and Pt [9]. To maintain the porous structure of nickel over long periods at elevated temperatures and to provide other desired properties for the anode, nickel is usually combined with a YSZ support [9,21]. However, the thermal mismatch between the Ni/YSZ support and the electrolyte can lead to stress, cracking and fabrication problems within the fuel cell.

Due to the large size of SOFCs the main use is envisaged to be in the area of stationary combined heat and power (CHP) generation [22]. Indeed, units are currently operating at a number of industrial sites globally. In 1992 Westinghouse installed two 25 kW units in Japan for a Japanese gas utility and an electrical utility. One of the plants set the record for SOFC
continuous operating time of 7,064 hours [22]. It is also believed that if the size and cost of SOFCs could be reduced they would be an attractive replacement for the internal combustion engine within road vehicles. Other types of fuel cell, in particular solid polymer fuel cells (SPFC), have already been demonstrated as power sources in buses by companies such as Ballard Power Systems [12]. Major car manufactures, including Daimler-Benz and Chrysler are joining the race to develop electric vehicles powered by fuel cells or hybrid vehicles utilising both gasoline and fuel cell technology, as recently reported in the international press [23] (Figure 1.4).

Figure 1.4 - The hybrid petrol/fuel cell electric vehicle as reported in *The Guardian* [23]
1.2.2 Oxygen Sensors

The monitoring of toxic gases and oxygen levels is an important issue in environmental monitoring. Electrochemical sensors are convenient and effective devices for this purpose, since they produce an electrical signal that can be related directly to the concentration of the compound being measured. One of the major achievements within air pollution monitoring is the introduction of the lambda sensor for monitoring oxygen in the exhaust gases from vehicle internal combustion engines, which is a prerequisite for the modern catalytic converter that reduces the emissions of pollutants such as CO, NOₓ, SO₂ and unburned hydrocarbons [24].

Potentiometric oxygen sensors are based on a specialised electrochemical cell. Figure 1.5 shows such a sensor, with two regions containing oxygen at different pressures separated by a stabilised zirconia electrolyte.

![Schematic representation of an oxygen sensor](image)

Figure 1.5 - Schematic representation of an oxygen sensor [25]

The stabilised zirconia electrolyte is an excellent oxygen ion conductor, and therefore as gas pressures equalise oxygen is able to pass from the left-hand side of the cell, through the solid electrolyte, to the right.
Since the oxygen ions are charged a potential difference is created, and a measurement of this difference indicates that oxygen is present in the sensor and gives a measure of the oxygen pressure difference. Current sensors employ calcia or yttria-stabilised zirconia which exhibits pure oxygen ion conductivity over a wide range of oxygen partial pressures. Recently, Ishihara and co-workers [26] have utilised the LaGaO$_3$-based electrolyte within a potentiometric oxygen sensor. This material exhibits almost pure oxygen ion conduction over a wide range of oxygen partial pressures, as well as being stable in both oxidising and reducing atmospheres.

1.2.3 Ceramic Oxygen Generators

The global market for oxygen is set to expand over the coming years. At present oxygen is separated from air by one of three process: cryogenic distillation of air, pressure swing adsorption and vacuum swing adsorption. The most appropriate method is dependant upon the amount and quality of the resulting oxygen, as well as on economic factors. Recently, Kilner et. al. [18] have reported a new type of separation process based on a gas-tight ceramic membrane operating at temperatures between 800 and 1000°C. These ceramic oxygen generators (COG) produce 100% pure oxygen in a single operation with the added benefit of providing a physical barrier to contaminants in the input stream.

The technology of electrically driven COGs is related closely to that of solid oxide fuel cells. An electrical potential is applied across an oxygen ion conducting electrolyte via electrodes, with oxygen from the air feed-stock being reduced at the cathode. Oxygen ions then travel through the electrolyte to the anode, where they are oxidised and recombined to produce oxygen molecules; electrons are able to transfer between the electrodes via an external circuit (Figure 1.6).
The electrolyte materials currently in use are based on fluorite-structured oxides, namely, stabilised zirconia and doped ceria. However, as with SOFC applications each of these materials have a number of disadvantages. Yttria or calcia-stabilised zirconia only exhibit appreciable ionic conductivity at temperatures above 900°C, while gadolina-doped ceria has substantial electronic conductivity under certain conditions. However, gadolina-doped ceria is still the favourable candidate at intermediate temperatures (600-800°C) as long as the applied voltage is not too high [18]. As already noted, of increasing interest as solid electrolytes are solid solutions based on the parent LaGaO₃ which adopts the perovskite structure [157-163,165,166]. These gallates have comparable ionic conductivity to doped ceria, without any appreciable electronic conductivity. Moreover, they show this superior ionic conductivity at temperatures lower than stabilised zirconias.

1.3 Fluorite Oxides: Structure and Defects

In the case of solid electrolytes for the above applications, the two most common electrolytes adopting the fluorite structure are based on stabilised ZrO₂ and doped CeO₂. The fluorite structure is named after the mineral form of calcium fluoride (CaF₂) and is shown in Figure [10].
1.7. It consists of a cubic close-packed array of cations in which all the tetrahedral sites are occupied by anions. In this structure each cation is in an eight-fold co-ordination with oxygen and the larger octahedral holes are vacant.

Oxides that crystallise in the fluorite structure (e.g. CeO₂, ThO₂ and stabilised ZrO₂) can accommodate a large fraction of lower valence cations such as alkaline-earth and rare-earth ions into solid solution. This results in oxygen deficiencies as high as 10-15 % which is the source of the high oxygen ion conductivities [154]. The defect chemistry of the fluorite-structured oxides is based on the replacement of the tetravalent host cation (M⁴⁺) with one of lower valency, e.g. Y³⁺ or Ca²⁺. The charge-imbalance that arises is compensated by the formation of highly mobile oxygen vacancies. This process can be represented by the following equation for Y₂O₃ doping of MO₂:

\[ Y₂O₃ + 2M^+_M + O^+_O \rightarrow 2Y^+_M + V^-_O + 2MO₂ \]  

(1.1)
where in Kröger-Vink notation \([27]\) the symbols are indicative of the type of defect, i.e. \(V\) for vacancy, the subscripts indicate the lattice site and the superscripts, \(x\) (neutral), \(\cdot\) (positive), \(\cdot\) (negative) indicate the charge of the defect relative to the normal site. With the creation of a vacant oxygen site it is possible for a neighbouring oxygen ion to migrate into this adjacent and equivalent site via a hopping mechanism \([28,29]\). It is the rapid movement of these vacancies that accounts for the high ionic conductivity exhibited by stabilised zirconia and other fluorite-structured oxides. The doping for \(M^{4+}\) with aliovalent cations not only introduces oxygen vacancies, but in \(ZrO_2\) also serves to stabilise the high temperature cubic phase at room temperature.

It has been shown that the ionic conductivity in fluorite-structured oxides increases with increasing dopant concentration due to an increase of ionic charge carriers (oxygen vacancies) \([58,128\text{-}132]\). However, the conductivity decreases after reaching a maximum at certain dopant concentrations, because the high concentration of oxygen vacancies begin to form defect associates, (e.g. \([YZr^- - V_0^-]\)); these can trap migrating vacancies and therefore lower ionic conductivity and increase the activation energy. The binding energy of these defect associates is dependent upon the degree of size mis-match between the dopant cation and host \(M^{4+}\), which should be a minimum to optimise the ionic conductivity values \([30]\). In general, studies in this area have aimed to enhance the oxygen ion conductivity of these compounds by varying the dopant ion and its concentration.

Clearly, the role of defects and dopants, as well as the mechanisms of ion transport are crucial for the complete understanding of their behaviour. To shed light on these issues, computer modelling techniques have been applied to Y/ZrO\(_2\) which are now well established tools in
probing materials properties at the atomic level. The reliability of such a modelling approach has been demonstrated by a wealth of similar work on a range of metal oxides [47,48,50-53,103,144-147].

In Chapter 3 we employ atomistic simulation techniques to examine the energetics of aliovalent dopant substitution in zirconia which is essential in increasing the concentration of mobile oxygen vacancies. Our study has extended the range of dopants beyond the commonly used stabilisers in zirconia (e.g. Ca$^{2+}$, Y$^{3+}$) to include a variety of di- and trivalent metal dopants. We also examine dopant-vacancy clustering, as well as the topical issue of Nb/Y codoping.

We proceed in Chapter 4 by undertaking a Molecular Dynamics (MD) study of oxygen ion diffusion in yttria-stabilised zirconia (YSZ). These simulations provide an insight into the effects of temperature on structural and ion transport properties. We also obtain oxygen diffusion coefficients over a greater range of temperatures than previous experimental and simulation studies on this material.

The ionic conductivity of electrolytes based on fluorite-structured oxides is high, as illustrated in Figure 1.1, but only at temperatures in excess of 900°C. The search is on for an electrolyte that can exhibit a similar stability in reducing and oxidising environments as yttria-stabilised zirconia, yet have appreciable oxygen ion conductivity at lower temperatures. A promising candidate is doped LaGaO$_3$, which belongs to the family of perovskite-structured oxides, as described in the next section.
1.4 Perovskite Oxides: Structure and Defects

The perovskite oxides constitute an important class of inorganic compound with the general formula ABO₃. Almost all the naturally occurring metallic elements in the periodic table are stable within this structure, and this, together with the whole host of elements that can be accommodated, accounts for the wide spectrum of properties exhibited by these oxides [31]. These materials are utilised within various solid state applications such as catalysts [32-35], ceramic membranes [36], gas sensors [37], fuel cells [38-39,161,162,165,166], dielectrics for capacitors [40] and, most recently, colossal magnetoresistance sensors [41]. Indeed, they have earned themselves the title of “Chemical Chameleons” [42], as well as being “materials for all seasons” [43].

Figure 1.8 - ABO₃ cubic perovskite structure (a) unit cell, (b) Structure depicted as BO₆ corner-sharing octahedra, with the A cations occupying the central interstice, and the B cations residing in the centre of the octahedra (A - green, B - blue and O - red)
The crystal structure of the perovskite oxides is related to that of the mineral perovskite (CaTiO$_3$) and is depicted in Figure 1.8. In its ideal form, the perovskite structure is cubic with the B cation octahedrally co-ordinated to six oxygens, and these octahedra are corner-shared. The A cation occupies the space between eight octahedra and has twelve nearest-neighbour oxygens.

For stoichiometric compounds the sum of the charges on the A and B atoms must be equal to six to preserve electroneutrality. This can be achieved in a number of ways: A$^{1+}$B$^{5+}$ (e.g. KTaO$_3$), A$^{2+}$B$^{4+}$ (e.g. BaTiO$_3$, SrCeO$_3$) and A$^{3+}$B$^{3+}$ (e.g. LaMnO$_3$, LaGaO$_3$). However, the occupancy of the A and B sites is not governed so much on the valence states of the cations, but rather it is governed by size effects. For an oxide of composition ABO$_3$ to form, the condition stated in the following equation must be satisfied:

$$r_A + r_0 = \sqrt{2}(r_B + r_0)$$  \hspace{1cm} (1.2)

where $r_A$, $r_B$ and $r_0$ are the radii of the A, B and oxygen ions, respectively. The tolerance factor, $t$, defined by Goldschmidt, sets the tolerance limits for the perovskite structure, and is given by:

$$t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}$$  \hspace{1cm} (1.3)

For the ideal structure it takes the value of unity, although the perovskite is obtained for 0.75 < $t$ < 1.0, as long as the radius of the A and B cations is greater than 0.9Å and 0.51Å, respectively [44].

The defect chemistry of ABO$_3$ perovskites is based on the substitution of the A and B cations by dopants of lower valency [45]. However, in perovskite oxides, acceptor dopants can be charge-compensated in a variety of ways. When the valence state of the dopant is fixed
electron neutrality is maintained by the formation of oxygen vacancies. For perovskites containing transition metal ions that can adopt a number of formal valence states, acceptor doping may lead to the oxidation of the transition metal ion, that is, electronic compensation [46]. In certain systems, such as \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \), a mixed compensation mechanism may be operative (i.e. electronic and vacancy compensation) leading to a mixed electronic/ionic conductor.

In our study of perovskite oxides, we have focused on the \( \text{LaGaO}_3 \) material, which is a promising new oxygen ion conductor, with an ionic transport number close to unity [160,163]. Acceptor doping on La and Ga sites leads to an increase in charge-compensating oxygen vacancies, and it is these vacancies that are responsible for high ionic conductivity exhibited by this material [157-160]. Considering Sr substitution of La as an example, this doping process can be represented by the following defect reaction:

\[
\text{SrO} + \text{La}^{3+}_\text{La} + \frac{1}{2} \, \text{O}^{2-}_\text{O} = \text{Sr}^{2+} + \frac{1}{2} \, \text{V}^{2-}_\text{O} + \frac{1}{2} \, \text{La}_2\text{O}_3
\]

(1.5)

where, in Kröger-Vink notation [27], \( \text{Sr}^{2+}_\text{La} \) signifies a dopant substitutional and \( \text{V}^{2-}_\text{O} \) an oxygen vacancy. As with the fluorite oxides described above, the movement of ions takes place by a hopping mechanism for oxygen vacancy migration.

Alkaline-earth dopants are usually acceptor-doped on both A and B sites in \( \text{LaGaO}_3 \) in order to enhance ion conductivity and in Chapter 5 we have evaluated the energetics of such substitution processes from static lattice simulations. Moreover, we have used our simulation methods as a predictive tool, and extended the range of dopants to include various transition metal cations. We have also examined the formation of holes in \( \text{LaGaO}_3 \) which are believed to form at high temperatures. In addition, the mechanistic features of ion transport, as well as
dopant-vacancy clustering which may have a direct effect on ion migration have been studied.

The theme of oxygen ion conduction continues in Chapter 6, where shell-model Molecular Dynamics (MD) techniques are used to explore the effects of temperature and of dopant concentration on oxygen diffusion in La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ} (LSGM). From MD we derive oxygen diffusion coefficients for several LSGM systems as well as information on migration mechanisms. It should be noted that this is the first static lattice and MD simulation study that has been carried out on the new LaGaO_3 material.

Before presenting the results of our work in detail, we will describe in the next chapter the principal methodologies employed in the computer simulations.
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Chapter 2: *Computer Simulation Methods*

2.1 Introduction

Over the last 15 years atomistic computer simulation techniques have become established tools in the fields of materials science and solid state chemistry. Increasingly, these techniques are being used to predict crystal structures and to examine the defect chemistry of technologically important materials. In part, this success can be attributed to the growth in affordable computing power, which has enabled increasingly complex solids to be successfully studied. Moreover, these methods are ideally suited to probing the structure of disordered solids at the atomic level, yielding data which is sometimes difficult to obtain experimentally. Atomistic simulation techniques have been successfully used to study a whole array of materials, including high-temperature superconductors [47-50], catalysts [51,52] and ionic conductors [53-56]. The starting point, and basis of any such study is the potential model, i.e. an analytical or possibly numerical description of the energy of the system as a function of atomic co-ordinates. The resulting computational model must accurately reproduce the crystal structure and physical properties of the system in question.

In this chapter, a description of the lattice simulation and the molecular dynamics methods used in the present study are presented, although more comprehensive reviews are given elsewhere [57-62].

2.2 Potential Model

The simulations are formulated within the framework of the Born Model, in which an ionic crystal is regarded as being comprised of discreet ions. The lattice energy ($U_L$) is defined as
the energy required to bring together gaseous ions from an infinite separation to their equilibrium positions within the crystal, and can be derived from a knowledge of the interatomic potential. A general expression for the lattice energy can be written as

\[ U_L = \sum_{i,j} \frac{q_i q_j}{r_{ij}} + \sum_{i,j} V(r_{ij}), \]

(2.1)

where the summations refer to all pairs of ions i and j. The terms in this equation refer to the Coulombic and short-range interactions between ions, respectively. However, materials which deviate from ionic bonding may require an additional three-body term which provides some degree of directionality. This usually takes the form of a angle-dependent ‘bond-bending’ function added to (2.1), which has been applied successfully to silicates and zeolites [59,62].

2.2.1 Coulombic Interactions

To evaluate the coulombic energy, charges must be assigned to all the ions present in the system. In this study we have used the fully ionic model, i.e. integral charges, as opposed to partial charges, have been assigned to ions corresponding to their formal oxidation states. If the summation of the coulombic interactions is carried out using conventional methods the results obtained can be unreliable. This is because the coulombic potential varies as 1/r, which if summed conventionally can be slow to converge. However, rapid convergence can be achieved by employing the Ewald method [63,64].

The Coulombic potential of an infinite crystal system can be calculated by superposing the coulombic potentials of the component Bravais lattices. The Ewald method transforms the potential of a Bravais lattice of unit point charges, neutralised by a uniform charge distribution, into an expression consisting of two rapidly converging series (one in real space...
Figure 2.1 - (i) Charge distribution of a one dimensional Bravais lattice. The vertical lines represent the point charges at the lattice sites, and the horizontal lines the neutralising uniform distribution of charge. (ii) The Ewald components of the charge distribution, each Gaussian is centred on a lattice site and normalised to unity.

and one in reciprocal space). This is achieved by splitting the charge distribution under consideration into two components, as illustrated in Figure 2.1, for a one dimensional lattice. To each Bravais lattice (real and reciprocal), a Gaussian distribution of the charge is superimposed, resulting in a smoothly variant function. The signs of the reciprocal space function and that of the real space function, are opposite, and therefore upon summation the functions cancel one another. The summation from 0 to $\infty$ of the $1/r$ term is expressed in integral form, and divided into the two spatial parts by a parameter $\eta$,

$$
\frac{1}{r} = \frac{2}{\pi^{\frac{3}{2}}} \left\{ \int_{0}^{\eta} \exp(-r^2t^2) dt + \int_{\eta}^{\infty} \exp(-r^2t^2) dt \right\}
$$

(2.2)
where \( r \) is the separation and \( t \) is the half-height width of the Gaussian function. Efficiency in the convergence is achieved from a knowledge of the unit cell volume, and from the number of species in the unit cell. Finally, the Fourier representation of the potential generated by the first component (0 to \( \eta \)) is added to the potential of the second component (\( \eta \) to \( \infty \)), and an appropriate value of the half-width of the Gaussian function chosen, so that both series may converge rapidly. Physically, the rapid convergence can be attributed to the fact that the first Ewald component of the charge distribution is smooth, while in the second component the neutralising charges are piled up around the point charges of the ions. This results in a rapidly-converging summation of the Coulombic potential.

2.2.2 Short-range Interactions

In contrast to the Coulombic potential, the short-range interactions are treated in real space by two-body models and pose no real problem on summation because of the short cut-off distances. In ionic crystal simulations the most common analytical potential is of the Buckingham form [57]:

\[
V_{ij}(r) = A \exp \left( -\frac{r}{\rho_{ij}} \right) - \frac{C_{ij}}{r^6}
\]  

(2.3)

where \( A, \rho \) and \( C \) are the potential parameters assigned to each ion-ion interaction. For the potential model to accurately describe a system, it is crucial that suitable values are assigned to these parameters (see §2.4). The exponential repulsive term of (2.3) describes the Pauli repulsion which occurs when atomic charge clouds interact. The attractive \( r^{-6} \) term describes the interactions of induced dipoles (Van-der Waals forces), that arise when electron clouds are in close proximity. However, these interactions are quite small, and dependent on the polarisability of the ion in question, and are therefore generally included for large polarisable
ions, such as $O^{2-}$.

2.2.3 Ionic Polarisability

The inclusion of ionic polarisability into the potential model is essential, since many of the properties we wish to model, such as dielectric constants and optical phonon modes, are dependent on its accurate description. Moreover, if we are to effectively model the response of the lattice to charged defects, which extensively polarise their surroundings, these properties must be accurately reproduced.

Earlier studies utilised the Point Polarisable Ion Model to describe ionic polarisability, but this was found to be unsatisfactory particularly in the calculation of defect energies. The Shell Model, originally developed by Dick and Overhauser [65], is superior to previous models because it allows the repulsive forces to act only between shells, thus short range repulsions and polarisation are coupled. Omission of this coupling by other models leads to an overestimation of the polarisation effects and therefore inaccuracies in the calculated physical properties.

Figure 2.2 - Schematic representation of the shell model
The shell model describes a polarisable ion in terms of a massive core of charge $X$, connected by a harmonic spring with force constant $k$, to a massless shell of charge $Y$; the formal charge on the ion is therefore given by $X + Y$ (Figure 2.2). When an electric field is applied to the ion, the shell is displaced relative to the core, creating a dipole moment. The polarisability of the free ion is given by

$$\alpha = \frac{Y^2}{k}$$  \hspace{1cm} (2.4)

Despite its simplicity, the shell model has enjoyed considerable success in modelling structural and defect properties of ionic halides and oxides [57-62].

2.3 Perfect Lattice Simulation

Once we have established high quality interatomic potentials for the system in question, it is possible to gain valuable structural and defect properties. This is achieved by employing energy minimisation techniques which calculate the equilibrium geometry, i.e. the minimum energy configuration of the system with respect to ion co-ordinates. Therefore, efficient energy minimisation is an essential part of any simulation and is necessary before any physical properties can be calculated.

2.3.1 Energy Minimisation

The concept of energy minimisation is simple: structural parameters, including ionic co-ordinates, are adjusted until a minimum energy configuration is attained. However, the energy of a crystal is a complicated, multidirectional function of the ionic co-ordinates, and this variance with the ionic co-ordinates results in a complex energy surface (sometimes called a hypersurface). We are concerned with the minimum points on this potential energy surface
that refer to the stable arrangement of the ions; any deviation from this minimum would result in a structure of higher energy and less stability. To identify the global energy minimum many minimisation algorithms are available, and choice of the right one requires careful consideration. The most widely used methods are those based on gradient techniques, which involve the use of the first derivatives of the energy function with respect to the structural parameters.

The *steepest descent method* is one of the simplest gradient techniques, and involves an iterative process, which is used to adjust various parameters through the utilisation of an expression of the form:

\[ x^{(p+1)} = x^p - g^p \delta \]  

(2.5)

where \( x^{(p+1)} \) is a vector whose components are variables for the \((p+1)^{th}\) iteration, \( x \) and \( g \) are variables along with their gradients for the \( p^{th} \) iteration, and \( \delta \) is a scalar parameter chosen so as to obtain a rapid convergence of the energy. Another first derivative method similar to steepest descents, which is sometimes employed, is the conjugate gradient method.

The most efficient, and hence most commonly used minimisers, are based on the Newton-Raphson method, which introduce second as well as first derivatives of the energy function. This method incorporates the hessian or some approximation of it, with the variables updated according to the formula:

\[ x^{p+1} = x^p - (H^p)^{-1} g^p \]  

(2.6)

where \( H \) represents the hessian matrix of the second derivatives of the energy function. When the energy drops below a certain criterion in one step or the angle between the gradient and search vectors becomes too large, the hessian is explicitly recalculated, leading to a rapid
convergence within a few cycles. One of the most intensive parts of the calculation is the inversion of the hessian matrix, especially if the unit cell contains a large number of ions. However, explicit calculation of the hessian matrix at each cycle is usually not necessary due to the Fletcher and Powell approximation [66]. This method updates the forces at each cycle, but only inverts the matrix at predetermined intervals, therefore improving convergence rates.

Most of the static lattice calculations in this study were carried out using the program GULP (General Utility Lattice Program) [67-69], which uses a symmetry-adapted energy minimisation technique. Symmetry information can be used to identify the minimum set of variables needed for the minimisation procedure, and to increase the rate of the calculation of the energy, and its first and second derivatives during optimisation. The list of variables for the minimisation only contains the fractional co-ordinates of the asymmetric unit as the internal parameters. This is because the total number of positions, $X_n$, can be related to those of the asymmetric unit, $X_a$, by a roto-translation which for the $n$th operator of the space group is given by:

$$X_n = R_n X_a + t_n$$

(2.7)

where $R_n$ is a 3 x 3 matrix and $t_n$ is the translational vector. Minimisations performed under constant pressure conditions occur through the use of a strain matrix, rather than by consideration of the cell parameters, and takes the form:

$$\begin{pmatrix}
1 + \varepsilon_1 & 1/2 \varepsilon_6 & 1/2 \varepsilon_5 \\
1/2 \varepsilon_6 & 1 + \varepsilon_2 & 1/2 \varepsilon_4 \\
1/2 \varepsilon_5 & 1/2 \varepsilon_4 & 1 + \varepsilon_3
\end{pmatrix}$$

(2.8)

The use of a strain matrix also reduces the number of variables in the minimisation and therefore lowers the number of optimisation cycles.
2.3.2 Physical Properties

Once the structure has been optimised, various physical properties, which are readily derived from the second derivative matrix, can be calculated and compared directly with experimental data. The elastic constants are defined as second derivatives of the lattice energy with respect to strain, normalised to the unit cell volume (V),

\[ C = \frac{1}{V} \left( W_{\text{II}} - W_{\text{IE}} \cdot W_{\text{IE}}^{-1} \cdot W_{\text{IE}} \right), \]  

(2.9)

where \( C \) is the elastic constant matrix and \( W \) the second derivative matrix of the lattice energy function. The dielectric constant, which is a function of polarisability, is given by

\[ K^{\alpha \beta} = \delta^{\alpha \beta} + \frac{4\pi}{V} \varepsilon \cdot \left[ W_{\text{IE}}^{-1} \right]^{\alpha \beta} \cdot q \]  

(2.10)

where \( K^{\alpha \beta} \) is the dielectric tensor, \( \delta^{\alpha \beta} \) the ion displacement, and \( q \) the charge.

Other physical properties which can be derived include piezoelectric constants and phonon frequencies. The calculation of these and other properties provides a useful test of the potential model, as well as providing predictive data in cases where there is a lack of experimental data.

2.4 Derivation of Interatomic Potentials

The reliability and the validity of any atomistic simulation technique is inherently dependent on the availability of quality interatomic potentials [67]. Moreover, the application of such models to complex solid-state problems demands the transferability of the potentials from the system they were derived to the system under examination. There are two main types of procedure available for the derivation of interatomic potentials; empirical and theoretical, both of which are described below.
2.4.1 Empirical Fitting

Empirical potentials are usually derived by ‘fitting’ the short range parameters $A$, $\rho$ and $C$, and the shell model parameters $Y$ and $K$, to experimental data and the crystal structure. In conventional fitting procedures, this involves the parameters being adjusted until good agreement is achieved between the calculated and observed experimental properties. This is usually achieved by using a least-squares procedure, which minimises the difference between the calculated and experimental properties:

$$ F = \sum_{\text{observables}} \omega (f_{\text{calc}} - f_{\text{obs}})^2 $$  \hspace{1cm} (2.11)

where $F$ is the sum of squares, $f_{\text{calc}}$ and $f_{\text{obs}}$ are the calculated and observed quantities and $\omega$ is the weighting factor. The properties must include the crystal structure and one or more of the following: elastic constants, static dielectric constants, piezoelectric constants and lattice energies. Obviously, if more properties are chosen during the fitting procedure, and the experimental data is of good quality, then the reliability of the resulting potentials will be improved. Also the transferability of the potential from the system it was derived for to any other system will be enhanced.

A problem arises when using the shell model; from the crystal structure the desired core positions, to which we wish to fit, can be ascertained. However, in the case of the shells, there is no a priori knowledge of their positions. If it is assumed that the cores and shells have the same positions, this can lead to a poor fit. One solution is to include the shell co-ordinates as fitted parameters, giving a more readily convergent and computationally efficient fit [68]. This fitting procedure, where the cores and shells are simultaneously relaxed, is embodied in the GULP code. [67,69].

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Empirical fitting procedures have been successfully used to derive potentials for a wide range of oxide and halide materials [70,71]. However, extraction of information about the potential over interatomic spacings different from those in the perfect lattice can be a problem. This can arise, for example, when defect interstitials are being investigated. Therefore, the validity of the empirical method of potential derivation depends on the accuracy of the analytical potential over a wide range of interatomic spacings. Knowledge of the potential over this wider range of interatomic separations improves the accuracy of the potential. This can be achieved either by; fitting a series of interatomic potentials to structural and crystal properties of several compounds containing the same interaction [70], or by fitting to a material that contains a sample of distances for the interacting ions, as is found in some low symmetry structures.

2.4.2 Theoretical Methods

The most widely used theoretical technique for the derivation of interatomic potentials is based on the electron-gas method of Wedepohl [72], and Gordon and Kim [73]. In these methods, the short-range potential acting between a pair of ions i and j is determined by calculating the electron densities [$\rho_i(r)$ and $\rho_j(r)$] of the isolated ions. This is normally achieved by solving the Hartree-Fock wave equations for each ion. The interaction energy, $E_{ij}$, is then calculated according to the formula:

$$E_{ij}(r) = E_{ij}^C(r) + E_{ij}^{KE}(r) + E_{ij}^{COR}(r) + E_{ij}^{EX}(r)$$

(2.12)

where $E_{ij}^C(r)$ is the Coulomb interaction between the two species i and j and $E_{ij}^{KE}(r), E_{ij}^{COR}(r)$ and $E_{ij}^{EX}(r)$ are the kinetic energy, correlation and exchange contributions to the interaction energy. A number of approximations are included in the above expressions which give the
interactions in terms of the densities [73]. Nevertheless, it has been shown [73,74] that these methods give adequate potentials for closed-shell interactions. A modification to the method is to obtain the Hartree-Fock wavefunctions for the interacting species performed on the species within an appropriate crystal environment. This effects the electron densities obtained and hence the calculated interatomic potentials. This is particularly true for the O$^{2-}$ ion, which is usually stabilised only by the crystal potential. Therefore, it has been suggested that both the Madelung and orthogonalisation effects due to surrounding ions may be important [75]. Using potentials derived from these crystal-adopted wave functions in defect calculations, it has been shown that there is very good agreement between calculated and experimental results [76]. A number of assumptions are made in these methods, including the neglect of distortion effects of the electron clouds when two ions are in close proximity, and the total electron density is simply the sum of the densities of isolated ions.

2.5 Modelling of Defects

The creation of a defect species in a crystal system causes a perturbation of the surrounding lattice. The nature of this perturbation or relaxation is mainly Coulombic in origin and therefore the effects are long range. Defect simulations accurately model this relaxation using the two region strategy based on the methodology of Mott and Littleton [77-79].

Defect energies are calculated by minimising the potential energy function Φ of the defective lattice, with respect to displacements of the ions that surround the defect. The corresponding defect energy is given by the difference in the minimum Φ for the perfect and defective lattices. The procedure for minimising Φ is simplified by partitioning the defective lattice into two regions (Figure 2.3).
Region I contains the defect and typically around 250 - 300 surrounding ions. All the ions in this inner region are relaxed explicitly using Newton-Raphson minimisation procedures, giving a minimum energy state. The forces exerted by the defect on the ions within region I are strong, and therefore the relaxation must be treated as accurately as possible. In contrast, in the more distant regions of the crystal outside the inner region the defect forces are relatively weak and may be treated using pseudo-continuum methods. The Mott-Littleton method describes the response of region II to the effective charge of the defect, entirely as a dielectric response. From dielectric continuum theory, the polarisation of the crystal P per unit cell, at a point r relative to the defect of charge q at the origin is given by:

\[
P = \frac{V}{4\pi} \left( 1 - \frac{1}{\varepsilon_0} \right) \frac{qr}{r^3},
\]

where \(V\) is the unit cell volume, \(q\) the effective charge of the defect, and \(\varepsilon_0\) the static dielectric constant. The total defect energy \(E_D\) after dividing the crystal into two regions, is evaluated using the expression:

\[
E_D = E_I(x) + E_{IIa}(x,y) + E_{IIb}(y),
\]
where $E_I$ is a function of the ion co-ordinates $(x)$, and of the dipole moments of ions in region
I only. $E_{\text{int}}(x,y)$ arises from interactions between regions I and II, and therefore it is necessary
to include an interface region (region IIa) between these regions, allowing for a smoother
convergence during minimisation. Displacements of ions within this interface region are
treated using the Mott-Littleton approximation, but the interaction with region I is handled
explicitly. $E_{\text{int}}(y)$ is dependent only on the displacements $(y)$ of ions in region IIb.

### 2.6 Molecular Dynamics Simulations

The simulation methods described in previous sections have been concerned with evaluating
potential energies of the system under investigation, with no explicit inclusion of temperature
effects. For many applications these 'static' methods perform well, giving useful data for the
system in question. However, in some cases, for example high temperature materials and/or
fast-ion conductors, it may become necessary to include explicitly thermal motions. The
Molecular Dynamics (MD) technique consists of an explicit dynamical simulation of an
ensemble of particles for which Newton's equations of motion are solved. This introduces a
kinetic energy term, and therefore introduces ion motion and temperature effects. MD
simulations allow a detailed picture of the evolution of the system, as function of time, to be
constructed. The MD simulations in this study were performed using the DL_POLY code
[80].

#### 2.6.1 Methodology

MD techniques assume that once an accurate potential model has been established, classical
mechanics can provide information about the dynamics of the system. Successive
configurations of the system are generated by integrating Newton’s equations of motion. The resulting trajectory specifies how the positions and velocities of the ions in the system vary with time. Initially a time step, $\Delta t$, is specified which must be smaller than the characteristic time of any important process in the system (e.g. the period of an atomic vibration) and is typically $10^{-14}$ to $10^{-15}$ seconds. The positions ($x_i$) and velocities ($v_i$) of a particle after each time step, which is applied thousands of times, are updated by applying the classical equations of motion, which in the limit of an infinitesimal $\Delta t$ would be:

$$x_i(t + \Delta t) = x_i(t) + v_i(t)\Delta t$$  \hspace{1cm} (2.15)$$

$$v_i(t + \Delta t) = v_i(t) + \frac{F_i}{m_i}(t)\Delta t$$  \hspace{1cm} (2.16)$$

where $F_i$ is the force, calculated by using the specified interatomic potentials, acting on the $i$th particle of mass $m_i$. In practice, the finite value of $\Delta t$ requires the use of terms in higher power of $\Delta t$. Before the MD simulation can commence, the system must be allowed to reach a state of thermodynamic equilibrium. This period of equilibration is usually assigned a time period of between 3 - 10ps. Following this, the production stage of the simulation proceeds for anywhere up to 100ps, although periods of 1ns are now becoming possible with recent advances in computing power.

An initial configuration, with ions assigned positions ($r_i$) and velocities ($v_i$), is constructed. The initial ion positions are usually obtained from crystallographic studies which are also used in the static lattice simulations. The ion velocities are obtained by randomly selecting from the Maxwell-Boltzmann distribution at the temperature of interest:

$$p(v_i) = \left( \frac{m_i}{2\pi k_b T} \right)^{\frac{3}{2}} \exp \left( -\frac{1}{2} \frac{m_i v_i^2}{k_b T} \right)$$  \hspace{1cm} (2.17)$$

This equation provides the probability that an ion $i$ of mass $m_i$ has a velocity $v_{ix}$ in the $x$
direction at temperature $T$.

The positions and velocities are updated using a numerical scheme, which breaks down the integration process into many smaller stages, separated by a fixed time step, $\delta t$. At a particular time $t$, the total force on any of the ions in the configuration can be calculated as the vector sum of the interactions with other ions. The accelerations of the ions are computed from these forces, and combined with the positions and velocities at a time $t$ to calculate the positions and velocities at time $t + \delta t$. During the timestep the force is assumed to be constant. The forces on the ions on their new positions is then determined, leading to new positions and velocities at time $t + 2\delta t$, and so on.

There are many algorithms available for the integration of the equations of motion using the finite difference method outlined above. Two of the most common algorithms utilised within MD simulations are the Predictor-corrector (Gear) and Verlet [81,82].

2.6.2 Periodic Boundary Conditions

The correct treatment of boundary effects is crucial to the simulation methods because it enables ‘macroscopic’ properties of the system to be calculated using a relatively small number of ions. The initial configurations in this study have consisted of a supercell containing between 1000 - 2560 ions, all located on their perfect lattice sites. Periodic boundary conditions (PBC) are applied to the supercell, which is repeated, in three dimensions, to infinity (Figure 2.4a) creating an unbounded system and eliminating surface effects. The use of PBC ensures that all the ions are considered to be embedded in the system under bulk conditions. Should an ion leave the simulation 'box', it is replaced by an image ion
Figure 2.4 - (a) Periodic boundary conditions. The simulation cell (heavy lines) is repeated (dotted lines) to infinity to create an unbounded system with no surfaces, (b) Number of ions in simulation cell remain constant.
that enters the box from the opposite side with an identical trajectory (Figure 2.4b). Therefore, the number of ions in the central simulation box remains constant.

MD simulations maybe performed under a wide range of conditions or ensembles [83-85]. Traditionally they are performed under conditions of constant number of ions (N), constant volume (V), and constant energy (E); the microcanonical or constant NVE ensemble. Another commonly used ensemble is the Berensden (NPT) [84], which corresponds to conditions of constant pressure (P) and constant temperature (T). Using this ensemble, energy can be exchanged with the surroundings and the cell dimensions modified to maintain a constant pressure. This is analogous to the idea of an ideal gas contained within a ‘box’ of variable dimensions, immersed in a temperature and pressure ‘bath’. The pressure within this box is caused by the particles colliding with the sides, resulting in a net force on the box. If the net force is greater than the theoretical force on the outside of the box, the box will expand. The system is kept at constant temperature by allowing energy to move in and out of the box and allowing for localised changes where the potential energy is converted to kinetic energy (heat exchange). We have utilised both ensembles mentioned above in our studies.

2.6.3 Shell Model Molecular Dynamics

The vast majority of MD simulations are rigid-ion simulations, i.e. there is no explicit inclusion of ion polarisability. This is usually due to the fact that such calculations would substantially increase the amount of computing time required to complete the simulation, and therefore be a great deal more expensive. However, with recent advances in parallel computing power and the subsequent decline in the cost of hardware production, shell model molecular dynamics is gaining ground.
Initial MD calculations outlined in this work have employed rigid-ion potentials, which are directly compatible with those used in our static lattice simulations. With respect to the cations the errors associated with the omission of polarisability are negligible; but the polarisability of the $O^{2-}$ ion will be significant. Nevertheless, it has been shown [139] that MD simulations of this type can adequately reproduce structural and dynamical properties of the system in question.

An ion is polarisable if it develops a dipole moment when placed in an electrical field. The polarisability is commonly given by:

$$\mu = \alpha E,$$  \hspace{1cm} (2.18)

where $\mu$ is the induced dipole, $E$ is the electric field, and the constant $\alpha$ represents the polarisability. The dynamical shell model is a method of incorporating polarisability into a MD simulation. The method employed in DL_POLY is called the adiabatic shell model, details of which are given by Collins et. al. [86]. In the static shell model (§2.2.3) the core and shell are connected by a harmonic spring. The effect of an electric field is to separate the core-shell unit, giving rise to a polarisation dipole. The condition of static equilibrium gives the polarisability ($\alpha$) as:

$$\alpha = \frac{(2q_s^2 - q_c^2)}{k},$$  \hspace{1cm} (2.19)

where $q_s$ and $q_c$ are the shell and core charges, and $k$ is the harmonic force constant. In the adiabatic method a dynamic description of shell model is set up by partitioning the total mass of the ion between the core and shell. Partitioning of the mass requires careful consideration, because the natural frequency of vibration $\nu$ of the harmonic spring, given by:
\[ v = \frac{1}{2\pi} \left[ \frac{k}{x(1-x)m} \right]^{1/2} \]  

(2.20)

where \( m \) is the atomic mass, must be well above the frequency of vibration of the whole ion in the bulk system. The dynamical core-shell unit can be likened to a diatomic molecule with a harmonic bond, however, the high vibrational frequency of the bond prevents effective exchange of kinetic energy. This means that throughout the simulation, from start to finish, the core-shell units will have negligible internal kinetic energy. This is essential, since the number of degrees of freedom of the core-shell units should not differ from the corresponding unpolarised unit.

### 2.6.4 Information from MD

Molecular dynamics simulations generate successive configurations of the system that are connected in time. The data from these simulations can provide an insight as to the microscopic dynamics of the system, and can be used to derive time dependent properties. Two valuable properties that can be obtained are the Radial Distribution Functions (RDF), and the Mean Square Displacements (MSD), each of which are described below.

Structural information is obtained from the pair RDF, which provides an insight into the long-range (dis)order of the crystal lattice, and is given by:

\[ g_{ij}(r) = \frac{\langle n_j(r) \rangle}{4\pi r^2 \langle n_i n_j \rangle^{1/2}} \]  

(2.21)

where \( i \) and \( j \) are ion types; \( \langle n_j(r) \rangle \) is the ensemble average of the number of species of type \( j \) in the radial shell of \( r \rightarrow r + dr \) with a central species of type \( i \) at the centre and \( n_i \) is the bulk density of ion type \( i \). Essentially, RDF provide information about ions surrounding a central
ion, and are plotted as a function of interatomic separation. For a perfect, crystalline solid, the RDF plot is usually sharp, and well-defined; in contrast to that of a liquid, which is rather less-defined and more diffuse. Fast-ion conductors usually have one mobile sub-lattice, and produce RDF plots that are commonly more liquid-like than those of normal solids.

MSD are time dependent, single particle averages, which describe the average displacement of an ion species from the initial position over a set period of time, and are given by:

$$\langle r_i^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} [r_i(t) - r_i(0)]^2$$

(2.22)

where $N$ is the total number of ions in the system. In the perfect lattice the MSD of component ions usually oscillates about a mean value. However, in a defective lattice, where there is a mobile species, such as $O^{2-}$ in stabilised zirconia, the MSD increases with time. MSD are usually plotted versus time, and from the gradient of such a plot, the diffusion coefficient ($D$) can obtained using the relationship:

$$\langle r^2(t) \rangle = 6Dt + B$$

(2.23)

where $B$ is the thermal Debye-Waller factor arising from lattice vibrations of ions. In addition to such information, mechanistic features may be obtained by analysis of ion trajectories, a procedure which is greatly assisted by modern graphics programs.
Chapter 3

Dopant Substitution and Defect Clustering in Zirconia

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Chapter 3: Dopant Substitution and Defect Clustering in Zirconia

3.1 Introduction

Interest in materials that exhibit high oxygen ion mobility has increased considerably over the last two decades. One of the primary reasons for this interest is that many new and developing technologies, such as fuel cells and oxygen sensors (as described in Chapter 1), depend on the greater understanding of the defect and ion transport processes in these materials. [6,87,88]. It is well established that doping zirconia (ZrO$_2$) with aliovalent cations (e.g. Y$^{3+}$, Ca$^{2+}$) increases the number of charge-compensating oxygen vacancies which are directly responsible for the ionic conduction in this system [89,90,91]. Indeed, stabilised ZrO$_2$ has found many uses as an electrolyte in solid oxide fuel cells (SOFC) and within oxygen sensors and generators, owing to its high oxygen ion conductivity [3,6,9,18,91].

It is clear that dopant incorporation has a major influence on the transport behaviour of oxygen ion conductors such as ZrO$_2$. However, the defect structure of stabilised ZrO$_2$ is still not fully characterised. Conductivity studies have shown that higher dopant concentrations (>10%) produce an increase in activation energy (and decrease in ionic conductivity), which is thought to arise from some form of vacancy-dopant association that traps the migrating oxygen vacancies [118]. There has been much debate on the nature of the interaction between the dopant cation and charge-compensating vacancies to form distinct clusters. It has been suggested that the oxygen vacancies sit at nearest-neighbour (NN) sites to the dopant ion, giving them seven-fold co-ordination [92,93,94]. In contrast, some studies indicate that anion vacancies sit on next-nearest-neighbour (NNN) sites with respect to the dopant, leading to eight-fold co-ordination [95,96]. It is therefore clear that consideration of local structure is...
crucial in order to fully understand the effect of dopants in ZrO₂.

However, in common with many materials, experimental data for ceramic oxides at the atomic level are difficult to obtain and hence there is considerable uncertainty as to the local structure. In an attempt to determine the defect and transport properties of pure and doped ZrO₂ atomistic simulation techniques have been applied, which are well suited to the study of electroceramics on the microscopic scale. Moreover, these techniques (described in Chapter 2) are now well established tools in the field of solid state chemistry, complimenting ‘traditional’ experimental methods.

In this chapter we examine the energetics of dopant substitution, dopant-vacancy clustering, and the mechanistic features of oxygen ion transport; this extends previous simulation studies on the ZrO₂ system [103] by considering a wider range of dopants, as well as the topical issue of Nb/Y co-doping. We start our account with some general comments on experimental work and technological applications of stabilised zirconia.

3.2 Experimental Background and Applications

A number of experimental studies, using a variety of techniques, have been carried out investigating the defect structure of stabilised ZrO₂. One of the most common experimental techniques employed has been extended X-ray absorption fine-structure (EXAFS) spectroscopy. The EXAFS technique provides a means to probe the local atomic structure and thus could be potentially used to directly investigate the defect structure of the oxygen sub-lattice of ZrO₂. Extensive studies by Catlow et. al. [95] and Veal et. al. [96] utilising this technique have been reported, which raise a number of interesting points regarding bond
lengths and the local environment of the dopant. Firstly, the dopant-O bond length is greater than the Zr-Zr bond length in the undoped system, and secondly the Zr-O bond length is smaller in the defective lattice compared to the perfect crystal. It is also suggested that dopants larger than the host Zr can only be accommodated in the lattice by displacements of the neighbouring anions. Both studies have suggested that a charge-compensating oxygen vacancy is preferentially located at a NNN site to the dopant ion, if the dopant radius is larger than the host Zr$^{4+}$ radius. This results in a 7-fold co-ordination of Zr$^{4+}$, similar to its structural environment in monoclinic zirconia. The same conclusion has been reached by Li and co-workers [97,98,99] using X-ray absorption spectroscopy (XAS), who go as far as saying that dopants larger than the host Zr$^{4+}$ are better stabilisers of the high temperature cubic phase. Impedance spectroscopy studies of Baumard and Abelard [100] have indicated that defect interactions, mainly dopant-vacancy attractive effects, play an important role in the transport properties of stabilised ZrO$_2$. The average structure in Ca/ZrO$_2$ and Y/ZrO$_2$ has been examined by X-ray diffraction techniques [92,93] from which the average displacement of anions surrounding the defect cation is calculated to be in the order of 0.065Å. Moreover, the anions immediately surrounding an anion vacancy tend to relax around it. However, the number of undisplaced anions in Ca/ZrO$_2$ is fewer than Y/ZrO$_2$, which is explained in terms of size effects: the larger Ca$^{2+}$ perturbs the surrounding anion sub-lattice to a greater degree than Y$^{3+}$. From this XRD study, Moringa and co-workers [92,93] also conclude that the charge-compensating anion vacancies are preferentially located at NNN sites to the dopant cation.

Stabilised ZrO$_2$, particularly ZrO$_2$-CaO and ZrO$_2$-Y$_2$O$_3$, has found many roles in applications requiring solid-state electrolytes. These have included galvanic cells, measurement of the oxygen content in metal melts, oxygen pressure monitoring in high-temperature gases, and
solid oxide fuel cells (SOFCs) [9,91,101]. However, it is in the field of high-temperature (1000 - 1200°C) SOFC technology that stabilised ZrO₂ has been applied the most, owing to the chemical, thermal and mechanical stability at elevated temperatures [9]. Yttria-stabilised ZrO₂ (YSZ) is the most common electrolyte because it possesses an adequate level of oxygen ion conductivity at typical operating temperatures, as well as stability in both an oxidising and reducing atmosphere. YSZ also has an extended oxygen partial pressure range (10⁵ - 10¹³ Pa) of ionic conduction which covers the conditions to which the electrolyte is exposed to the fuel. Because of the reducing conditions of the fuel gas, metals are used for the anode. During the normal operation of a SOFC based on YSZ suitable metals are limited mainly to nickel, cobalt and noble metals [9]. The cathode material is usually based on perovskite-structured compounds, namely doped LaMnO₃ and LaCoO₃. The interconnect material, used to combine individual fuel cell units to produce larger stacks, is doped LaCrO₃, which also adopts the perovskite structure. The major drawbacks of ZrO₂-based SOFCs are the high-operating temperatures that result in material and fabrication problems of the cell, as well as unreliability during prolonged periods of operation [9].

3.3 Crystal Structure and Potentials

At room temperature, pure ZrO₂ adopts the monoclinic (P2₁/c) crystal structure, which at temperatures above 1170°C changes to the tetragonal (P4₂/mnc) form. Above 2370°C a cubic (Fm3m) fluorite structure is observed which exists up to the melting point of 2680°C [9,91,102]. The high temperature cubic phase can be stabilised at room temperature by the addition of cations with a lower valence state than the host Zr⁴⁺ (Figure 1.7). It can be thought of as related to a cubic close-packed array of zirconium ions with oxygens occupying all the tetrahedral holes. In the centre of the structure lies a large, empty octahedral interstitial space.
(hole) which plays an important part in oxygen ion migration.

The short-range potential parameters assigned to each ion-ion interaction were transferred directly from a previous simulation study by Dwivedi and Cormack [103], and are listed in Table 3.1.

Table 3.1 - Potential parameters for ZrO$_2$

(i) Short-range

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>$\rho$ (Å)</th>
<th>C (eV Å$^6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr$^{4+}$...O$^{2-}$</td>
<td>985.869</td>
<td>0.3760</td>
<td>0.000</td>
</tr>
<tr>
<td>O$^{2-}$...O$^{2-}$</td>
<td>22764.300</td>
<td>0.1490</td>
<td>27.890</td>
</tr>
</tbody>
</table>

(ii) Shell Model$^a$

<table>
<thead>
<tr>
<th>Species</th>
<th>Y (e)</th>
<th>k (eVÅ$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr$^{4+}$</td>
<td>1.350</td>
<td>169.617</td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>-2.077</td>
<td>27.290</td>
</tr>
</tbody>
</table>

$^a$ Y and k refer to the shell charge and harmonic force constant respectively; Note: Region I = 300 ions; Potential cut-off = 10.254 Å

The cell dimensions and ion positions were then equilibrated under conditions of constant pressure. The resulting bond distances and other properties are displayed in Table 3.2, along with experimental values where available. Examination of the differences between the calculated and observed separations and properties, shows that these potentials have accurately reproduced the cubic fluorite phase. We note that the calculated static dielectric constant accords well with the observed value, although additional experimental data is
always useful in further validating and refining the potential model.

Table 3.2 - Calculated and observed properties of cubic ZrO$_2$

(i) Interatomic separations (Å)

| Separation | $r$ (calc.) | $r$ (expt.)$^a$ | $|\Delta|$ |
|------------|-------------|----------------|----------|
| Zr-O       | 2.176       | 2.204$^a$      | 0.028    |
| O-O        | 2.538       | 2.563$^a$      | 0.025    |
| Zr-Zr      | 3.620       | 3.589$^b$      | 0.031    |

$^a$ Data from [103]; $^b$ [104]

(ii) Calculated properties of the perfect crystal

<table>
<thead>
<tr>
<th>Property</th>
<th>ZrO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice energy per formula unit (eV)</td>
<td>-109.76</td>
</tr>
<tr>
<td>$a = b = c$ (Å)</td>
<td>5.076 (5.07)$^c$</td>
</tr>
<tr>
<td>Elastic constants ($10^{11}$ dyn cm$^{-2}$)</td>
<td></td>
</tr>
<tr>
<td>$c_{11}$</td>
<td>61.63 (40.09)$^d$</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>11.96</td>
</tr>
<tr>
<td>$c_{13}$</td>
<td>11.96</td>
</tr>
<tr>
<td>$c_{33}$</td>
<td>61.63</td>
</tr>
<tr>
<td>$c_{44}$</td>
<td>10.08</td>
</tr>
<tr>
<td>$c_{66}$</td>
<td>10.08</td>
</tr>
<tr>
<td>Dielectric constants</td>
<td></td>
</tr>
<tr>
<td>$\langle \varepsilon_0 \rangle$</td>
<td>26.90 (29.3)$^d$</td>
</tr>
<tr>
<td>$\langle \varepsilon_{oo} \rangle$</td>
<td>2.63</td>
</tr>
</tbody>
</table>

$^c$ Experimental value from [89]; $^d$ [103]
3.4 Intrinsic Atomic Defects

Initial calculations evaluated the energetics of the creation of isolated point defects, i.e. vacancies and interstitials; the resulting energies are reported in Table 3.3. The vacancy energy consists of removing a host ion, from the perfect crystal, to infinity; likewise the interstitial energy corresponds to bringing in an ion, from infinity, into the perfect crystal. In all cases the interstitial site is located at \((\frac{1}{2}, 0, 0)\), which is at the centre of the empty, eight coordination site in the oxygen sub-lattice (Figure 1.7). All the calculations employed full lattice relaxation around the defect, as described in Chapter 2.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vacancy</strong></td>
<td></td>
</tr>
<tr>
<td>Zr(^{4+})</td>
<td>86.05</td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>15.00</td>
</tr>
<tr>
<td><strong>Interstitial</strong></td>
<td></td>
</tr>
<tr>
<td>Zr(^{4+})</td>
<td>-65.58</td>
</tr>
<tr>
<td>O(^{2-})</td>
<td>-9.34</td>
</tr>
</tbody>
</table>

The individual point defect energies were combined to give formation energies for Frenkel \([105]\) and Schottky \([106]\) disorder. These disorders are represented by the reactions, given by equations 3.1 - 3.3, using Kröger-Vink notation \([27]\), with their formation energies reported in Table 3.4.

\[
\text{Schottky defect} \quad \text{Zr}_{\text{int}}^{4+} + 2\text{O}_{\text{int}}^{2-} \leftrightarrow \text{V}_{\text{Zr}}^{\text{m}} + 2\text{V}_{\text{o}}^\text{m} + \text{ZrO}_{2\text{ vacancy}} \quad (3.1)
\]

\[
\text{Cation Frenkel} \quad \text{Zr}_{\text{int}}^{4+} \leftrightarrow \text{Zr}_{\text{int}}^{4+} \quad \text{V}_{\text{Zr}}^{\text{m}} \quad (3.2)
\]
Anion Frenkel \[ \text{O}^{2-}_{\text{int}} \leftrightarrow \text{O}^{+}_{i} + \text{V}_{o} \] (3.3)

where the symbols are indicative of the type of defect, i.e. V for vacancy, i for interstitial and the superscripts, * (positive), ' (negative) indicate the charge of the defect relative to the normal site [27].

Table 3.4 - Calculated formation energies for intrinsic disorder

<table>
<thead>
<tr>
<th>Type of defect</th>
<th>Energy (eV/defect)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky</td>
<td>2.10</td>
</tr>
<tr>
<td>Frenkel</td>
<td></td>
</tr>
<tr>
<td>Cation</td>
<td>10.23</td>
</tr>
<tr>
<td>Anion</td>
<td>2.80</td>
</tr>
</tbody>
</table>

It is apparent that the Schottky disorder energy is slightly lower than the anion Frenkel energy as was found by Dwivedi and Cormack [103] and Mackrodt and Woodrow [107]. This is interesting because this is not the case in many fluorite-structured oxides. This may be explained in terms of ion size factors: the Zr\(^{4+}\) (0.72\(\text{Å}\)) is much smaller than most cations in fluorite-structured compounds, hence because of its small radii, it has a natural tendency to transform the surrounding lattice into the monoclinic form. In this form Zr\(^{4+}\) is sevenfold coordinated by oxygen ions, providing a closer packing of oxygen ions around the cation. The closer packing can be improved by the removal of an oxygen ion (creating an oxygen vacancy), but is impaired by the creation of an oxygen interstitial. In any case, the magnitude of the formation energies suggest a low concentration of intrinsic defects in ZrO\(_2\). The defect chemistry of ZrO\(_2\) will therefore be dominated by the incorporation of dopants.
3.5 Dopant Substitution

It is well established that the addition of aliovalent dopant ions (e.g. Ca\(^{2+}\), Y\(^{3+}\)) to ZrO\(_2\) act to stabilise the high temperature cubic polymorph at ambient temperatures [96]. To maintain charge neutrality, anion vacancies are created which are distributed randomly in the lattice, and are the main reason for the outstanding ionic conduction exhibited by stabilised ZrO\(_2\) [97-99,108,109]. The most straight forward mode of dopant incorporation into the host lattice is as a substitutional ion at a Zr\(^{4+}\) site with compensating oxygen vacancies. This process of dopant substitution can be represented by the following defect equations:

\[
\text{MO} + \text{Zr} + \rightarrow \text{MZr} + \text{V}_0 + \text{ZrO}_2 \\
\text{M}_2\text{O}_3 + 2\text{Zr} \rightarrow 2\text{MZr} + \text{V}_0 + 2\text{ZrO}_2
\]

where M\(^{2+}\) and M\(^{3+}\) represent di- and trivalent dopant substitution, respectively. From our simulation approach we can calculate the energetics of these ‘solution’ reactions (\(E_{\text{soln}}\)) by combining the appropriate defect and lattice energy terms (\(U_L\)), as represented by the following equations:

\[
E_{\text{soln}} = E(M^{2+}) + E(V_0) + U_L(ZrO_2) - U_L(MO) \\
E_{\text{soln}} = 2E(M^{3+}) + E(V_0) + 2U_L(ZrO_2) - U_L(M_2O_3)
\]

It is well documented that some of the most favourable dopants in ZrO\(_2\) are the alkaline-earth and rare-earth ions [6,9,89,90,91,100]. Therefore, we have examined the substitution of these dopants into ZrO\(_2\) in detail, as well as extending the study to include a range of di- and trivalent metal dopants.

3.5.1 Alkaline-earth Dopants

Our calculated energies of solution for the alkaline-earth dopants (Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\) and Ba\(^{2+}\)) are reported in Table 3.5, and plotted versus ion radius in Figure 3.1. As an initial test of our
simulation methods, we have employed two sets of potential parameters for the dopant species derived by Lewis and Catlow [71], which are listed in Appendix 1.

Table 3.5 - Energies of solution for the alkaline-earth metals

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$E_{\text{soln}}$ (eV/dopant)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Potential Set 1</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>1.43</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1.29</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>2.27</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>6.96</td>
</tr>
</tbody>
</table>

Figure 3.1 - Energies of solution for the alkaline-earth dopants as a function of dopant radius (lines are guides to the eye)
From an examination of the results it is clear that the most favourable solution energy, and hence the highest solubility is predicted for Ca$^{2+}$. The favourable solubility of Ca$^{2+}$ is clearly illustrated in Figure 3.1 which shows a strong degree of correlation between the solution energy and dopant size, with a clear minimum at Ca$^{2+}$. Moreover, our results accord well with experimental studies which have demonstrated how the addition of Ca$^{2+}$ to ZrO$_2$ not only stabilises the cubic phase, but improves ionic conduction [9,90,91,100-108,110-113]. In addition, we find that the two sets of potentials for the alkaline-earth dopants produce good quantitative agreement which provides further support for our simulation methods. It is noted that Mg$^{2+}$ also shows a relatively low solution energy in ZrO$_2$ which suggests that this dopant could be used as a stabiliser. However, experimental work has shown the instability of ZrO$_2$-MgO solid solutions at high temperatures [91], whilst any significant solubility of Sr$^{2+}$ has been discounted experimentally [114,115]. The incorporation of Ba$^{2+}$ (ionic radius 1.36\AA) into the host lattice is highly unfavourable, and this is probably due to the large size ‘mismatch’ with the host Zr$^{4+}$ (0.72\AA).

3.5.2 Rare-earth Dopants

The calculated solution energies for the rare-earth dopants (Y$^{3+}$, La$^{3+}$, Nd$^{3+}$ and Gd$^{3+}$) are shown in Table 3.6 and plotted versus dopant radius in Figure 3.2. The potential parameters utilised for the rare-earth dopants were also taken directly from Lewis and Catlow [71] and are listed in Appendix 1. The lowest solution energy, and therefore highest solubility, is predicted for Y$^{3+}$. Figure 3.2 shows a clear minimum at this dopant, as well as a degree of correlation between the solution energy and dopant size. The negative solution energy would suggest that Y$^{3+}$ would be a very favourable stabilising agent in ZrO$_2$. Indeed, this result accords well with experimental work in which yttria-stabilised ZrO$_2$ is one of the most widely used solid
electrolytes for applications requiring high oxygen ion conductivity [9,91,95,96,100,108,116-123]. Gd$^{3+}$ also has a fairly favourable solution energy, and an ionic radius similar to Y$^{3+}$. However, there are no reports of ZrO$_2$-Gd$_2$O$_3$ being utilised for electrolyte applications, although Gd$^{3+}$ is widely used as a dopant in the CeO$_2$-based oxygen ion conductor [129,130].

Table 3.6 - Energies of solution for the rare-earth metal ions

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$E_{\text{soln}}$ (eV/dopant)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$^{3+}$</td>
<td>-3.13</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>0.39</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>3.99</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>5.28</td>
</tr>
</tbody>
</table>

Figure 3.2 - Energies of solution for the rare-earth dopants as a function of dopant radius
3.5.3 Transition Metal Dopants

A variety of cations are known to act as stabilisers in ZrO₂, preventing unfavourable transformations at lower temperatures [124]. As a possible predictive tool, we have incorporated a range of transition metal ions and Al³⁺ into ZrO₂, and calculated the energetics of solution for these dopants. To our knowledge, this is largest range of dopants in ZrO₂ that have been investigated using simulation techniques. The potential parameters for this set of dopants are again listed in Appendix 1. Tables 3.7 and 3.8 show our calculated energies of solution for the di- and trivalent metal dopants, respectively. These energies are plotted as a function dopant size in Figures 3.3 and 3.4.

<table>
<thead>
<tr>
<th>Divalent Metal Dopant</th>
<th>E_{soln} (eV/dopant)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn²⁺</td>
<td>1.42</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>1.89</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>2.22</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>2.57</td>
</tr>
<tr>
<td>aCu²⁺</td>
<td>1.79</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>1.88</td>
</tr>
</tbody>
</table>

* Potential parameter from [125]

<table>
<thead>
<tr>
<th>Trivalent Metal Dopant</th>
<th>E_{soln} (eV/dopant)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al³⁺</td>
<td>4.27</td>
</tr>
<tr>
<td>Sc³⁺</td>
<td>-0.01</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>1.82</td>
</tr>
<tr>
<td>Mn³⁺</td>
<td>1.21</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>2.20</td>
</tr>
</tbody>
</table>
Figure 3.3 - Energies of solution for divalent metal dopants as a function of dopant radius

Figure 3.4 - Energies of solution for trivalent metal dopants as a function of dopant radius
From an examination of the results, Sc$^{3+}$ exhibits the lowest solution energy, and therefore, it may be suggested that scandia-stabilised zirconia could be a promising electrolyte. Indeed, it has been shown that this material exhibits a higher conductivity than both yttria and calcia-stabilised zirconia [91]. However, it is not widely utilised within SOFC configurations, largely due to cost considerations and economic factors. Experimental studies of Al$_2$O$_3$, Fe$_2$O$_3$ and Cr$_2$O$_3$ have found that the solubility of these compounds in ZrO$_2$ to be in the range of 0.6 - 3.0 mol% [97,126]. Mn$^{3+}$ shows a fairly favourable solution energy, although a study by Dravid et. al. [127] on the valence state of manganese in ZrO$_2$ states that the dopant is present as Mn$^{2+}$.

### 3.6 Dopant-Vacancy Clustering

From experimental studies it is has been shown that interactions between dopant ions and their charge-compensating vacancies lead to distinct dopant-vacancy clusters. For example, in yttria doped ceria it has been shown that the conductivity is controlled by the extent of dopant-vacancy interactions [58,128-131]. This effect is believed to be due to the variation in the strength of the 'trapping' of the mobile oxygen vacancy by the dopant ion, and therefore having a direct effect on oxygen vacancy migration [54]. At low defect concentrations simple clusters are formed, which add a binding energy term to the Arrhenius energy of ionic conduction. It has been demonstrated, both experimentally and theoretically, that the elastic strain energy between the dopant and the oxygen vacancy is at least as important as the electrostatic term [58,128,132].

Consequently, we have considered various cluster configurations in ZrO$_2$ involving the dopants considered above (§3.5). The first set of clusters involve an oxygen vacancy located at
Dopant Substitution and Defect Clustering in Zirconia

either a nearest-neighbour (NN) or next-nearest-neighbour (NNN) sites to the dopant ion. These simple pair clusters are illustrated in Figure 3.5. The cluster binding energies (with respect to isolated defects) are calculated using equations 3.8 and 3.9 for di- and trivalent dopants, respectively. The corresponding binding energies \( (E_{\text{bind}}) \) are reported in Tables 3.9 and 3.10.

\[
\text{divalent dopant:} \quad E_{\text{bind}} = \left[ M_{\text{Zr}} \cdot V_{\text{O}}^\ast \right] - M_{\text{Zr}} - V_{\text{O}} \quad (3.8)
\]

\[
\text{trivalent dopant:} \quad E_{\text{bind}} = \left[ M_{\text{Zr}}' \cdot V_{\text{O}}^\ast \right] - M_{\text{Zr}}' - V_{\text{O}} \quad (3.9)
\]

![Figure 3.5 - Schematic of simple pair clusters in ZrO2](image)

Focusing on the results for the NN and NNN clusters, several interesting points arise. The negative binding energies show that the clusters are generally bound. In particular, the binding energy of \(-0.26 \text{ eV}\) for \(Y^{3+}\) accords with recent conductivity studies [100,136]. In addition, the stronger binding energy for \(Mn^{2+}\) in comparison with \(Mn^{3+}\) will enhance the solubility of
Mn$^{2+}$ to a greater extent. This is in accord with the observation of the Mn$^{2+}$ state in ZrO$_2$ [127]. In general, our results show that the larger ("oversized") dopants are more strongly bound to an oxygen vacancy at the NNN site, whereas the smaller trivalent metal ions generally favour the cluster with a NN vacancy.

Table 3.9 - Binding energies for dopant-vacancy pair clusters: alkaline- and rare-earth metals

<table>
<thead>
<tr>
<th>Dopant Ion</th>
<th>E$_{\text{bind}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NN</td>
</tr>
<tr>
<td><strong>Alkaline-earths</strong></td>
<td></td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>-0.43</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>-0.31</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>-0.43</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>-0.79</td>
</tr>
<tr>
<td><strong>Rare-earths</strong></td>
<td></td>
</tr>
<tr>
<td>Y$^{3+}$</td>
<td>0.18</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>0.20</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>0.21</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 3.10 - Binding energies for dopant-vacancy pair clusters: di- and trivalent metal ions

<table>
<thead>
<tr>
<th>Divalent metal dopants</th>
<th>E$_{\text{bind}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NN</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>-0.39</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>-0.42</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>-0.44</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>-0.47</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>-0.58</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>-0.47</td>
</tr>
<tr>
<td><strong>Trivalent metal dopants</strong></td>
<td></td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>-0.53</td>
</tr>
<tr>
<td>Sc$^{3+}$</td>
<td>-0.04</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>-0.29</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>-0.26</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>-0.28</td>
</tr>
</tbody>
</table>
This observation can be explained in co-ordination terms: the trivalent metal dopants have a smaller radius than Zr$^{4+}$ (0.72 Å) and prefer to be seven-fold co-ordinated. The larger dopants prefer to be eight-fold co-ordination and therefore impose a cubic symmetry on the surrounding anion sub-lattice. This may be one of the reasons why they act as good stabilisers of the cubic phase. Moreover, these observations are in agreement with recent experimental and theoretical studies [97,103] as discussed in section 3.2. To summarise the results, Figure 3.6 shows the variation of the dopant-vacancy binding energies with ion radius for the most favourable dopants (in terms of their solution energy). It is interesting to note that for the stability of the NN and NNN configurations the "crossover" point is at a radius of approximately 0.7 Å which corresponds closely to the radius of Zr$^{4+}$ (0.72 Å). This is consistent with the view that Zr$^{4+}$ is the smallest ion possible in maintaining the fluorite structure [97,103].

![Figure 3.6 - Variation of dopant-vacancy binding energies with dopant radius for favourable dopants](image)

Figure 3.6 - Variation of dopant-vacancy binding energies with dopant radius for favourable dopants
Having investigated pair clusters, we now examine larger neutral clusters involving di- and trivalent dopants but focusing our attention on dopants that were found to have favourable solution energies. Figure 3.7 depicts a schematic of two configurations of a neutral cluster involving trivalent dopants of the form \([M_{Zr}^3 \cdot V_0^+ \cdot M_{Zr}^3]^\nu\) in which the oxygen vacancy is at two different positions; in Table 3.11 we list calculated binding energies for these configurations.

![Schematic of a neutral cluster involving trivalent dopants with an oxygen vacancy located at positions 1 or 2](image)

**Figure 3.7 - Schematic of a neutral cluster involving trivalent dopants with an oxygen vacancy located at positions 1 or 2**

**Table 3.11 - Binding energies for neutral trivalent dopant-vacancy clusters**

<table>
<thead>
<tr>
<th>Trivalent dopant ion</th>
<th>(E_{\text{bind}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(V_0^- (1))</td>
</tr>
<tr>
<td>Sc(^{3+})</td>
<td>-0.08</td>
</tr>
<tr>
<td>Mn(^{3+})</td>
<td>-0.56</td>
</tr>
<tr>
<td>Y(^{3+})</td>
<td>0.31</td>
</tr>
<tr>
<td>Gd(^{3+})</td>
<td>0.26</td>
</tr>
</tbody>
</table>
As expected, the larger dopants prefer configuration 2, owing to the vacancy being at a NNN site, which leaves the dopant in an eight-fold co-ordination. The smaller Mn$^{3+}$ ion prefers configuration 1 because it is able to remain in a seven-fold co-ordination. It is worth noting that configuration 1 is comparable to a pair cluster where the oxygen vacancy is at a NN site to the dopant, while configuration 2 is comparable to an oxygen vacancy at a NNN site to the dopant. Therefore, on comparing the results in Table 3.11 with pair cluster binding energies (Tables 3.9 and 3.10), indicates that the pair clusters are bound to a lesser degree and that we would expect larger, stable clusters at higher dopant levels. This suggests that short-range ordering could occur as a precursor to the final 'stabilised' phase.

3.7 Local Structure Around Clusters

Insertion of a dopant ion that differs in size to Zr$^{4+}$ perturbs the surrounding host lattice [95], which in turn may effect the mobility of a migrating oxygen. A number of experimental techniques are available to examine this distorted local structure including EXAFS (as discussed in §3.2). In previous sections we have shown that Ca$^{2+}$, Sc$^{3+}$, Mn$^{2+}$ and Y$^{3+}$ have the most favourable dopant solution energies. We have therefore examined, in detail, the local structure around simple pair clusters involving these four dopants. As already noted, the pair clusters are of the form \([M_z\cdot V_o]^n\) and \([M_z\cdot V_o^-]\) for di- and trivalent dopants, respectively. We have focused on clusters where the oxygen vacancy is located at either a NN or NNN site to the dopant (Figure 3.5), and calculated the interatomic separations (Table 3.12).
Table 3.12 - Calculated and experimental interatomic separations

(a) - Oxygen vacancy located at a NN site to the dopant

<table>
<thead>
<tr>
<th>Separation</th>
<th>$r$ (calc.) / Å</th>
<th>$r$ (expt.) / Å</th>
<th>$\Delta r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^a$Ca-O</td>
<td>2.377</td>
<td>2.230</td>
<td>0.147</td>
</tr>
<tr>
<td>Zr-O</td>
<td>2.117</td>
<td>2.120</td>
<td>0.003</td>
</tr>
<tr>
<td>Zr-Ca</td>
<td>3.680</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^b$Y-O</td>
<td>2.267</td>
<td>2.330</td>
<td>0.340</td>
</tr>
<tr>
<td>Zr-O</td>
<td>2.119</td>
<td>2.150</td>
<td>0.031</td>
</tr>
<tr>
<td>Zr-Y</td>
<td>3.724</td>
<td>3.580</td>
<td>0.144</td>
</tr>
<tr>
<td>Mn-O</td>
<td>2.310</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-O</td>
<td>2.047</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-Mn</td>
<td>3.751</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc-O</td>
<td>2.185</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-O</td>
<td>2.047</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-Sc</td>
<td>3.746</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) - Oxygen vacancy located at a NNN site to the dopant

<table>
<thead>
<tr>
<th>Separation</th>
<th>$r$ (calc.) / Å</th>
<th>$r$ (expt.) / Å</th>
<th>$\Delta r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^a$Ca-O</td>
<td>2.437</td>
<td>2.230</td>
<td>0.207</td>
</tr>
<tr>
<td>Zr-O</td>
<td>2.120</td>
<td>2.120</td>
<td>0.000</td>
</tr>
<tr>
<td>Zr-Ca</td>
<td>3.550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^b$Y-O</td>
<td>2.340</td>
<td>2.330</td>
<td>0.010</td>
</tr>
<tr>
<td>Zr-O</td>
<td>2.117</td>
<td>2.150</td>
<td>0.033</td>
</tr>
<tr>
<td>Zr-Y</td>
<td>3.576</td>
<td>3.580</td>
<td>0.004</td>
</tr>
<tr>
<td>Mn-O</td>
<td>2.394</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-O</td>
<td>2.121</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-Mn</td>
<td>3.597</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc-O</td>
<td>2.278</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-O</td>
<td>2.119</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-Sc</td>
<td>3.590</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Experimental values from [97]; $^b$ [95]; Note: All separations refer to NN oxygen ions.
Several key results emerge from our analysis. The average Zr-O bond lengths presented in Table 3.12 are lower than the Zr-O bond lengths in the pure crystal which is in accord with EXAFS measurements [95]. In the NN case the dopant-O bond lengths are less than the Zr-O bond lengths in the pure crystal, whereas in the NNN case the dopant-O bond length is greater. This result can be accounted for by considering the co-ordination number of the dopant cation and the Zr\(^{4+}\) at the NN site: when either ion is in a seven-fold co-ordination a lower average bond length is expected. Li et. al. [97] suggest that when an oxygen vacancy is sited NNN to the dopant cation, the Zr-dopant bond length decreases to between 3.58 and 3.60\(\text{Å}\). Our results are in accord with this observation which give the mean Zr-dopant bond length as 3.58\(\text{Å}\).

From the data collected we have also investigated the displacement of ions surrounding the dopant and our findings are depicted graphically in Figure 3.8. The results are supported by XAS data from Li et. al. [97] who find that oxygen ions adjacent to an oxygen vacancy are displaced towards it. We also find an off-centre displacement of the dopant cation, which is also consistent with the findings of Li et. al. [97]. Note that for Sc\(^{3+}\), which has an ionic radius close to Zr\(^{4+}\), we find the distortion of the host lattice is very severe. Therefore we suggest that dopants with an ionic radius similar or smaller than Zr\(^{4+}\), cause greater distortions than larger dopants. Table 3.13 lists the average displacement of oxygen ions that immediately surround the oxygen vacancy. We only present the values for the NNN case which is found to be the most stable configuration.
Figure 3.8 - Displacement of ions (a) an oxygen vacancy at a NN site to the dopant, (b) an oxygen vacancy at a NNN site to the dopant

Table 3.13 - Average displacement of oxygen ions surrounding an oxygen vacancy located at a NNN site to the dopant

<table>
<thead>
<tr>
<th>Dopant ion</th>
<th>Average oxygen ion displacement (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>0.44</td>
</tr>
<tr>
<td>Sc$^{3+}$</td>
<td>0.42</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>0.43</td>
</tr>
<tr>
<td>Y$^{3+}$</td>
<td>0.41</td>
</tr>
</tbody>
</table>
It is clear from Table 3.13 that there is significant oxygen ion displacement within the defect cluster. Therefore, these lower-valent dopants lead to considerable perturbation of the local structure.

3.8 Nb/Y co-doping

The anode material for solid oxide fuel cells should exhibit good mixed conducting properties at low oxygen partial pressures [9]. The combination of good oxygen ion conductivity with high electronic conductivity affords a greatly increased effective surface area for the electrode reaction and, hence improves efficiency [133]. Fluorite-based oxides, such as doped CeO$_2$ and stabilised ZrO$_2$, offer exceptionally high oxygen ion conductivity, and it is possible to induce electronic conductivity in reducing environments by doping these materials with early transition metals, e.g. Nb$^{5+}$ and Ti$^{4+}$. However, the solubility of these ions is low in both CeO$_2$ and ZrO$_2$ [134,135], and large quantities are required to achieve a reasonable level of electronic conductivity. Such high levels of pentavalent dopant are also believed to be detrimental to ionic conductivity.

A recent ac impedance spectroscopy and neutron powder diffraction study by Irvine et. al. [136] proposed that co-doping with Nb$^{5+}$ in cubic Y/ZrO$_2$ would be less detrimental to ionic conductivity based on electrostatic and size considerations. They have gone as far as saying that the introduction of Nb$^{5+}$ into heavily doped Y/ZrO$_2$ may reduce dopant-vacancy associations and therefore increase oxygen ion conductivity.

We have therefore carried out a preliminary study of the Nb$_2$O$_5$:Y$_2$O$_3$:ZrO$_2$ system. The GULP code [68,69] has been employed which allows fractional occupancies to be specified
for crystallographic sites, implemented through a mean field approach. This consists of scaling the interatomic potentials by the product of the site occupancies. For example, in the case of ZrO$_2$ containing Y, this feature allows homogenous distributions of the dopant.

In the co-doped system there will exist two types of substitution: zirconium being replaced by the pentavalent niobium and the trivalent yttrium. Therefore, there will be three types of defect in this system: Nb$_{Zr}$, Y$_{Zr}$ and V$_{O}$. As a significant population of oxygen vacancies are required to stabilise the cubic fluorite structure, the concentration of trivalent dopant must always be significantly higher than that of the pentavalent ion [136]. The equation for the incorporation of the two dopants can be written as:

$$\frac{1}{2} \text{Nb}_2\text{O}_5 + \frac{3}{2} \text{Y}_2\text{O}_3 + 4\text{Zr}_{Zr} + \text{O}_0^x \rightarrow \text{Nb}_{Zr}^x + 3\text{Y}_{Zr}^x + \text{V}_{O}^x + 4\text{Zr}_2\text{O}_2$$  \hspace{1cm} (3.10)

where we have considered a higher level for Y doping. The use of the mean field approach involved an additional step in evaluating defect energies, which needs to be described briefly. If we indicate with a M the “hybrid” Zr/Y cation present at each cationic site of the Zr$_{1-x}$Y$_x$O$_2$.8 solid solution, then the substitution of a lattice Zr$^{4+}$ with a Nb$^{5+}$ must be preceded by the substitution of a “hybrid” cation with a Zr$^{4+}$ according to: $M^x_M \rightarrow \text{Zr}^x_M \rightarrow \text{Nb}_{Zr}$. Using this approach allows us to set up a ‘baseline’ for our defect calculations. The resulting vacancy and substitution energies for various Y levels (x) in Zr$_{1-x}$Y$_x$O$_2$.8 are listed in Table 3.14.

<table>
<thead>
<tr>
<th>x</th>
<th>Nb$_{Zr}$ energy (eV)</th>
<th>V$_{O}$ energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-44.98</td>
<td>15.00</td>
</tr>
<tr>
<td>0.10</td>
<td>-43.37</td>
<td>15.64</td>
</tr>
<tr>
<td>0.25</td>
<td>-43.02</td>
<td>15.95</td>
</tr>
</tbody>
</table>
Chapter 3  
Dopant Substitution and Defect Clustering in Zirconia

As with our previous dopant calculations (§3.5), the energetics of solution for reaction (3.10) were evaluated from the following equation:

\[ E_{\text{soln}} = E(\text{Nb}_2\text{Zr}) + 3(\text{Y}_2\text{Zr}) + E(\text{Y}_{\text{O}}) + 4U_{\text{L}}(\text{ZrO}_2) - \frac{1}{2}U_{\text{L}}(\text{Nb}_2\text{O}_5) - \frac{3}{2}(\text{Y}_2\text{O}_3) \]  

(3.11)

The resulting energies of solution are presented in Table 3.15, from which it is clear that as yttria content increases from \( x = 0.0 \) to \( x = 0.25 \), there is a significant decrease in solution energy. Therefore, the calculations suggest that (on energetic grounds) the presence of yttrium promotes the solution of Nb\(^{5+}\) in zirconia. This is consistent with observation which finds that the solubility of such pentavalent ions is low in pure ZrO\(_2\).

Table 3.15 - Solution energy of Nb\(^{5+}\) in \( \text{Zr}_{1-x}\text{Y}_x\text{O}_{2.8} \)

<table>
<thead>
<tr>
<th>( x )</th>
<th>( E_{\text{soln}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>3.24</td>
</tr>
<tr>
<td>0.10</td>
<td>-3.66</td>
</tr>
<tr>
<td>0.25</td>
<td>-3.00</td>
</tr>
</tbody>
</table>

Extending the experimental work on the Nb/Y/ZrO\(_2\) system [136], we have investigated the local structure around the Nb substitutional with the average displacements of lattice species reported in Table 3.16. The largest displacements occur for the nearest-neighbour (NN) anions which can be rationalised in terms of ion size effects. The Nb\(^{5+}\) (0.64\(\text{Å}\)) has a smaller ionic radius than the host cations, and as we have shown previously (§3.7) this size mismatch can cause severe distortions of the surrounding anion sub-lattice. However, the perturbation of the local structure is not as severe as that calculated for the lower valent dopants such as Ca\(^{2+}\) and Mn\(^{2+}\) (Table 3.13).
Table 3.16 - Average displacements due to the Nb dopant in Zr$_{0.9}$Y$_{0.1}$O$_{2.8}$

<table>
<thead>
<tr>
<th>Species</th>
<th>Displacement (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$^{5+}$</td>
<td>0.09</td>
</tr>
<tr>
<td>Y$^{3+}$ and Zr$^{4+}$ (NN)</td>
<td>0.09</td>
</tr>
<tr>
<td>O$^{2-}$ (NN)</td>
<td>0.12</td>
</tr>
<tr>
<td>O$^{2-}$ (NNN)</td>
<td>0.09</td>
</tr>
</tbody>
</table>

3.9 Summary

In this Chapter we have demonstrated the application of atomistic simulation techniques to the study of the defect chemistry of zirconia. We also note that in this investigation we have examined a wider range of dopants than previous experimental work; the following conclusions can be drawn:

(i) Favourable dopants (on energetic grounds) are calculated to be: MgO, CaO, MnO, Mn$_2$O$_3$, Y$_2$O$_3$, Gd$_2$O$_3$ and Sc$_2$O$_3$. The ‘solution’ of these dopants will enhance oxygen diffusivity owing to the increase in the oxygen vacancy concentration. These results accord with experimental work in which these dopants are used to enhance oxygen ion conductivity in zirconia.

(ii) The calculations on defect clusters find that cation dopants with a larger ionic radii than the host Zr$^{4+}$ prefer the charge-compensating vacancy to be at a next-nearest-neighbour (NNN) site, leaving them in an eight-fold co-ordination; conversely “undersized” dopants prefer the vacancy to be situated at nearest-neighbour (NN) positions. Moreover, this observation is in accord with EXAFS studies on calcia- and yttria-stabilised zirconia.
(iii) Dopants with similar or smaller ionic radii than the host $\text{Zr}^{4+}$ cause a greater perturbation of the host lattice than larger dopants. The ion displacement trends produced by our simulation techniques have reproduced similar trends found from XAS studies.

(iv) From our Nb/Y co-doping simulations we have shown how the presence of yttria greatly promotes the solution of Nb in cubic zirconia. We have also shown that Nb substitution for zirconium leads to only minor distortions in the surrounding anion sub-lattice.
Chapter 4

Molecular Dynamics Study of Oxygen Diffusion in Stabilised Zirconia

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Chapter 4: *Molecular Dynamics Study of Oxygen Diffusion in Stabilised Zirconia*

### 4.1 Introduction

As discussed in earlier chapters, the wide spread use of yttria-stabilised zirconia (YSZ) can be attributed to exceptionally high oxygen ion conductivity, adequate stability within both oxidising and reducing atmospheres and negligible electronic conductivity [9,91]. Because of the technological importance of this system there is a need to obtain a greater insight as to the oxygen transport properties.

We have already obtained, via static lattice simulations, valuable information on some of the factors controlling oxygen transport in stabilised zirconia, as well as on the effects of dopant substitution (Chapter 3). To further amplify this knowledge we have employed Molecular Dynamics (MD) techniques which are well-suited to probing ion transport on the atomic scale and include thermal effects explicitly. The temperature and concentration of charge carriers can have a direct effect on ion diffusion and can be modelled by MD methods; the results obtained are also directly comparable with experimental diffusion data. Whereas static lattice methods are used to probe the energetics and pathway of a single migrating ion, MD can view the time evolution of the whole system. Moreover, these techniques have been complimentary to static lattice simulations by providing information on the mechanisms of diffusion in a wide of range materials, particularly fast-ion conductors such as Ag$_2$Te [137,138], $\beta$"-Al$_2$O$_3$ [139], Li$_3$N [140] and CaF$_2$ [141,142]. This study is analogous to previous MD work on yttria-stabilised zirconia [143-147] and is a natural extension of our simulations on dopants and cluster formation.
4.2 Simulation Model

In the present simulations we have constructed a supercell consisting of 6x6x6 fluorite unit cells, approximately 30Å in dimension, and containing 2592 ions (864 Zr⁴⁺ and 1728 O²⁻ ions) located at crystallographic sites. As detailed in Chapter 2 (Simulation Methods), the supercell is then repeated by applying periodic boundary conditions, which generate an unbounded system, and therefore eliminate any surface interactions. As with most MD simulations to date we have treated ion-ion interactions using the rigid ion model. The potential parameters are those that were successfully employed in our previous static lattice calculations on zirconia (Chapter 3) and have been transferred directly, excluding the shell model parameters (Table 4.1).

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A(eV)</th>
<th>ρ(Å)</th>
<th>C(eVÅ⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr⁴⁺...O²⁻</td>
<td>985.869</td>
<td>0.3760</td>
<td>0.000</td>
</tr>
<tr>
<td>O²⁻...O²⁻</td>
<td>22764.300</td>
<td>0.1490</td>
<td>27.890</td>
</tr>
<tr>
<td>Y³⁺...O²⁻</td>
<td>1345.100</td>
<td>0.3491</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The simulations were performed using the DL_POLY [80] code and under conditions of constant temperature (T) and pressure (P) by utilising the NPT ensemble of Berendsen [84]. The temperature was varied between 873 and 2073K, and the pressure kept constant at 1.0 atm. The simulations were run for a total of 53ps, with the system allowed to reach a state of equilibrium within the first 3ps. A time-step (δt) of 1fs (1 x 10⁻¹⁵s) was used; data collection occurred over a period of 50ps immediately after the 3ps equilibration period.
Chapter 4

Oxygen Diffusion in Stabilised Zirconia

Unit Cell Parameter

![Graph of Unit Cell Parameter vs Time (ps)]

Total Energy

![Graph of Total Energy vs Time (ps)]
Figure 4.1 - Time evolution of calculated properties (unit cell parameter, total energy, temperature and pressure) for undoped zirconia at 1000K
4.3 Pure Zirconia

Preliminary simulations were first performed on undoped zirconia at 1000K. The purpose of these calculations was to check the validity of the model and determine the correct values of any variables within the datasets (for example, the Ewald parameters which control Coulombic summations). The simulation time was reduced to 1ps, including a 1/3ps equilibration period, to allow us to diagnose any problems in an effective manner. The time evolution of several properties that were calculated during these ‘test’ runs is shown in Figure 4.1.

On inspection of Figure 4.1 it is clear that all the calculated physical properties are well within acceptable mean values. The temperature and pressure rapidly attain their predefined equilibrium values, as does the total energy of the system, which approaches a constant value in a very short span of time. The unit cell parameter shows slightly more deviation before reaching a value that is slightly increased from the mean crystallographic value of 5.127Å. This is to be expected since the interatomic potential parameters were effectively derived at 0K, and therefore at higher temperatures we would expect a degree of cell expansion.

4.3.1 Structural Information

Structural information, such as bond distances and local structure around a particular ion, can be derived from experimental techniques such as x-ray absorption spectroscopy (XAS) and extended x-ray absorption fine structure (EXAFS). From MD simulations, we can obtain similar information from the pair radial distribution function (RDF), which provides an insight into the long-range order (or disorder) of the crystal lattice. The partial pair distribution functions g(r), defined in Chapter 2, for Zr-Zr and O-O pairs are shown in Figure 4.2.
The Zr-Zr pair RDF reveals a series of sharp, well-defined peaks, which correspond to successive nearest-neighbour distances, and is normal for an ordered solid. In between the peaks the RDF falls to approximately zero which is typical for a high symmetry solid. In contrast, the O-O pair RDF shows some loss of long-range order in the oxygen sub-lattice.
which can be rationalised in terms of size effects. In Chapter 3 we have already shown that
cation dopants with an ionic radii larger than Zr$^{4+}$ are better stabilisers of the cubic phase than
smaller dopants. These larger dopants impose a cubic symmetry on the surrounding oxygen
sub-lattice, while the smaller dopants cause a perturbation of this lattice. Therefore, the lack of
an effective stabiliser in the undoped system, and the small size of the Zr$^{4+}$ ion causes an
extensive perturbation within the oxygen sub-lattice which is shown in Figure 4.2. With the
absence of any dopants, and the associated charge-compensating vacancies, we would expect
our calculated bond lengths derived from the RDF data to be in good agreement with those in
pure zirconia. Indeed, this is borne out in Table 4.2 which shows negligible deviation between
the reported and calculated separations of the cubic structure. Having established the validity
of our MD simulation model, we then focused our attention on the doped system.

| Separation | $r$ (calc.) | $r$ (expt.) | $|\Delta|$ |
|------------|------------|------------|---------|
| Zr - Zr    | 3.620      | 3.589$^a$  | 0.031   |
| O - O      | 2.570      | 2.563$^b$  | 0.007   |

$^a$[104], $^b$[103]

4.4 Yttria-stabilised Zirconia

Experimental conductivity measurements on YSZ utilising a variety of techniques including
low field dc conduction [120], quasielectric light scattering [116], impedance spectroscopy
[148] and tracer diffusion methods [152] have found that a maximum in the conductivity
occurs at about 8-10 mol% yttria doping [149,150]. In the simulation cell we randomly
replaced the required number of Zr$^{4+}$ ions with Y$^{3+}$ ions to give a dopant level of 10%.
Figure 4.3 - Radial distribution functions for Zr-Zr and Y-Y in 10YSZ at 1273K
introducing $\text{Y}^{3+}$ a charge imbalance arises and this is compensated by the introduction oxygen vacancies resulting in a cell containing 2549 ions ($86 \text{Y}^{3+}, 778 \text{Zr}^{4+}$ and $1685 \text{O}^{2-}$); this system was designated 10YSZ. The simulations were carried for a total of 53ps (including 3ps for equilibration) at a range of temperatures from 873 - 2073K covering those that typically occur for fuel cell applications. We note that previous MD simulations of YSZ carried out by Li and Hafskjold [143], Shimojo et. al. [144,145] and Okazaki et. al. [146,147] have utilised smaller cells and shorter simulation times compared to our model.

4.4.1 Structural Information

The cation-cation RDFs are shown in Figure 4.3, which reveal a series of sharp, well ordered peaks corresponding to successive nearest-neighbour distances. In contrast, the oxygen-oxygen RDF (Figure 4.4) show weak, diffuse structure for separations greater than nearest -
neighbour, indicating some loss of long-range order on the mobile oxygen sub-lattice. As the
temperature increases from 1273K to 2073K the first peak decreases in height, while
subsequent peaks broaden suggesting greater disorder and increased oxygen diffusion at
higher temperatures.

The calculated nearest-neighbour distances for all pair functions at 1273, 1773 and 2073K are
given in Table 4.3. On examination of these results we can see that as the temperature
increases there is a slight increase in the host Zr-Zr and O-O separations which is probably
due to cell expansion. The Zr-Y separation remains constant throughout the temperature
range, indicating that there is little cation displacement. The cation-oxygen separations show a
slight amount of variation which may be indicative of the greater disorder in the oxygen sub-
lattice. Comparing the calculated separations with those from x-ray absorption spectroscopy
(XAS) measurements [97] in Table 4.3 shows good agreement, which lends further support to
our simulations.

<table>
<thead>
<tr>
<th>Separation</th>
<th>1273K</th>
<th>1773K</th>
<th>2073K</th>
<th>Experimenta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Zr</td>
<td>3.64</td>
<td>3.64</td>
<td>3.65</td>
<td></td>
</tr>
<tr>
<td>Zr-O</td>
<td>2.11</td>
<td>2.09</td>
<td>2.07</td>
<td>2.15</td>
</tr>
<tr>
<td>Zr-Y</td>
<td>3.64</td>
<td>3.64</td>
<td>3.64</td>
<td>3.58</td>
</tr>
<tr>
<td>Y-O</td>
<td>2.32</td>
<td>2.30</td>
<td>2.32</td>
<td>2.33</td>
</tr>
<tr>
<td>Y-Y</td>
<td>3.65</td>
<td>3.67</td>
<td>3.64</td>
<td></td>
</tr>
<tr>
<td>O-O</td>
<td>2.60</td>
<td>2.61</td>
<td>2.63</td>
<td></td>
</tr>
</tbody>
</table>

a From [97] for 10mol% Y2O3-ZrO2
Within a solid oxide fuel cell configuration the thermal expansion of the electrolyte must be similar to the electrodes and interconnect materials, otherwise the cell may fracture [9]. For example, the typical anode material is a Ni/YSZ cermet which has a thermal expansion coefficient of about $12 \times 10^{-6}\ \text{K}^{-1}$ [151], which is close to that of YSZ. Figure 4.5 depicts our calculated variation of the lattice parameter with temperature in 10YSZ; this reveals the process of thermal expansion over the simulation temperature range is fairly linear. From Figure 4.5 we derive a thermal expansion coefficient of $11.09 \times 10^{-6}\ \text{K}^{-1}$, which compares well with a observed value for YSZ of $10.5 \times 10^{-6}\ \text{K}^{-1}$ [9].

![Figure 4.5 - Thermal expansion in 10YSZ](image)

4.4.2 Ion Diffusion

The dynamics of all ions in 10YSZ can be obtained from mean square displacement (MSD) data (Chapter 2). In Figure 4.6, the MSD data is plotted as a function of time for 10YSZ at 1273K. After the initial equilibration, the cation functions rapidly tend to a constant value with time, which confirms that there is no significant cation diffusion in 10YSZ. In contrast,
the oxygen function increases rapidly as a function of time, indicating significant ion diffusion. Therefore, it is clear that the presence of yttria as a stabiliser in zirconia enhances oxygen ion diffusion.

Figure 4.6 - Mean square displacement of all ion species in 10YSZ at 1273K

Figure 4.7 depicts the MSD of oxygen ions at 1273, 1773 and 2073K. The cations, which do not diffuse, have been omitted for clarity. It is clear that with an increase in temperature, there is an accompanied increase in oxygen diffusion.

From the slope of the MSD plot we may obtain the diffusion coefficient (D) according to the Einstein relationship:

\[
\langle r^2(t) \rangle = 6Dt + B
\]  

(4.1)

where B is the thermal (Debye-Waller) factor arising from atomic vibrations. The calculated diffusion coefficients at all simulation temperatures are listed in Table 4.4.
Figure 4.7 - Mean square displacement of oxygen ions in 10YSZ at 1273, 1773 and 2073K

Table 4.4 - Calculated rates of diffusion in 10YSZ

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>D (cm².s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>873K</td>
<td>0.19 x 10⁻⁶</td>
</tr>
<tr>
<td>1073K</td>
<td>0.34 x 10⁻⁶</td>
</tr>
<tr>
<td>1273K</td>
<td>0.70 x 10⁻⁶</td>
</tr>
<tr>
<td>1773K</td>
<td>2.12 x 10⁻⁶</td>
</tr>
<tr>
<td>2073K</td>
<td>3.00 x 10⁻⁶</td>
</tr>
</tbody>
</table>

From the calculated diffusion data we may evaluate an activation energy for oxygen migration using the standard Arrhenius relation,

\[ D = A \exp\left(\frac{-E_{\text{act}}}{kT}\right) \]  \hspace{1cm} (4.2)

where \( E_{\text{act}} \) is the activation energy, \( k \) the Boltzmann constant and \( A \) the pre-exponential factor.

Figure 4.8 shows an Arrhenius plot (\( \ln D \) versus \( 1/T \)), onto which data from experimental and
previous theoretical studies have been included. Our calculated slope is compatible with the available tracer experiments of Oishi and Ando [152] and the simulations of Li and Hafskjold [143]. Moreover, we find good quantitative agreement with calculated values at the highest temperature from studies of Okazaki et. al [147] and Shimojo et. al [144]. We should note that our simulations here have covered a wider temperature range than the tracer diffusion experiments and previous simulation studies [152].

![Figure 4.8 - Arrhenius plot for 10YSZ](image)

From our data in Figure 4.8 we derive an activation energy of 0.37 eV. This value is in reasonable agreement with an activation energy of 0.44 eV derived from tracer diffusion experiments [152]. Our results are also consistent with the MD study by Li and Hafskjold [143] which employed several sets of potential parameters and found that the calculated diffusion coefficients yielded activation energies in the range of 0.2 to 0.8 eV. However, this
value is lower than activation energies derived from bulk conductivity and ac impedance spectroscopy measurements which show significant scatter: values range from 0.79 to 1.12 eV [108,118,153]. One reason for this variation could be the incorporation of a binding energy term which arises from the 'trapping' of oxygen vacancies by the Y$^{3+}$ dopant to form defect clusters as discussed in the preceding chapter. It is also worth noting that a study by Adler and Smith [10] on oxygen transport in fluorite-structured Y/CeO$_2$ found an activation energy of 0.49 eV, with a corresponding binding energy of 0.49 eV.

4.5 Summary

Molecular dynamics techniques have been used to investigate structural and transport properties of oxygen ion diffusion in yttria-stabilised zirconia. Our study has covered a wider range of temperatures than both experimental and simulation work on this system. Several key points emerge:

(i) The pair distribution functions show considerable disorder in the oxygen sub-lattice. The degree of disorder increases with increasing temperature associated with enhanced oxygen diffusion. Calculated nearest-neighbour separations are in accord with EXAFS data on yttria-stabilised zirconia.

(ii) Oxygen diffusion coefficients have been calculated for Y/ZrO$_2$ between 873 and 2073K, and indicate rapid oxygen transport. Ion diffusion was not observed within the undoped system, confirming the need for yttria stabilisation to increase ionic conductivity.
(iii) Calculated activation energies, derived from our Arrhenius plots, are lower than most values derived from ionic conductivity studies. However, they accord well with energies derived from tracer diffusion experiments, and are within the range of energies computed by other groups.
Chapter 5

Defect Properties of the LaGaO$_3$-based Oxygen Ion Conductor

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<th>Page</th>
</tr>
</thead>
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</tbody>
</table>
Chapter 5: Defect Properties of the LaGaO$_3$-based Oxygen Ion Conductor

5.1 Introduction

It is generally accepted that if the operating temperature of the solid oxide fuel cell (SOFC) could be reduced from the high temperatures required (typically 1000°C) this would be a significant practical advance [9,154-156]. However, the conventional zirconia electrolyte does not exhibit sufficient oxygen ion conductivity to be used at lower temperatures.

Recent investigations [157-163] have discovered extremely high oxygen ion conductivity in the doped LaGaO$_3$ perovskite which is superior to that of Y/ZrO$_2$ at the lower operating temperature of 800°C. The incorporation of cation dopants (particularly Sr at La sites and Mg at Ga sites) gives rise to the highly mobile oxygen vacancies which are responsible for the observed ionic conductivity. More recent studies [162,163] have investigated the solid solution range of the La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$ system (LSGM) as a means of optimising the conduction properties. Tracer diffusion experiments at 1073K on the La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ system resulted in a diffusion coefficient of $3.24 \times 10^{-7}$ cm$^2$/s, with a calculated activation enthalpy of 0.79 eV, which is less than most reported values for yttria-stabilised zirconia [108,153]. It has been noted that the perovskite structure of LaGaO$_3$ also allows for a wider range in the choice of electrode materials than the fluorite-structured electrolytes [164]. For example, the fuel cell performance of a LSGM electrolyte coupled with Pt, LaMnO$_3$ or LaCoO$_3$ cathodes has been investigated [157-159,165-167].

The defect and ion transport properties of the perovskite-structured LaMO$_3$ oxides (where $M$ = Cr, Mn, Fe, Co) [53,54,168-170] have been studied previously by Islam and co-workers using...
computer simulation techniques. In this chapter we extend this work by a detailed investigation of the LaGaO$_3$-based system which is viewed as a promising oxygen ion conductor. Here we have focused our attention on the substitution of a range of dopant ions and the formation of dopant-vacancy clusters, as well as the energetics of oxygen ion migration. To our knowledge these studies are the first detailed survey of the LaGaO$_3$ material employing simulation methods.

5.2 Structure and Potentials

LaGaO$_3$ adopts the perovskite structure (§1.4) and contains double oxides of trivalent ions, La$_2$O$_3$ and Ga$_2$O$_3$. At room temperature LaGaO$_3$ has the orthorhombic structure (Pbnm) with lattice constants $a=5.487$, $b=5.520$ and $c=7.752\,\text{Å}$ [162]. Several authors have reported the lattice constants for this phase which show small differences.

![Perovskite structure of LaGaO$_3$](image.png)

Figure 5.1 - Perovskite structure of LaGaO$_3$ (a) cubic (b) orthorhombic (GaO$_6$ octahedron - yellow, La - green)

The structure of LaGaO$_3$ is built upon a framework of corner linked GaO$_6$ octahedra; the orthorhombic phase can be considered as due purely to tilts of these octahedra from the ideal
cubic structure (Figure 5.1). However, with the substitution of La and Ga by aliovalent dopants, the lattice parameters systematically change until eventually the ideal cubic structure results [162].

Table 5.1 - Interatomic potentials for LaGaO₃

(i) Short-range

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>ρ (Å)</th>
<th>C (eVÅ⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La³⁺ ... O²⁻</td>
<td>1545.21</td>
<td>0.3590</td>
<td>0</td>
</tr>
<tr>
<td>Ga³⁺ ... O²⁻</td>
<td>2901.12</td>
<td>0.2742</td>
<td>0</td>
</tr>
<tr>
<td>O²⁻ ... O²⁻</td>
<td>22764.30</td>
<td>0.1490</td>
<td>43.0</td>
</tr>
</tbody>
</table>

(ii) Shell model

<table>
<thead>
<tr>
<th>Species</th>
<th>Y (e)</th>
<th>k (eVÅ⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La³⁺</td>
<td>-0.25</td>
<td>145.0</td>
</tr>
<tr>
<td>Ga³⁺</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>O²⁻</td>
<td>-2.239</td>
<td>42.0</td>
</tr>
</tbody>
</table>

Potential cutoff = 12 Å; Y and k refer to the shell charge and harmonic spring constant, respectively.

The potential parameters for LaGaO₃ were derived by empirical procedures using the observed perovskite structure [171]. The potentials for the La-O and O-O interactions were transferred directly from the analogous simulation study of the LaMₐO₃ (where M = Cr, Mn, Fe, Co) perovskites [53,168] and are listed in Table 5.1. The calculated bond distances and lattice parameters are listed in Table 5.2, along with available experimental data. Examination of the differences shows good agreement between experimental and simulated structures. It is interesting to note that the mean value of our calculated static dielectric constants for cubic
and orthorhombic LaGaO$_3$ is 23.6 which is close to the observed value of ~ 25.

Table 5.2 - Calculated and Experimental Properties of Orthorhombic and Cubic LaGaO$_3$

<table>
<thead>
<tr>
<th>Property</th>
<th>Orthorhombic Calculated</th>
<th>Orthorhombic Experimental</th>
<th>Cubic Calculated</th>
<th>Cubic Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell parameters</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.485</td>
<td>5.527</td>
<td>3.875</td>
<td>3.875</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.752</td>
<td>7.781</td>
<td>3.875</td>
<td>3.875</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.481</td>
<td>5.496</td>
<td>3.875</td>
<td>3.875</td>
</tr>
<tr>
<td>α = β = γ</td>
<td>90.0</td>
<td>90.0</td>
<td>90.0</td>
<td>90.0</td>
</tr>
<tr>
<td>Bond distances (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La - O(1)</td>
<td>2.538</td>
<td>2.418</td>
<td>2.740</td>
<td>2.740</td>
</tr>
<tr>
<td>La - O(2)</td>
<td>2.541</td>
<td>2.400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga - O(1)</td>
<td>1.958</td>
<td>1.977</td>
<td>1.937</td>
<td>1.937</td>
</tr>
<tr>
<td>Ga - O(2)</td>
<td>1.960</td>
<td>1.956</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice energy (eV)</td>
<td>143.250</td>
<td>-</td>
<td>143.160</td>
<td>-</td>
</tr>
<tr>
<td>Dielectric constants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Static &lt;ε₀&gt;</td>
<td>16.79</td>
<td>~25$^c$</td>
<td>30.48</td>
<td>~25$^c$</td>
</tr>
<tr>
<td>High frequency &lt;ε₁&gt;</td>
<td>2.02</td>
<td>-</td>
<td>2.01</td>
<td></td>
</tr>
</tbody>
</table>

*a O'Bryan et. al. [172]; *b Geller [173]; *c Dube et. al. [174]

5.3 Intrinsic Defects

Initial calculations were performed to evaluate the energetics of formation of isolated point defects in the orthorhombic system, with the results listed in Table 5.3. It is important to stress that all the calculations employed full lattice relaxation around the defect (Chapter 2).
Table 5.3 - Calculated energies of isolated point defects

<table>
<thead>
<tr>
<th>Defect</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancy</td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>20.65</td>
</tr>
<tr>
<td>O(2)</td>
<td>20.62</td>
</tr>
<tr>
<td>Ga</td>
<td>60.80</td>
</tr>
<tr>
<td>La</td>
<td>43.21</td>
</tr>
<tr>
<td>Interstitial</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>-22.65</td>
</tr>
<tr>
<td>Ga</td>
<td>-41.30</td>
</tr>
<tr>
<td>O</td>
<td>-10.73</td>
</tr>
</tbody>
</table>

Combination of the isolated point defects with the appropriate lattice energy terms allows us to evaluate the formation energies for Schottky and Frenkel disorder in LaGaO₃. These types of disorder can be represented, using Kρger-Vink notation [27], by the following reactions:

**Schottky Disorder**

\[
\text{La}_{i_a}^{x_a} + \text{Ga}_{i_a}^{x_a} + 3\text{O}_0^x = \text{V}_{i_a}^x + \text{V}_{i_a}^x + 3\text{V}_0^- + \text{LaGaO}_3
\]  \hspace{1cm} (5.1)

\[
2\text{La}_{i_a}^{x_a} + 3\text{O}_0^x = 2\text{V}_{i_a}^- + 3\text{V}_0^- + \text{La}_2\text{O}_3
\]  \hspace{1cm} (5.2)

\[
2\text{Ga}_{i_a}^{x_a} + 3\text{O}_0^x = 2\text{V}_{i_a}^- + 3\text{V}_0^- + \text{Ga}_2\text{O}_3
\]  \hspace{1cm} (5.3)

**Frenkel Disorder**

\[
\text{La}_{i_a}^{x_a} = \text{V}_{i_a}^- + \text{La}_i^+
\]  \hspace{1cm} (5.4)
Defect Properties of the LaGaO$_3$-based Oxygen Ion Conductor

\[ \text{Ga}^{\alpha}_{\text{dG}} = V_{\text{Ga}}^– + \text{Ga}^+ \quad (5.5) \]
\[ O^{\alpha}_0 = V^–_0 + O^+_i \quad (5.6) \]

where the symbols indicate the type of defect, i.e. V for vacancy, i for interstitial and the superscripts, • (positive), ' (negative) indicate the charge of the defect relative to the normal site.

Table 5.4 - Calculated formation energies for intrinsic disorder

<table>
<thead>
<tr>
<th>Disorder</th>
<th>Energy (eV/defect)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Schottky</strong></td>
<td></td>
</tr>
<tr>
<td>LaGaO$_3$</td>
<td>4.52</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>3.55</td>
</tr>
<tr>
<td>Ga$_2$O$_3$</td>
<td>5.96</td>
</tr>
<tr>
<td><strong>Frenkel</strong></td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>10.28</td>
</tr>
<tr>
<td>Ga</td>
<td>9.75</td>
</tr>
<tr>
<td>O</td>
<td>4.94</td>
</tr>
</tbody>
</table>

The calculated formation energies, presented in Table 5.4, clearly show that the most favourable intrinsic disorder is of the La$_2$O$_3$ Schottky-type. The higher formation energies for Frenkel disorder are consistent with observation, where interstitial formation is believed to be unfavourable in the close-packed perovskite structure. In any case, the magnitude of the energies suggests that intrinsic disorder is not significant in LaGaO$_3$. Consequently, the defect properties of this material will be dominated by extrinsic disorder including the incorporation of dopants.
5.4 Dopant Substitution

It has been clearly shown that the addition of aliovalent dopants (especially Sr for La and Mg for Ga) is crucial to the high oxygen ion conductivity in LaGaO₃ [157-163]. Our simulation approach to dopant substitution follows that of our successful study of impurities in stabilised zirconia (Chapter 3) and in LaMO₃ [53,168,169]. The cations are incorporated into the lattice at either La³⁺ or Ga³⁺ sites with the creation of oxygen vacancies as charge-compensating defects. Considering Sr²⁺ substitution of La³⁺ as an example, this doping process can be represented by the following defect reaction:

\[
\text{SrO} + \text{La}^{3+} + \frac{1}{2} \text{O}_2^- = \text{Sr}^{2+} + \frac{1}{2} \text{V}_0^- + \frac{1}{2} \text{La}_2\text{O}_3
\]

where, in Kröger-Vink notation [27], Sr⁺⁺ signifies a dopant substitutional and \( V_0^- \) an oxygen vacancy. The energies of this “solution” reaction can be evaluated by combining appropriate defect and lattice energy terms. In this way such an approach provides a useful systematic guide to the relative energies for different dopant species at the same site. The resulting solution energies for a series of alkaline-earth metal and alkali metal ions in orthorhombic LaGaO₃ are listed in Table 5.5, and presented graphically in Figure 5.2 as a function of dopant radius.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La site</td>
</tr>
<tr>
<td>Li⁺</td>
<td>4.71</td>
</tr>
<tr>
<td>Na⁺</td>
<td>3.46</td>
</tr>
<tr>
<td>K⁺</td>
<td>4.49</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>5.48</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>3.49</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.86</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>0.31</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>4.18</td>
</tr>
</tbody>
</table>
Figure 5.2 - Calculated energies of solution as a function of dopant radius for alkali and alkaline-earth cations (a) La site (b) Ga site
Figure 5.3 - Calculated energies of solution as a function of dopant radius (a) La site (b) Ga site

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We note that the interatomic potentials for the dopant ions are exactly those of corresponding binary metal oxides [71] which have been applied to analogous studies of the LaMO$_3$ perovskites [53,54,168] and other ceramic oxides (Appendix 1). Examination of the results (Figure 5.2) reveals that the lowest and most favourable solution energies are predicted for Sr at the La site and Mg at the Ga site. The favourable incorporation of these two ions will therefore enhance oxygen diffusivity owing to the increase in the concentration of oxygen vacancies. These results accord well with experimental work [157-163] in which Sr and Mg are the favoured acceptor dopants used to produce high oxygen ion conductivity. It is also apparent from Figure 5.2 that a degree of correlation is found between the calculated solution energy and the dopant size with minima near the radii of the host cations. We note that the solution energy for the alkali metal dopants in LaGaO$_3$ are appreciably endothermic, in line with their observed low solubility.

As a possible predictive tool, this approach was then extended to a wider range of low-valent ions substituting at both La and Ga sites; the calculated solution energies are presented in Figure 5.3 which includes the Sr and Mg ions as reference points. Examination of the results confirms that Sr is the most favourable dopant on the La site. In contrast, we find that Cu$^{2+}$ and Hg$^{2+}$ have lower solution energies than Mg$^{2+}$ on the Ga sub-lattice. This predicts that both Cu and Hg ions are potential candidates for use as acceptor dopants in LaGaO$_3$ to enhance the oxygen diffusivity. It is worth noting that a related system, LaSrCuGaO$_5$, has been synthesised and adopts the brownmillerite structure [175]. While we recognise the possible electronic contribution from mixed-valence copper, these results suggest that Cu or Hg doped La$_{1-x}$Sr$_x$GaO$_{3.5}$ warrants further experimental investigation. In this respect, it is interesting to note that one of the highest oxygen ion conductivities is observed in the Aurivillius phase Cu-doped Bi$_4$V$_2$O$_{11}$ ('BICUVOX') (Appendix 3). Transport number measurements indicate that
the oxygen ions are the predominant charge-carriers in this material with a very small electronic contribution related to the vanadium ions [176].

5.5 Dopant-vacancy Clusters

As discussed in Chapter 3, it is well known that interactions between dopant ions and their charge-compensating defects can lead to the formation of distinct clusters which can 'trap' the migrating species. For example, the ionic conductivity of fluorite-structured oxides (such as Y-doped CeO₂) is largely controlled by the extent of dopant-vacancy interactions [38,154,157-159]. These have been described in terms of the formation of dopant-oxygen vacancy pair clusters for low dopant concentrations, which add a binding energy term (E_{bind}) to the conduction activation energy.

From ionic conductivity measurements of La₁₋xSrₓGa₁₋yMgₓO₃₋₅, Huang and Petrie [162] find significant differences in the activation energy as a function of the Sr and Mg content. Drennan et. al. [163] also observe a large difference in the conduction activation energy between data at low temperature (E_{act} = 1.13 eV) and at high temperature (E_{act} = 0.66 eV). Feng and Goodenough [161] have noted the importance of the possible trapping of an oxygen vacancy at a divalent-cation impurity. Consequently, we undertook a series of calculations on defect pair clusters in the LaGaO₃ system comprised of a dopant substitutional and an oxygen vacancy at nearest-neighbour sites (Figure 5.4). Since Sr on La and Mg on Ga are the most commonly used acceptor dopants, and Cu and Hg are also calculated to be favourable, we have focused our attention on these substitutionals.
Figure 5.4 - Schematic of defect clusters shown for Sr on La and Mg on Ga, with an oxygen vacancy (□) (La - green, Ga - dark blue, Sr - cyan, Mg - pink)

X-ray diffraction data [162] of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3.5}$ indicate a transition from an orthorhombic to cubic structure at higher dopant levels corresponding to $x + y = 0.35$. We have therefore considered cluster formation in both the orthorhombic and cubic phases of $\text{LaGaO}_3$, with calculated cluster binding energies with respect to the component isolated defects reported in Table 5.6.

Table 5.6 - Calculated binding energies for dopant-oxygen vacancy pair clusters in cubic and orthorhombic $\text{LaGaO}_3$

<table>
<thead>
<tr>
<th>Dopant site</th>
<th>Cluster$^a$</th>
<th>$E_{\text{bind}}$ (eV)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Sr on La</td>
<td>$(\text{Sr}_{\text{La}}' \text{V}_0''')$</td>
<td>-0.37</td>
</tr>
<tr>
<td>Mg on Ga</td>
<td>$(\text{Mg}_{\text{Ga}}' \text{V}_0''')$</td>
<td>-1.77</td>
</tr>
<tr>
<td>Cu on Ga</td>
<td>$(\text{Cu}_{\text{Ga}}' \text{V}_0''')$</td>
<td>-1.50</td>
</tr>
<tr>
<td>Hg on Ga</td>
<td>$(\text{Hg}_{\text{Ga}}' \text{V}_0''')$</td>
<td>-1.90</td>
</tr>
</tbody>
</table>

$^a$ Oxygen vacancy is at nearest-neighbour site; $^b$ Sign convention: negative value indicates system is bound
The results reveal that all the pair clusters are bound with the lowest binding energy for the Sr-vacancy configuration. In particular, we find a near-zero value for \( \text{Sr}_{La}V_{O} \) in the cubic structure although it is possible that other types of aggregate could have greater stability. This suggests a negligible change in conduction activation energy with Sr level for compositions with cubic symmetry. Any change with activation energy with increasing Sr dopant concentration may be linked to the changes in the overall crystal structure. In any case these findings suggest that the oxygen vacancies originating from Sr doping will optimise the ionic conductivity to a greater degree owing to the minimum binding energy term. By contrast, we find that Mg-vacancy clusters have much higher binding energies; this points to strong ‘trapping’ of the migrating oxygen vacancies with increasing Mg concentration. This result is consistent with the observed increase in the conduction activation energy and decrease in conductivity at higher Mg doping levels in \( La_{0.8}Sr_{0.2}Ga_{1.9}Mg_{y}O_{3.6} \) [162]. We should note that it is has been observed that Mg doping is important in promoting the introduction of a higher concentration of Sr into LaGaO\(_3\). This indicates a synergy effect when doping simultaneously both A (La) and B (Ga) lattice sites, so that the solubility limit for each dopant increases relative to the singly-doped material.

Whilst our calculations also find high cluster binding energies for both Cu and Hg ions, the magnitude for Cu is less than the commonly used Mg dopant. Previous work on dopants in fluorite oxides have indicated that the elastic strain field around the defects in the cluster is at least as important as the electrostatic interaction [132]. The binding energy is therefore dependent upon the ion size ‘mismatch’ between the host and dopant cation with the expectation of a minimum when the ionic radii are approximately the same. This is borne out here with the greater ion size mismatch for the \( Mg^{2+} \) (0.72Å) on the small Ga\(^{3+}\) site (0.62Å).
5.6 Solid Solutions

We have shown that doping LaGaO$_3$ on both the La and Ga sites by aliovalent ions is crucial to increasing the conductivity of this material. Previously our calculations have focused on isolated defects within the undoped cubic or orthorhombic systems. However, within the GULP code [67-69] there is a facility for setting up complex solid solutions by adopting a ‘mean field’ approach which we employed for Nb/Y co-doping of ZrO$_2$ (§3.8). This feature allows the simulation of homogenous distributions of Sr and Mg dopants in the LaGaO$_3$ lattice.

We initially concentrated on the cubic La$_{1-x}$Sr$_x$GaO$_3$.§ system. However, there were problems achieving a valid energy minimisation which was partially solved by assigning Sr as a rigid ion. First, the La$_{1-x}$Sr$_x$GaO$_3$.§ system was investigated with an isolated Mg impurity introduced onto a Ga site, with the resulting energies of solution presented in Table 5.7. For comparison we have included the solution energy for Mg in undoped LaGaO$_3$ (x = 0.0), and indicated the difference between this value and the energies computed here. The results indicate that an increase in the amount of Sr dopant from x = 0.0 to 0.2 lowers slightly the solution of Mg. This result accords with Huang and Petrie [162] in which they state that the solubility of Mg on Ga sites varies with Sr concentration on La sites.

<table>
<thead>
<tr>
<th>x</th>
<th>Solution energy (eV)</th>
<th>$\Delta$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>6.05</td>
<td>0.00</td>
</tr>
<tr>
<td>0.10</td>
<td>5.92</td>
<td>-0.13</td>
</tr>
<tr>
<td>0.20</td>
<td>5.70</td>
<td>-0.35</td>
</tr>
</tbody>
</table>
In a similar fashion the Mg doped system (LaGa$_{1-y}$Mg$_y$O$_{3.8}$) was examined with an isolated Sr impurity introduced on La sites as $y$ varied from 0.0 to 0.2; Table 5.8 lists the results obtained. Again the calculations suggest that the presence of Mg on Ga promotes the solubility of Sr into the material. In this case the enhancement of the solution energy is much more significant.

<table>
<thead>
<tr>
<th>$y$</th>
<th>Solution energy (eV)</th>
<th>$\Delta$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.46</td>
<td>0.00</td>
</tr>
<tr>
<td>0.10</td>
<td>-1.05</td>
<td>-0.59</td>
</tr>
<tr>
<td>0.20</td>
<td>-1.64</td>
<td>-1.18</td>
</tr>
</tbody>
</table>

The major contribution to the lower solution energies in Table 5.8 seems to be the formation of the oxygen vacancy becoming more favourable. For example, in LaGa$_{1-y}$Mg$_y$O$_{3.8}$ the energy for an isolated oxygen vacancy decreases from 19.62 eV ($y = 0.0$) to 17.51 eV for ($y = 0.2$). It has been suggested by Huang and Petrie [162] that the oxygen vacancies originating from Sr doping are directly responsible for increases in ionic conductivity. They go as far as saying that an increase in Mg doping on Ga aids the substitution of Sr on La. Indeed, this is borne out by our results in Table 5.8.

### 5.7 Anion and Cation Migration

Despite the conductivity studies on LaGaO$_3$ referred to above, fundamental mechanistic features of oxygen transport are not well characterised. Calculations can greatly enhance our understanding of this problem by probing the energetics of oxygen vacancy migration which
effects the transport of lattice $O^{2-}$. It is worth recalling that the simulation approach is able to model lattice relaxation about the migrating ion and treats ionic polarisability by the shell model. In this way, the LaGaO$_3$ structure is not considered simply as a hard-sphere lattice with fixed ions.

Table 5.9 - Calculated and experimental energies for oxygen ion and cation vacancy migration in LaGaO$_3$

<table>
<thead>
<tr>
<th>Ion</th>
<th>$E_{\text{calc}}$ (eV)</th>
<th>$E_{\text{exp}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O^{2-}$</td>
<td>0.73</td>
<td>0.79$^a$, 1.07$^b$, 0.81-1.17$^c$; 0.66$^d$, 1.13$^d$</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>4.66</td>
<td>-</td>
</tr>
<tr>
<td>Ga$^{3+}$</td>
<td>16.92</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Ishihara et. al. [160]; $^b$ Feng and Goodenough [161]; $^c$ Huang and Petrie [162]; $^d$ Drennan et. al. [163]

The saddle-point configuration to vacancy migration in the cubic structure has been identified from which the energy barrier was derived. In Table 5.9 we report the calculated migration energies ($E_{\text{mig}}$) together with available activation energies ($E_{\text{act}}$) from experimental studies. Our calculated migration energy (0.73 eV) for oxygen transport accords well with activation energies of 0.79 eV and 0.66 eV from SIMS measurements of oxygen self-diffusion [160] and dc conductivity studies over a high temperature range (850 - 1000°C) [163] respectively. However, we recognise that direct comparison is not straightforward since the observed values show significant scatter. Such variation may reflect differences in synthesis conditions and doping levels, as well as problems associated with deviations from ideal stoichiometry. It is important to stress that $E_{\text{mig}}$ relates purely to migration of the oxygen vacancy and does not include a binding (or association) term. Examination of Table 5.9 also reveals that some experimental studies find higher activation energies of ca. 1.1 eV. As earlier studies of fluorite
Figure 5.5 - Schematic representation of the curved path for oxygen vacancy migration (a)

GaO$_6$ octahedron (b) [Ga-O] ab plane
oxides have already shown [9,132,154], the formation of \((M^{+}\overline{V}_O)\) pair clusters adds a term equal to half the binding energy \(E_{\text{bind}}\) to the Arrhenius energy of the conductivity. Our strong binding energy term for the \((M_{Ga}^{+}\overline{V}_O)\) cluster may help to rationalise the increase in \(E_{\text{act}}\) with increasing Mg content in LSGM. In general, the increase in activation energy at higher doping levels may be attributed to the onset of significant defect clustering.

Analysis of the calculated migration mechanism along the \(<110>\) edge of the GaO\(_6\) octahedron reveals that the pathway is not strictly linear. Rather, the simulations suggest a curved route with the saddle-point slightly bowed away from the neighbouring Ga ion (Figure 5.5) which results in a significantly lower oxygen migration energy. In the saddle-point configuration, the migrating oxygen ion must pass through the opening of a triangle defined by two La\(^{3+}\) ions and one Ga\(^{3+}\) ion (Figure 5.6). We find significant outward relaxation (-0.1Å) of these cations away from the mobile oxygen ion which probably reduces any
repulsive overlap interactions. Previous work on ABO$_3$ show a strong relationship between the perovskite tolerance factor (t) and the migration energy, in which the minimum seems to correspond to the most effective balance of the relaxation of A and B cations [53,168].

Despite numerous studies devoted to oxygen transport, little attention has been paid to cation diffusion in LaGaO$_3$, notwithstanding its significance to the reliability of technological applications. Knowledge of cation diffusion is central to high temperature processes such as sintering, creep and grain growth, as well as to interactions at the electrolyte-electrode interface. The existence of cation vacancies may become particularly important in LaGaO$_3$ samples that deviate from ideal cation stoichiometry, as is observed in similar perovskite oxides [177]. In a preliminary attempt to shed light on this problem we have undertaken atomistic simulations of vacancy migration on the La and Ga lattices. Possible vacancy jumps between neighbouring cation sites have been identified with resulting migration energies included in Table 5.9.

As was expected, the calculations reveal high migration energies for cation vacancy transport which confirms the much slower diffusion rates in comparison to oxygen. Analysis of the crystal structure indicates that the jump distance for La motion (3.87Å) is shorter than that for Ga motion (5.48Å), and that the saddle-point for a migrating Ga ion is very close to two La lattice ions. While there is no experimental data for direct comparison, the magnitude of the calculated values is consistent with observed activation energies of $> 4$ eV for cation diffusion in other perovskite-type oxides [178]. In view of the high migration energy for Ga, we anticipate the diffusion coefficients following the order $D_o >> D_{La} > D_{Ga}$. The diffusion of Ga is therefore likely to be rate-controlling for processes such as creep or grain growth.
In Chapter 6 we have extended the study of ion migration presented here by employing Molecular Dynamics (MD) techniques to examine oxygen diffusion as a function of temperature.

5.8 Holes and Protons in the Doped Oxide

It has been reported that doped LaGaO$_3$ shows a small amount of hole conductivity at high oxygen partial pressures [157-159]. However, recent studies suggest this is not the case by comparison of the oxygen self-diffusivity obtained from tracer and ionic conductivity measurements [160]. We have therefore examined the energetics of hole formation in LaGaO$_3$ via the following oxidation reaction:

$$V_0^+ + \frac{1}{2} O_{2(g)} = O_0^\times + 2 h^-' \quad (5.8)$$

which involves the ‘filling’ of oxygen vacancies to create holes (h'). Our approach to electronic defects follows that used for LaM$_2$O$_3$ and Ba$_2$In$_2$O$_5$ [54,175] in which we model the hole centre as Ga$^{4+}$ or O$^-$. The resulting energies, listed in Table 5.10, favour creation of oxygen holes. This is not too surprising since it is known that the Group 13/III elements have a maximum oxidation state of +III.

Table 5.10 - Calculated Energies of Hole Formation

<table>
<thead>
<tr>
<th>Defect Process$^a$</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga$^{4+}$ (h')</td>
<td>19.52</td>
</tr>
<tr>
<td>O$^-$ (h')</td>
<td>7.88</td>
</tr>
<tr>
<td>$V_0^+ + \frac{1}{2} O_{2(g)} = O_0^\times + 2 h'$</td>
<td>3.78</td>
</tr>
</tbody>
</table>

$^a$ Ionisation energy (Ga IV 64 eV); Electron affinity (O II 8.75 eV)
Using the oxygen hole term, the energy for the oxidation reaction (5.8) can be evaluated and is found to be 3.78 eV (Table 5.10). This result suggests a highly unfavourable process, indicating that ionic rather than electronic compensation (and hence ionic rather than p-type conductivity) predominates in doped LaGaO₃, which is in agreement with recent tracer experiments [160]. Such redox behaviour is in contrast to that found in the perovskite-oxides containing transition-metal ions at the B-site (e.g. LaCoO₃), but is similar to the properties of LaAlO₃ [54]. It has been reported that an advantage of acceptor-doped LaGaO₃ over similar CeO₂-based electrolytes is that it is stable in both oxidising and reducing atmospheres [157-159]. In general, our calculations are consistent with experimental findings which show that the LaGaO₃ system is mainly an ionic conductor with an ionic transport number close to unity [160,163].

In addition to hole formation, there is also the question of whether there is any evidence of protons in this material. Perovskite-structured oxides, particularly BaCeO₃ and SrCeO₃, have already received considerable attention as high temperature proton conductors [37,179]. Protons are introduced into these doped materials by treatment in water vapour, whereby oxygen vacancies are filled by hydroxyl ions. The defect is described as a hydroxyl group as the interstitial proton is clearly associated with the neighbouring oxygen ion. The water incorporation reaction can be described as follows:

$$\text{H}_2\text{O} + \text{V}_\text{O} + \text{O}_\text{O}^x = 2\text{OH}_\text{O}$$

We have investigated this problem by evaluating the energy for this incorporation reaction ($E_{\text{H}_2\text{O}}$) by using the following reaction:

$$E_{\text{H}_2\text{O}} = 2E_{\text{OH}} - E_{\text{V}_\text{O}} + E_{\text{PT}}$$

(5.10)
where $E_{\text{OH}}$ is the energy associated with substitution by the hydroxyl group, $E_{\text{Vo}}$ the energy of an oxygen vacancy and $E_{\text{PT}}$ the energy of the proton transfer reaction: $\text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$. These component energy terms and the calculated value of $E_{\text{H}_2\text{O}}$ are given in Table 5.11. Analogous to previous simulation studies of protons in perovskite-oxides, the O-H interaction is modelled as a Morse potential [169,170].

**Table 5.11 - Terms used in the calculation of the energy of water incorporation ($E_{\text{H}_2\text{O}}$)**

<table>
<thead>
<tr>
<th>Term</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{OH}}$</td>
<td>17.24$^a$</td>
</tr>
<tr>
<td>$E_{\text{Vo}}$</td>
<td>19.62</td>
</tr>
<tr>
<td>$E_{\text{PT}}$</td>
<td>-11.77</td>
</tr>
<tr>
<td>$E_{\text{H}_2\text{O}}$</td>
<td>3.10</td>
</tr>
</tbody>
</table>

$^a$ Includes D of Morse potential [169,170]

There are, of course, uncertainties in the absolute values due to the free-ion energies employed. However, the endothermic energy for $E_{\text{H}_2\text{O}}$ suggests that the dissolution of protons at the expense of oxygen vacancies is highly unfavourable. Although quantitative data for doped LaGaO$_3$ is limited, our result is consistent with the work of Feng and Goodenough [161] who found no evidence of proton conduction in LSGM by examining the conductivity in three different air atmospheres: dry, ambient and water-saturated.
Chapter 5  
Defect Properties of the LaGaO$_3$-based Oxygen Ion Conductor

5.9 Summary

The present study illustrates how atomistic simulation modelling techniques can contribute to the understanding of key aspects of LaGaO$_3$ that are relevant to its potential use in fuel cells and other similar applications. The following points have emerged from our results:

(i) Favourable acceptor-dopants are Sr$^{2+}$ at La and Mg$^{2+}$ at Ga; these results accord well with experimental work that find the highest ionic conductivity in the (La,Sr)(Ga,Mg)O$_{3.8}$ system. The favourable ‘solution’ of these dopants will enhance oxygen diffusivity owing to the increase in the oxygen vacancy concentration. We also suggest that Cu$^{2+}$ and Hg$^{2+}$ warrant further investigation as potential candidates as acceptor dopants (at the Ga site).

(ii) The binding energies for defect clusters indicate that the Mg$^{2+}$ substitutional has a strong tendency to ‘trap’ the migrating oxygen vacancy. This result is compatible with the observed increase in activation energy and decrease in conductivity at higher Mg doping levels in La$_{0.8}$Sr$_{0.2}$Ga$_{1-y}$Mg$_y$O$_{3.8}$. However, Sr doping will enhance oxygen ion conductivity to a greater degree owing to the minimum binding energy term.

(iii) We find that the presence of Mg on Ga sites is important in enhancing the uptake of Sr on La sites. The results also reveal an improved solubility of Mg on Ga sites as the concentration of Sr on La is increased. This is indicative of a synergy effect when doping simultaneously both La and Ga lattice sites, so that the solubility limit of each dopant increases relative to the singly-doped material. Moreover, this observation is line with recent XRD measurements.
(iv) Our calculated migration energy (0.73 eV) for oxygen vacancy transport is generally consistent with measured values. Higher activation energies from experiment may be related to dopant-vacancy association at higher dopant concentrations. The mechanism for oxygen vacancy migration is along the GaO$_6$ octahedron edge, but following a slightly curved trajectory with significant outward relaxation of adjacent cations.

(v) The first reported examination of cation transport in LaGaO$_3$ reveals high vacancy migration energies (>4 eV) and confirms the much slower diffusion rates in comparison to oxygen. The diffusion of Ga$^{3+}$ is likely to be rate-controlling for processes such as creep or grain growth.

(vi) Oxidation with the formation of holes is an energetically unfavourable process. This is consistent with experimental findings that show doped LaGaO$_3$ to be almost a pure ionic conductor. Preliminary calculations find that the incorporation of water is appreciably endothermic, which suggests that proton conduction will not be significant in this material.
Chapter 6

Molecular Dynamics Study of Oxygen Diffusion in LaGaO$_3$

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Chapter 6: Molecular Dynamics Study of Oxygen Diffusion in LaGaO$_3$

6.1 Introduction

Recent studies [157,162,163] have investigated the solid solution range La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3.5}$ system (LSGM) as a means of optimising conduction properties. However, despite several reports of electrical conductivity in LSGM [157,161-163] there are far fewer studies of oxygen diffusion and limited information on the mechanistic features at the atomic level.

In this Chapter we expand on our static lattice simulations (Chapter 5) by employing Molecular Dynamics (MD) techniques which are well-suited to examining ion transport on the atomic scale. Through the use of MD methods, which explicitly include temperature effects, we can obtain valuable diffusion and structural information which can be compared directly to available experimental data. The temperature and concentration of charge carriers are important aspects of ion diffusion in perovskite oxides, and these factors can be investigated by these simulations. In the past MD methods have been applied to a number of fast-ion conductors [137-142], but have not been widely applied to perovskite-type oxides. A notable exception is a study by Islam et. al. [168] in which MD simulations were undertaken on doped LaMnO$_3$ and LaCoO$_3$. We note that previous MD studies have excluded the shell model (to treat ionic polarisation) usually due hardware limitations. However, in the present study our simulation model incorporates anion polarisability by application of the shell model.
6.2 Simulation Model

A simulation supercell consisting of 5x5x5 cubic perovskite unit cells, and approximately 19Å in dimension, was constructed. As described in Chapter 2 (Simulation Methods), the cell is repeated by applying periodic boundary conditions (PBC) to generate an unbounded system with no surfaces. In most MD studies to date ion-ion interactions have been treated by using a rigid-ion model. Here we have employed the shell model (Chapter 2) for the anion species, with the cations treated by a rigid-ion model. Essentially the shell is represented as a separate species connected by a harmonic spring to the core with the total mass of the anion proportioned over both the core and shell in the ratio 9:1, in favour of the core. Therefore, interactions between the anion and the other species occurs via the shell species. The total number of ions in the supercell is as follows: 125 La$^{3+}$, 125 Ga$^{3+}$, 375 $O_{\text{core}}^{2-}$ and 375 $O_{\text{shell}}^{2-}$ giving a total number of 1000 ion species. The potential parameters are those that were successfully employed in our previous static lattice calculations (Chapter 5) and have been transferred directly and are given in Table 6.1.

The simulations were performed using the DL_POLY [80] code (on the Intel parallel supercomputer at Daresbury) and under conditions of constant volume (V) and energy (E) by utilising the NVE ensemble. We note that to date most MD calculations have been performed utilising this ensemble. Initially the pressure was set to 1 atm and the temperature varied between 873 and 1173 K. All the simulations were run for a total of 60ps, with the system allowed to equilibrate in the first 3ps. A time-step ($\delta t$) of 1fs ($1x10^{-15}$ s) was used; data for subsequent analysis was collected between 3 and 40ps which was found to be satisfactory since data in the last 10ps was found to fluctuate as the calculation neared completion. This phenomenon was observed for all ion species, and at all temperatures and may be caused by
the way the simulation is terminated by DL_POLY. We note that the simulations were extremely complex and required a large amount of hardware resources. Each simulation utilised approximately 20 hours of processor time and required about 30 MB of free disk space for output files. Therefore, before extensive work on doped LaGaO₃ was undertaken our simulation model had to be tested. This was done by performing initial runs on undoped LaGaO₃.

Table 6.1 - Interatomic potential parameters

(i) Short-range

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>p (Å)</th>
<th>C (eVÅ⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La³⁺ ... O²⁻</td>
<td>1545.21</td>
<td>0.3590</td>
<td>0</td>
</tr>
<tr>
<td>Ga³⁺ ... O²⁻</td>
<td>2901.12</td>
<td>0.2742</td>
<td>0</td>
</tr>
<tr>
<td>O²⁻ ... O²⁻</td>
<td>22764.30</td>
<td>0.1490</td>
<td>43.0</td>
</tr>
</tbody>
</table>

(ii) Shell model

<table>
<thead>
<tr>
<th>Species</th>
<th>Y (e)</th>
<th>k (eVÅ⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O²⁻</td>
<td>-2.239</td>
<td>42.0</td>
</tr>
</tbody>
</table>

* Y and k refer to the shell charge and harmonic spring constant, respectively

6.3 Undoped LaGaO₃

Preliminary simulations were first performed on undoped LaGaO₃ at 1073K. The results from this simulation were used to confirm the validity of the model and to check that certain parameters within the datasets were set to appropriate values (for example, the Ewald parameters which control Coulombic interactions). The setting up of a shell model MD
simulation was not a trivial task and therefore the results from these simulations proved invaluable in "debugging" the set-up files.

Firstly, the time evolution of certain properties was examined. As expected, the volume of the simulation cell remained constant (58.16Å³ per unit cell) throughout the entire simulation run. Comparing this unit cell volume with the volume derived from our static lattice calculations (58.18Å³) we find negligible difference. The energy of the system also remained constant at -17800 eV, giving a unit cell lattice energy of -142.50 eV. Again this accords favourably with our previous simulations in which we derived a lattice energy of -143.16 eV. The small differences between the results obtained from the static lattice simulations (which employed the shell model for all ion species) and those presented here shows that treating the cations as rigid ions has a negligible effect on the calculated properties.

6.3.1 Structural Information

Experimental techniques such as extended x-ray absorption fine structure (EXAFS) can provide information about the local structure around dopant species and bond distances within defective solids. Similar structural information can be obtained from MD simulations by way of the Radial Distribution Function (RDF), defined in Chapter 2. The RDF provides an insight into the long-range order (or disorder) of the crystal lattice. The partial pair distribution functions, g(r), were calculated for La-La and Ga-Ga and O-O pairs, and are presented in Figure 6.1.
Chapter 6  

Molecular Dynamics Study of Oxygen Diffusion in LaGaO$_3$

![Graph of La-La interatomic separation](image)

![Graph of Ga-Ga interatomic separation](image)
Figure 6.1 - Radial distribution functions for undoped LaGaO$_3$

Examination of the cation RDFs (Figure 6.1) reveals a series of sharp, well defined peaks, corresponding to successive nearest-neighbour distances. Furthermore, in between peaks the RDF tends to zero, which is also characteristic for a high symmetry solid. In contrast, the O-O pair functions show weak structure after the first nearest-neighbour peak.

Further evidence for possible distortions of the oxygen octahedron is given in Table 6.2 which lists the nearest-neighbour (NN) separations for all ion pairs. It is clear that there are no significant distortions with the cation sub-lattices. However, the cation-anion and anion-anion separations show deviations from crystallographic NN separations, which is consistent with a distortion of the oxygen octahedron.
Table 6.2 - Calculated and crystallographic nearest-neighbour separations (Å) for undoped LaGaO₃

| Separation | Calculated | Crystallographic | $|\Delta|$ |
|------------|------------|------------------|-----------|
| La - La    | 3.875      | 3.875            | 0.000     |
| Ga - Ga    | 3.875      | 3.875            | 0.000     |
| La - Ga    | 3.365      | 3.360            | 0.005     |
| La - O     | 2.675      | 2.740            | 0.065     |
| Ga - O     | 1.925      | 1.937            | 0.012     |
| O - O      | 2.725      | 2.740            | 0.015     |

6.3.2 Ion Diffusion

The mean square displacement (MSD) describes the average displacement of an ion relative to its initial position over a set period of time. The MSDs for all ions in undoped LaGaO₃ at 1073K are given in Figure 6.2.

![Figure 6.2 - Mean square displacements for all ions in undoped LaGaO₃ at 1073K](image-url)
Examination of Figure 6.2 reveals that after the initial 3ps equilibration period all the ions rapidly tend to a constant value. This result is indicative of a lack of any ion diffusion process in the undoped system as expected. It is important to stress that the oxygen core and shell species remain coupled together over the duration of the simulation.

From this section we can conclude that our potentials have accurately reproduced the cubic perovskite structure of LaGaO$_3$. Furthermore, we have shown that the undoped material does not exhibit any ionic conductivity due to the lack of any mobile oxygen vacancies, and therefore the addition of aliovalent dopants is needed to introduce these vacancies for ionic diffusion.

### 6.4 Acceptor Doped LaGaO$_3$

The preliminary MD simulations on undoped LaGaO$_3$ have clearly demonstrated that defects are essential in promoting appreciable ionic diffusion in this material. As discussed in Chapter 5, LaGaO$_3$ can be acceptor doped with Sr on La and Mg on Ga sites, leading to the formation of mobile oxygen vacancies.

From dc conductivity measurements Ishihara et. al. have identified superior conductivity in La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3-\delta}$ at temperatures lower than conventional stabilised zirconias [157-160,165-167], and have also reported oxygen diffusion data at 1073K [160]. A detailed conductivity study by Huang and Petric [162] on La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$ (where $x = 0.1 - 0.25$ and $y = 0.0 - 0.15$) concludes that at temperatures below 973K the highest conductivity is demonstrated by the composition where $x = 0.2$ and $y = 0.1$, while at temperatures above 973K the highest conductivity is exhibited by the system where $x = 0.2$ and $y = 0.15$. 

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Figure 6.3 - Pair functions for all ion species in $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3.8}$ (LSGM12) at 1073K
Therefore, three La_{1-x}Sr_xGa_{1-y}Mg_yO_{3.8} systems chosen for our study are: x = 0.1 and y = 0.2 (which we assign LSGM12), x = 0.2 and y = 0.1 (LSGM21), and x = 0.2 and y = 0.15 (LSGM215) as they relate directly to these recent experimental studies.

From the perfect cell the appropriate number of Sr and Mg dopants were randomly substituted for La and Ga, respectively. To preserve neutrality the corresponding number of oxygen ions were removed to create oxygen vacancies. All the simulations were performed at temperatures between 873 and 1173K for a total of 60ps (with 3ps for equilibration) with data collection occurring between 3 and 60ps. For post-simulation analysis purposes we only examined data between 3 and 40ps for reasons mentioned above (§6.2).

6.4.1 Structural Information

The pair radial distribution functions (RDF) for all like ions in LSGM12 at 1073K are illustrated in Figure 6.3. The cation-cation pair functions show sharp, well defined peaks which correspond to successive nearest-neighbour separations. This suggests that the cation sub-lattices are not involved in the diffusion process which accords with our previous atomistic calculations (Chapter 5) in which we showed that cation diffusion is highly unfavourable in this material. In contrast, the oxygen-oxygen pair function shows weak, diffuse structure for separations greater than nearest-neighbour; this indicates some loss of long range order on the mobile oxygen sub-lattice. This is further exemplified in Figure 6.4 which compares the RDFs computed for undoped LaGaO_3 with those from LSGM12 at 1073K. For LSGM12 the first peak has decreased in height compared to the undoped system (Figure 6.4), while the general profile broadens in the doped system indicating a greater
degree of disorder associated with oxygen diffusion. Moreover, this trend in the oxygen-oxygen RDF was calculated in all three of the doped systems under study here.

Figure 6.4 - Radial distribution functions for undoped LaGaO$_3$ and LSGM12 at 1073K

6.4.2 Ion Diffusion in Doped LaGaO$_3$

Molecular Dynamics (MD) simulation techniques allow valuable transport data to be collected with the possible derivation of diffusion coefficients for direct comparison with experimental data. The time dependent mean square displacements (MSD) of all ions at 1073K in the LSGM12, LSGM21 and LSGM215 are given in Figure 6.5.

Figure 6.5 clearly shows that the cation MSDs rapidly tend to a constant value following equilibration and this confirms that there is no cation diffusion in these systems. However, the Mg MSDs exhibit a slight increase, and we return to this point later. The oxygen functions increase sharply with time indicating significant ion diffusion; this type of behaviour was also
observed in the simulation of Y/ZrO$_2$ (Chapter 4). We note that the basic features of the above plots are very similar for all temperatures considered between 873 and 1173K.
Huang and Petrie [162] have suggested that acceptor doping on both La and Ga sites leads to an increase in the concentration of mobile oxygen vacancies, and therefore enhanced conductivity. However, they state that the two dopants have significantly different effects on activation energy; Sr addition lowers the mobility barrier while Mg addition increases it. They suggest that the reason for this is an increased binding (association) energy between Mg and an oxygen vacancy compared to Sr and a vacancy. From our previous static simulations (Chapter 5) we have calculated binding energies for \((\text{Sr}_{\text{La}} V_{O}^{-})\) and \((\text{Mg}_{\text{Ga}} V_{O}^{-})\) clusters to be -0.02 and -1.83 eV, respectively. The greater binding between the Mg substitutional and an oxygen vacancy may be the cause of the very slight increase in the Mg MSDs shown in Figure 6.5 and expanded in Figure 6.6. Indeed, the largest displacements are shown for LSGM215 (Figure 6.6) in which there is a greater concentration of oxygen vacancies compared with the other two systems, and also an increased amount of Mg dopant.
We now focus on the anion sub-lattice in LSGM12, LSGM21 and LSGM215 between 873 and 1073K; the MSDs for oxygen ions are presented in Figure 6.7. The rapid increase in the MSD data in these systems indicates rapid oxygen diffusion.
Figure 6.7 - Mean square displacements of oxygen ions in LSGM12, LSGM21 and LSGM215 at 873, 973 and 1073K (cations have been omitted for clarity)
From the slope of these plots, we can obtain the oxygen diffusion coefficient (D) according to the Einstein relation (Equation 4.1). We note that our study has covered a wider temperature range (873 to 1173K) than previous experimental studies. In Table 6.3 we have focused on three temperatures, and have listed the calculated diffusion coefficients derived from our MSD plots (Figure 6.7).

Table 6.3 - Calculated rates of diffusion in $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3.8}$

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>LSGM12</th>
<th>LSGM21</th>
<th>LSGM215</th>
<th>Exptl.\textsuperscript{a} LSGM12</th>
</tr>
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<tr>
<td>873K</td>
<td>$1.85 \times 10^{-7}$</td>
<td>$1.51 \times 10^{-7}$</td>
<td>$3.86 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>973K</td>
<td>$2.00 \times 10^{-7}$</td>
<td>$3.86 \times 10^{-7}$</td>
<td>$4.65 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>1073K</td>
<td>$4.12 \times 10^{-7}$</td>
<td>$4.97 \times 10^{-7}$</td>
<td>$6.35 \times 10^{-7}$</td>
<td>$3.24 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Ishihara et al. [160] for $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3.8}$

The first point to note about the diffusion coefficients presented in Table 6.3 is that as expected there is a temperature dependence, i.e. oxygen ion diffusion increases with increasing temperature. The calculated diffusion coefficient for LSGM12 at 1073K is in good agreement with SIMS measurements of oxygen self-diffusion [160] for the same system. To our knowledge this is the only experimental diffusion data available for doped LaGaO$_3$. It is worth noting that a diffusion coefficient of $8.50 \times 10^{-7}$ cm$^2$/s was evaluated for LSGM12 using a rigid-ion model. Conductivity measurements by Huang and Petrie [162] on a wide range of compositions of doped LaGaO$_3$ have identified LSGM215 as having superior oxygen ion conductivity at temperatures greater than 973K. Moreover, this observation is borne out in Table 6.3 in which we find the greatest diffusion in LSGM215 not only at 1073K, but across all the temperatures studied. This is probably due to an increased concentration of oxygen
vacancies compared to the other two systems. An interesting point arises when comparing the oxygen diffusion coefficients in LSGM12 and LSGM21; both systems contain the same concentration of oxygen vacancies but with differing amounts of dopant on La and Ga sites. At elevated temperatures (≥ 973K) LSGM21 exhibits superior oxygen ion diffusion, which is probably due to an increased amount of Sr on La. This observation is consistent with conductivity studies [162] which state that Sr addition lowers the mobility energy barrier to oxygen vacancy migration while Mg addition increases this barrier.

The MD simulations show that diffusion occurs via a conventional hopping mechanism involving discrete jumps of oxygen ions, which allows us to evaluate an activation energy for oxygen migration using the standard Arrhenius relationship (Equation 4.2), with the resulting energies presented in Table 6.4.

Table 6.4 - Calculated activation energies for oxygen ion migration in LSGM12, LSGM21 and LSGM215

<table>
<thead>
<tr>
<th>System</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSGM12</td>
<td>0.32 - 0.64</td>
</tr>
<tr>
<td>LSGM21</td>
<td>0.35 - 0.48</td>
</tr>
<tr>
<td>LSGM215</td>
<td>0.20 - 0.58</td>
</tr>
</tbody>
</table>

Our calculated activation energies when compared directly with those from experiment are somewhat lower. However, activation energies from both simulation and experiment show a degree of scatter indicating that direct comparison is not straightforward, and therefore it is difficult to draw any firm conclusions. One reason for the lower values may be due to
increased dopant-vacancy clustering in the experimental systems. Indeed, it is well known that in fluorite-structured ion conductors, e.g. Y/ZrO₂, the ionic conductivity is dependent on the extent of defect clustering which adds a binding (or association) term to the Arrhenius energy [132].

6.4.3 Migration Mechanism

The use of MD simulations has enabled us to investigate the effects of temperature and of dopant concentration in LaGaO₃. In order to gain a further insight into the mechanism of oxygen ion migration we can extract ion trajectories from MD simulations which help build a detailed picture of ion motion at the atomic level. Indeed, a significant thrust of basic transport studies has been the determination of the mechanisms controlling bulk transport phenomena.

During the progress of a Molecular Dynamics (MD) simulation a vast amount of information is produced, so we concentrate on one simulation run, namely La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃.₈ (LSGM12) at 1073K. An examination of individual configurations from this simulation allows us to build a picture of ion motion. Moreover, using the Insight II package [180] we are able to visualise an animated sequence, in three dimensions, of ion motion as a function of time.

Analysis of the trajectory information using animation confirmed that there are small distortions in the oxygen octahedra. The distortions are more apparent near an oxygen vacancy, with neighbouring oxygen ions drawn towards the vacancy. During the course of the animation the existence of extensive motion in the oxygen sublattice is clear, which is consistent with the MSD and RDF data (§6.4). In contrast, the cation motions are restricted to
a small volume about their lattice sites, which is indicative of an ordered crystal structure as shown by the RDF data. The NVE ensemble also constrains the volume of the cell and this is observed in the animation where the volume of the supercell remains constant.

Oxygen diffusion occurs by discrete hops of oxygen ions from lattice sites into vacant sites, with no indication of correlated motion. Previously in Figure 5.5b we presented a schematic of oxygen ion migration along an edge of an oxygen octahedron. The migrating ion passes through a saddle-point that is located between three cations (Figure 5.6) which in previous static lattice simulations (Chapter 5) were shown to relax outwards away from the migrating ion. Indeed, inspection of the migration pathway observed in animations from MD simulations is in direct agreement with our previous calculations presented earlier (Chapter 5). A useful way of visualising the motions of selected ions in the simulation supercell is by plotting the ion displacements in two-dimensions as ‘trajectory’ plots. It is important to note that these plots do not represent a single plane in the cell, rather they depict the direction the cell is viewed (Figure 6.8).

Figure 6.8 - Cubic perovskite unit cell (La - green, Ga - blue and O - red)
Figures 6.9 to 6.12 show the positions of ions every 10 time steps over a period of 5ps. Therefore, a plot of the cation positions viewed down the x,y plane would show the Ga$^{3+}$ cations in the first z plane and the central La$^{3+}$ ion in the second z plane. Figure 6.9 shows a trajectory plot for the cations, and it is clear from the dense distribution of points that there is relatively little displacement of these ions from their lattice sites. This verifies the retention of an ordered cation sublattice as shown by the RDF results. Furthermore, there is no evidence of diffusion which is consistent with the MSD data presented earlier. Trajectory plots involving dopant and lattice cations (Figures 6.10 and 6.11) reveal similar trends, with motion restricted to a small volume about their normal positions. In contrast, the oxygen trajectory plots (Figure 6.12) are more diffuse indicating considerable displacement of the oxygen ions from their perfect lattice sites. It is clear that during the simulation an oxygen ion hops into the adjacent site along the octahedron edge. Furthermore, we find no evidence of correlated motion for oxygen ion migration, rather our results point to a conventional hopping mechanism of vacancies.

A plot of the x,y,z co-ordinates of the migrating oxygen ion (Figure 6.13) shows that the migration occurs in the y-z plane, with the x co-ordinate remaining fairly constant. Figure 6.13 indicates that the migrating ion hops after approximately 1ps and immediately hops back to the original lattice site. This observation further supports a hopping model for ion diffusion, although we need to consider a longer time scale for the trajectory plots in order to visualise long range diffusion through the lattice.
Figure 6.9 - (a) Trajectory plot of host cations in LSGM12 (b) Schematic of ion positions in unit cell.

Figure 6.10 - (a) Trajectory plot of La and Mg positions in LSGM12 (b) Schematic of ion positions in unit cell.
Figure 6.11 - (a) Trajectory plot of La and Mg positions in LSGM12 (b) Schematic of ion positions in unit cell.

Figure 6.12 - (a) Trajectory plot of oxygen positions in LSGM12 (b) Schematic of ion positions in unit cell with an oxygen vacancy.
6.5 Summary

In this Chapter we have used shell model Molecular Dynamics (MD) techniques to investigate the structural and transport properties of doped LaGaO$_3$. Our discussion has drawn attention to the following points:

(i) The pair correlation functions indicate considerable disorder on the oxygen sublattice in the doped material which is typical of a fast oxygen ion conductor. In the undoped system we find only slight disorder in the oxygen sublattice which is due to tilts of the oxygen octahedra.

(ii) Oxygen diffusion coefficients have been calculated over a wider range of temperatures and systems than the available experimental data and indicate rapid oxygen transport. We find no sign of oxygen ion diffusion in the undoped material and confirms the need for acceptor
doping in promoting enhanced ionic conductivity. The calculated activation energies show significant scatter and are somewhat lower than observed values.

(iii) Analysis of the ion trajectory data, aided by visualisation software, indicates that oxygen ion migration occurs along the edge of a GaO$_6$ octahedron. There is no evidence of correlated motion for oxygen ion migration, rather our results point to a conventional hopping mechanism of vacancies.
Chapter 7

Conclusions and Future Work
Chapter 7: Conclusions and Future Work

7.1 General Remarks

In broad terms, the research presented in this thesis has demonstrated how advanced computer simulation techniques can be used to investigate the structural, defect and transport properties of ZrO₂ and LaGaO₃-based oxygen ion conductors. As detailed in the Introduction (Chapter 1), these solid electrolytes find application within a host of applications including solid oxide fuel cells (SOFC) and oxygen sensors. It is appropriate to end this thesis by reviewing the main results obtained and briefly discuss how any future studies could extend the present work.

7.2 Stabilised Zirconia

In Chapter 3 we began by studying the energetics of solution of some alkaline-earth and rare-earth metals in zirconia. The ‘solution’ of these dopants will enhance oxygen diffusivity owing to an increase in mobile oxygen vacancies. We found that the most favourable dopants (on energetic grounds) were CaO, Y₂O₃ and Gd₂O₃; indeed, calcia- and yttria-stabilised zirconia are the two most common electrolytes used within fuel cell configurations. The range of dopants was then extended beyond any previous experimental work to include various low-valent metal ions; subsequent calculations revealed that MgO, MnO, Mn₂O₃ and Sc₂O₃ are favourable dopants. It has been shown experimentally that scandia-stabilised zirconia has a higher oxygen ion conductivity than yttria-stabilised zirconia, but is not used as a solid electrolyte due to cost considerations.
Our detailed examination of defect clustering revealed that dopant size plays an important part in stabilising the cubic structure of zirconia. We found that cation dopants with a larger ionic radii than the host Zr\(^{4+}\) prefer the charge-compensating vacancy to be at a next-nearest-neighbour (NNN) site to them, leaving them in an eight-fold co-ordination; conversely "undersized" dopants prefer the vacancy to be situated at nearest-neighbour (NN) positions. Moreover, the perturbation of the host lattice caused by these smaller dopants was quite severe and this will probably interfere with any transport process.

The topical area of Nb/Y co-doping was also investigated by using the mean field approach embodied in the GULP code. We showed that the presence of yttria greatly promotes the solution of Nb in cubic zirconia, and that Nb substitution only causes minor distortions in the surrounding anion sub-lattice. Moreover, these results accord with a recent study using ac impedance and neutron powder diffraction techniques.

In Chapter 4 we extended our techniques to include Molecular Dynamics (MD) and carried out a detailed study of 10mol% yttria-stabilised zirconia (YSZ). MD allowed us to examine the effects of yttria doping on structure and oxygen transport as a function of temperature. The rigid-ion potentials accurately reproduced the cubic structure of zirconia, and on comparing the calculated bond distances with those from experiment we found good agreement. The pair distribution functions showed considerable disorder in the oxygen sub-lattice. The degree of disorder increased with increasing temperature associated with enhanced oxygen diffusion. Within a solid oxide fuel cell (SOFC) configuration the thermal expansion of YSZ must be similar to the other components, and therefore we derived a thermal expansion coefficient over typical SOFC operating temperatures. Our value compared well with observed values which provided further support for our potential model. The main objective of the MD
Conclusions and Future Work

Chapter 7

simulations was to calculate oxygen ion diffusion coefficients over a wider temperature range than experiment. Moreover, our calculated oxygen diffusion coefficients were in accord with those from available tracer diffusion studies, as was the activation energy. To summarise, we found that yttria doping is crucial in increasing the concentration of oxygen vacancies, which in turn will enhance oxygen ion conductivity.

In terms of future work, a natural progression from our MD study of oxygen ion diffusion in 10mol% YSZ would be to examine the effects of yttria concentration as a function of temperature. It would also be interesting to apply the shell model to this system and examine the difference in results (if any) with our rigid-ion calculations. An extension of the work presented in Chapter 3 would be to examine oxygen ion diffusion in Gd/ZrO$_2$ by application of MD techniques. Gd$_2$O$_3$ has already been successfully used as a dopant in fluorite-structured ceria (CeO$_2$). MD studies would provide a valuable insight into the rates of diffusion and the mechanistic features of oxygen transport in Gd/ZrO$_2$ (and Gd/CeO$_2$). Since it is believed that the introduction of Nb into Y/ZrO$_2$ may reduce dopant-vacancy associations, and therefore increase oxygen ion conductivity, a MD study of this system would also be warranted.

The present work has focused on the bulk properties of solid electrolyte materials. Future simulations should also consider aspects of the structure and stability of the electrode/electrolyte interface.

7.3 Doped LaGaO$_3$

Chapter 5 illustrated how atomistic simulation techniques can contribute to the understanding of key aspects of LaGaO$_3$ that are relevant to its potential use in fuel cells. We began our
investigation by exploring dopant substitution (alkali and alkaline-earth metals), and found that favourable dopants were Sr on La and Mg on Ga; these results agreed well with experimental work that found the highest ionic conductivity in the $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3.8}$ system. The solution energies for the alkali metal dopants were appreciably endothermic, in line with their observed low solubility. By using computer simulation as a possible predictive tool, we extended the range of dopants to include various low-valent ions substituting at both La and Ga sites. Results revealed that Sr is still the most favourable dopant on the La site. In contrast, we found that Cu and Hg had lower solution energies than Mg on the Ga sub-lattice. This suggests that both Cu and Hg are potential candidates as acceptor-dopants in $\text{LaGaO}_3$ and could enhance oxygen diffusivity.

The effects of dopant-vacancy clustering were examined and computed binding energies revealed that the Mg substitutional has a strong tendency to ‘trap’ the migrating oxygen vacancy. This is in agreement with an observed increase in activation energy and decrease in conductivity at higher Mg levels of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3.8}$ system. However, Sr will enhance oxygen ion conductivity to a greater extent owing to the minimum binding energy term. To investigate the effects of dopant substitution on both La and Ga sites, the mean field approach was employed, which allowed us to set up solid solutions with varying concentrations of dopant ions. Results showed that Mg doping is important in promoting the introduction of higher concentrations of Sr in $\text{LaGaO}_3$.

Our calculated migration energy (0.73 eV) for oxygen vacancy transport was generally consistent with measured values. Higher activation energies from experiment may be related to increased dopant-vacancy association at higher dopant concentrations. Simulation techniques are ideally suited to probing transport mechanisms at the atomic level, and
revealed that oxygen vacancy migration occurs along the GaO$_6$ octahedron edge. However, this route was not linear, but slightly curved away from the central Ga cation. An examination of cations adjacent to the migration pathway indicated significant outward relaxation.

Simulations show that oxidation with the formation of holes is an energetically unfavourable process. This is consistent with experimental findings that show doped LaGaO$_3$ to be almost a pure ionic conductor. Preliminary calculations found that the incorporation of water is appreciably endothermic, which suggests that proton conduction will not be significant in this material.

Since we were primarily concerned with the study of oxygen ion conductivity in LaGaO$_3$, we used Molecular Dynamics (MD) simulations to gain valuable structural and ion transport information. In the past MD simulations have neglected ion polarisation effects and have used short simulation times (typically less than 20 ps), usually due to the lack of processing power. However, our calculations were run for 60 ps and employed the shell model for oxygen species which allowed for anion polarisability effects.

Simulations were performed on La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3.5}$ at a range of temperatures. The pair correlation functions indicated considerable disorder on the oxygen sub-lattice in the doped material which is typical for a fast oxygen ion conductor. Oxygen diffusion coefficients were calculated over a wider range of temperature and dopant compositions than available experimental data, and showed rapid oxygen transport. In the undoped system there was no sign of ion diffusion and this confirmed the need for acceptor-doping to enhance ionic conductivity. The highest conductivity was exhibited by La$_{0.8}$Sr$_{0.2}$Ga$_{0.85}$Mg$_{0.15}$O$_{3.5}$ over all the simulation temperatures; this is consistent with conductivity measurements. Calculated
activation energies showed significant scatter, although there is also wide scatter in experimental values, and therefore comparison was not straightforward. MD simulations produced a vast amount of data, including individual ion trajectories, which provided a detailed insight into oxygen ion migration mechanisms. By coupling this trajectory data with visualisation software we verified that oxygen ion migration occurs along the edge of a GaO₆ octahedron. We found no evidence of correlated motion for oxygen transport, rather our results pointed to a conventional hopping mechanism.

Future work should use MD techniques to explore the findings we make here regarding Cu and Hg doping on the Ga sites. Both ions were shown to have higher solubility than Mg and lower binding energies. Experimental conductivity measurements on Cu or Hg doped La₁₋ₓ-SrₓGaO₃ would be extremely useful to gauge the suitability of these ions as acceptor-dopants. While we recognise the possible electronic contribution from mixed-valence copper, it is worth pointing out that one of the highest oxygen ion conductivities is observed in the Aurivillius phase Cu-doped Bi₄V₂O₁₁ (‘BICUVOX’).
Appendices

Appendix 1: \textit{Interatomic Potentials}

Appendix 2: \textit{Calcia-stabilised Zirconia}

Appendix 3: \textit{Modelling of Bi}_4\textit{V}_2\textit{O}_{11}

Appendix 4: \textit{Internet Fuel Cell Resources}

Appendix 5: \textit{Presentations and Publications}
Appendix 1: *Interatomic Potentials*
Appendix 1: Interatomic Potentials

The short-range interatomic potentials used in this study, along with the lattice energies used in the defect reactions are reported in this Appendix.

Table A1.1 - Monovalent cations

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>ρ (Å)</th>
<th>C (eVÅ⁶)</th>
<th>Y (e)</th>
<th>k (eVÅ⁻²)</th>
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<tr>
<td>Li⁺...O²⁻</td>
<td>292.3</td>
<td>0.3472</td>
<td>0.0</td>
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<td>99999</td>
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<td>Na⁺...O²⁻</td>
<td>611.1</td>
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<td>0.0</td>
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<td>99999</td>
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<td>K⁺...O²⁻</td>
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<td>Rb⁺...O²⁻</td>
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<td>1.00</td>
<td>99999</td>
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<td>Ag⁺...O²⁻</td>
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<td>331.5715</td>
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Table A1.2 - Divalent cations

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<th>Interaction</th>
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<td>Sr²⁺...O²⁻</td>
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<td>Ba²⁺...O²⁻</td>
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<tr>
<td>Mn²⁺...O²⁻</td>
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<tr>
<td>Fe²⁺...O²⁻</td>
<td>694.1</td>
<td>0.3399</td>
<td>0.0</td>
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<tr>
<td>Co²⁺...O²⁻</td>
<td>696.3</td>
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<tr>
<td>Ni²⁺...O²⁻</td>
<td>683.5</td>
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<td>Zn²⁺...O²⁻</td>
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<td>0.2427</td>
<td>0.0</td>
<td>2.00</td>
<td>99999</td>
</tr>
<tr>
<td>Cd²⁺...O²⁻</td>
<td>499.6</td>
<td>0.3595</td>
<td>0.0</td>
<td>2.05</td>
<td>10.28</td>
</tr>
<tr>
<td>Hg²⁺...O²⁻</td>
<td>1725.99</td>
<td>0.3497</td>
<td>13.91</td>
<td>-6.10</td>
<td>840.00</td>
</tr>
<tr>
<td>Pb²⁺...O²⁻</td>
<td>648.5</td>
<td>0.3251</td>
<td>0.0</td>
<td>1.50</td>
<td>598.00</td>
</tr>
<tr>
<td>5Pb²⁺...O²⁻</td>
<td>5444.4</td>
<td>0.2994</td>
<td>0.0</td>
<td>2.00</td>
<td>99999</td>
</tr>
</tbody>
</table>
### Table A1.3 - Trivalent cations

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>( \rho ) (Å)</th>
<th>C (eVÅ(^6))</th>
<th>Y (e)</th>
<th>k (eVÅ(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Al^{3+}\ldots O^2^- )</td>
<td>1114.9</td>
<td>0.3118</td>
<td>0.0</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>( Sc^{3+}\ldots O^2^- )</td>
<td>1299.4</td>
<td>0.3312</td>
<td>0.0</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>( Cr^{3+}\ldots O^2^- )</td>
<td>1734.1</td>
<td>0.3010</td>
<td>0.0</td>
<td>0.97</td>
<td>67.00</td>
</tr>
<tr>
<td>( Mn^{3+}\ldots O^2^- )</td>
<td>1257.9</td>
<td>0.3214</td>
<td>0.0</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>( Fe^{3+}\ldots O^2^- )</td>
<td>1102.4</td>
<td>0.3299</td>
<td>0.0</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>( ^5 Ga^{3+}\ldots O^2^- )</td>
<td>2901.244</td>
<td>0.2742</td>
<td>0.0</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>( ^6 Ga^{3+}\ldots O^2^- )</td>
<td>2339.8</td>
<td>0.2742</td>
<td>0.0</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>( Y^{3+}\ldots O^2^- )</td>
<td>1345.1</td>
<td>0.3491</td>
<td>0.0</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>( La^{3+}\ldots O^2^- )</td>
<td>1545.213</td>
<td>0.35898</td>
<td>0.0</td>
<td>-0.25</td>
<td>145.00</td>
</tr>
<tr>
<td>( La^{3+}\ldots O^2^- )</td>
<td>1439.7</td>
<td>0.3651</td>
<td>0.0</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>( Nd^{3+}\ldots O^2^- )</td>
<td>1379.9</td>
<td>0.3601</td>
<td>0.0</td>
<td>3.00</td>
<td>99999</td>
</tr>
<tr>
<td>( Bi^{3+}\ldots O^2^- )</td>
<td>1644.98</td>
<td>0.34350</td>
<td>0.0</td>
<td>-0.25</td>
<td>145.00</td>
</tr>
<tr>
<td>( ^5 Bi^{3+}\ldots O^2^- )</td>
<td>1682.6731</td>
<td>0.3276</td>
<td>0.0</td>
<td>-0.25</td>
<td>145.00</td>
</tr>
</tbody>
</table>

### Table A1.4 - Tetravalent cation

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>( \rho ) (Å)</th>
<th>C (eVÅ(^6))</th>
<th>Y (e)</th>
<th>k (eVÅ(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Zr^{4+}\ldots O^2^- )</td>
<td>985.869</td>
<td>0.3760</td>
<td>0.000</td>
<td>1.350</td>
<td>169.617</td>
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</table>

### Table A1.5 - Pentavalent cation

<table>
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<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>( \rho ) (Å)</th>
<th>C (eVÅ(^6))</th>
<th>Y (e)</th>
<th>k (eVÅ(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^5 V^{5+}\ldots O^2^- )</td>
<td>2543.4541</td>
<td>0.2680</td>
<td>0.0</td>
<td>-4.497</td>
<td>145.00</td>
</tr>
<tr>
<td>( Nb^{5+}\ldots O^2^- )</td>
<td>1796.3</td>
<td>0.34598</td>
<td>0.0</td>
<td>-4.497</td>
<td>1358.58</td>
</tr>
</tbody>
</table>

### Table A1.6 - Oxygen - oxygen short-range interatomic potentials

<table>
<thead>
<tr>
<th>Interaction</th>
<th>A (eV)</th>
<th>( \rho ) (Å)</th>
<th>C (eVÅ(^6))</th>
<th>Y (e)</th>
<th>k (eVÅ(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^5 O^2^-\ldots O^2^- )</td>
<td>22764.30</td>
<td>0.1490</td>
<td>43.0</td>
<td>-2.2389</td>
<td>42.00</td>
</tr>
<tr>
<td>( ^8 O^2^-\ldots O^2^- )</td>
<td>22764.30</td>
<td>0.1490</td>
<td>27.89</td>
<td>-2.077</td>
<td>27.29</td>
</tr>
</tbody>
</table>
Table A1.7 - Lattice energies used in defect reactions

<table>
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<tr>
<th>Compound</th>
<th>( U_L ) (eV)</th>
<th>Compound</th>
<th>( U_L ) (eV)</th>
<th>Compound</th>
<th>( U_L ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_2)O</td>
<td>-29.98</td>
<td>MgO</td>
<td>-41.29</td>
<td>Al(_2)O(_3)</td>
<td>-160.50</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>-24.75</td>
<td>CaO</td>
<td>-35.95</td>
<td>Sc(_2)O(_3)</td>
<td>-144.47</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>-22.18</td>
<td>SrO</td>
<td>-33.42</td>
<td>Cr(_2)O(_3)</td>
<td>-154.21</td>
</tr>
<tr>
<td>Rb(_2)O</td>
<td>-21.18</td>
<td>BaO</td>
<td>-33.74</td>
<td>Mn(_2)O(_3)</td>
<td>-150.82</td>
</tr>
<tr>
<td>(^a)Ag(_2)O</td>
<td>-26.01</td>
<td>MnO</td>
<td>-38.73</td>
<td>Fe(_2)O(_3)</td>
<td>-150.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FeO</td>
<td>-40.12</td>
<td>(^i)Ga(_2)O(_3)</td>
<td>-153.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CoO</td>
<td>-40.83</td>
<td>Y(_2)O(_3)</td>
<td>-134.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NiO</td>
<td>-41.58</td>
<td>La(_2)O(_3)</td>
<td>-130.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^d)CuO</td>
<td>-43.79</td>
<td>Nd(_2)O(_3)</td>
<td>-129.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZnO</td>
<td>-39.80</td>
<td>(^h)ZrO(_2)</td>
<td>-109.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^h)CdO</td>
<td>-39.45</td>
<td>(^a)ZrO(_2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^h)HgO</td>
<td>-40.49</td>
<td>Nb(_2)O(_5)</td>
<td>-322.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PbO</td>
<td>-36.48</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All interatomic potentials taken from [71] and all lattice energies taken from [181] unless otherwise stated.

\(^a\) This study; \(^b\) [47], \(^c\) [70], \(^d\) [125], \(^e\) [182], \(^f\) [183], \(^g\) [103], \(^h\) [184], \(^i\) [185], \(^j\) [200]
Appendix 2: *Calcia-stabilised Zirconia*
Appendix 2: Molecular Dynamics Study of Calcia-stabilised Zirconia

Another common electrolyte utilised within fuel cell configurations and within other applications requiring high oxygen conduction is calcia-stabilised zirconia (CSZ) [9,91]. Ionic conductivity in CSZ reaches a maximum at about 12-15mol% calcia [91,111], with typical activation energies of 1.11 - 1.35 eV [108,111].

To our knowledge MD simulations have not been undertaken on CSZ, and therefore, following on from our successful study of YSZ we carried out extensive simulations on this system. The interatomic potential parameters were transferred directly from the simulation study of Ca/ZrO\textsubscript{2} by Dwivedi and Cormack [103], and are listed in Table A2.1. The simulation model was identical to that employed in the Y/ZrO\textsubscript{2} study. Configurations corresponding to calcia-doping levels between 1 to 30mol% in zirconia were set-up. Each configuration was run for 50ps within a temperature range of 1023 - 1773K. However, the results produced an unusually wide range of scatter in the calculated oxygen diffusion coefficients, with corresponding activation energies ranging between 0.15 - 0.30 eV. This study raised questions regarding the nature of calcia-doping in zirconia and warrants further investigation.

Table A2.1 - Interatomic potentials for Ca/ZrO\textsubscript{2} (rigid-ion)

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Short-range parameters</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A(eV)</td>
<td>ρ(Å)</td>
<td>C(eVÅ\textsuperscript{6})</td>
</tr>
<tr>
<td>Zr\textsuperscript{4+}...O\textsuperscript{2-}</td>
<td>985.869</td>
<td>0.3760</td>
<td>0.000</td>
</tr>
<tr>
<td>O\textsuperscript{2-}...O\textsuperscript{2-}</td>
<td>22764.300</td>
<td>0.1490</td>
<td>27.890</td>
</tr>
<tr>
<td>Ca\textsuperscript{2+}...O\textsuperscript{2-}</td>
<td>1090.4</td>
<td>0.3437</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Appendix 3: Modelling of $Bi_4V_2O_{11}$
Appendix 3: Modelling of Bi$_4$V$_2$O$_{11}$

A3.1 Introduction

The bismuth vanadate compound, Bi$_4$V$_2$O$_{11}$, has been shown to be the parent phase for a new family of oxide ion conductors known as BIMEVOX [186,187]. These systems, in which vanadium is partially substituted by aliovalent metal ions (ME = Co, Zn, Ni, Ca, Sr or Ge), have generated a great deal of interest [176,188-194]. The highest conductivity is exhibited in the Cu substituted compound (BICUVOX) and is found to be nearly two orders of magnitude higher than zirconia based electrolytes at 500K [195]. This compound has an activation energy of approximately 0.5 eV [196] compared to a value of around 1 eV [108] for yttria-stabilised zirconia.

It is the high conductivity at low temperatures which makes the BIMEVOX family very attractive for use as electrolytes in applications such as oxygen sensors and SOFC. The high conductivity is related to the stabilisation of the high temperature tetragonal $\gamma$ phase by aliovalent metal dopants which results in highly mobile, charge-compensating oxygen vacancies within the disordered perovskite-like layers [186].

However, in common with many ceramic materials, high quality structural data for these complex oxides are difficult to obtain. For example, experimental structural studies on Bi$_4$V$_2$O$_{11}$ and the BIMEVOX phases have been incomplete due to twinning [197], the occurrence of an incommensurate supercell and the disorder of both cations and oxygens [186]. In this study we have attempted to model the $\gamma$-Bi$_4$V$_2$O$_{11}$ using atomistic computer...
Appendix 3

Modelling of Bi$_4$V$_2$O$_{11}$

simulation techniques, which has never been performed before on this system. The reliability and quality of simulation results are ultimately dependent upon the potential model employed to describe the material under investigation. However, it is known that obtaining effective potentials for materials containing Bi and/or V can be difficult. In the present study we have attempted to derive effective potentials for Bi$_4$V$_2$O$_{11}$ using the relaxed fitting procedure embodied in the GULP code [68,69]. Essentially, this allows the simultaneous relaxation of the shells during the fitting routine to achieve a better fit.

A3.2 Crystal Structure

The crystal structure of Bi$_4$V$_2$O$_{11}$ can be formulated as (Bi$_2$O$_2$)$_{2+}$,(VO$_{3.5}$$\cdot 0.5$)$_{2-}$ and therefore can be considered as derived from $\gamma$-Bi$_2$MoO$_6$, the n=1 member of the Aurivillius compounds (Bi$_2$O$_2$)$_{2+}$,(An$_{n-1}$B$_n$O$_{3n+1}$) [198].

Depending on the temperature, Bi$_4$V$_2$O$_{11}$ exhibits three different polymorphs, $\alpha$, $\beta$ and $\gamma$. Their crystal structures can be described in an orthorhombic “mean cell” $a_m = 5.53$, $b_m = 5.61$ and $c_m = 15.28\text{Å}$ [198]. By far the most studied phase is the high temperature $\gamma$ phase, which can be stabilised at room temperature by the substitution of vanadium by various aliovalent transition metals. On stabilisation an apparent tetragonal unit cell ($I4/mmm$ space group) is observed from X-ray powder diffraction studies with $a_{tet} = a_m/\sqrt{2}$. The crystal structure of $\gamma$-BIMEVOX can be viewed as composed of Bi$_2$O$_2^{2+}$ layers interleaved with anion-deficient perovskite-like sheets. The bismuthate layer is fully ordered with Bi in a square pyramidal coordination to four O(1) atoms, while the O(2) and O(3) atoms in the vanadate layer occupy split sites [186,195,199]. This structure is illustrated in figure A3.1. The crystallographic coordinates used in this study for the $\gamma$ phase of Bi$_4$V$_2$O$_{11}$ were derived from data on the
Appendix 3

Modelling of Bi\textsubscript{4}V\textsubscript{2}O\textsubscript{11}

BICOVOX system obtained by Abrahams et. al. [199] and are given in Table A3.1.

Table A3.1 - Atomic parameters for $\gamma$-Bi\textsubscript{4}V\textsubscript{2}O\textsubscript{11}

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>4e</td>
<td>0.00</td>
<td>0.00</td>
<td>0.16863(6)</td>
<td>1.00(-)</td>
</tr>
<tr>
<td>V</td>
<td>2b</td>
<td>0.50</td>
<td>0.50</td>
<td>0.00(-)</td>
<td>1.00(-)</td>
</tr>
<tr>
<td>O(1)</td>
<td>4d</td>
<td>0.00</td>
<td>0.50</td>
<td>0.25(-)</td>
<td>1.00(-)</td>
</tr>
<tr>
<td>O(2)</td>
<td>4e</td>
<td>0.50</td>
<td>0.50</td>
<td>0.1053(6)</td>
<td>0.332(7)</td>
</tr>
<tr>
<td>O(3)</td>
<td>8g</td>
<td>0.50</td>
<td>0.00</td>
<td>0.0285(3)</td>
<td>0.338(-)</td>
</tr>
</tbody>
</table>

Figure A3.1 - Idealised structure of $\gamma$-Bi\textsubscript{4}V\textsubscript{2}O\textsubscript{11} [186]
Table A3.2 - Interatomic potentials for $\gamma$-$\text{Bi}_4\text{V}_2\text{O}_{11}$

(a) Starting potentials

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Short range potentials</th>
<th>Shell model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (eV)</td>
<td>$\rho$ (Å)</td>
</tr>
<tr>
<td>$^{\text{a}}$Bi$^{3+}$...Bi$^{3+}$</td>
<td>24244.50</td>
<td>0.32840</td>
</tr>
<tr>
<td>$^{\text{b}}$Bi$^{3+}$...O$^{2-}$</td>
<td>1644.98</td>
<td>0.34350</td>
</tr>
<tr>
<td>$^{\text{c}}$V$^{5+}$...O$^{2-}$</td>
<td>5312.99</td>
<td>0.26797</td>
</tr>
<tr>
<td>$^{\text{d}}$O$^{2-}$...O$^{2-}$</td>
<td>22764.30</td>
<td>0.14900</td>
</tr>
</tbody>
</table>

$^{\text{a}}$(200), $^{\text{b}}$starting values same as Bi$^{3+}$...Bi$^{3+}$ $^{\text{210}}, ^{\text{c}}$(52), $^{\text{d}}$(53), $^{\text{e}}$(201)

(b) Derived potentials

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Short range potentials</th>
<th>Shell model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (eV)</td>
<td>$\rho$ (Å)</td>
</tr>
<tr>
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<td>0.4017</td>
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<tr>
<td>Bi$^{3+}$...O$^{2-}$</td>
<td>1682.6731</td>
<td>0.3276</td>
</tr>
<tr>
<td>V$^{5+}$...V$^{5+}$</td>
<td>24244.5000</td>
<td>0.3284</td>
</tr>
<tr>
<td>V$^{5+}$...O$^{2-}$</td>
<td>2543.4541</td>
<td>0.2680</td>
</tr>
<tr>
<td>O$^{2-}$...O$^{2-}$</td>
<td>22764.3000</td>
<td>0.14900</td>
</tr>
</tbody>
</table>

A3.3 Interatomic Potential Parameters

The potential parameters assigned to each ion-ion interaction were derived empirically by a least-squares fitting routine to minimise the strains acting on the ions within the unit cell (i.e., internal basis strains) and on the unit cell as a whole (i.e., bulk lattice strains). This procedure adjusts the potential parameters so as to achieve the best possible agreement between...
calculated and experimental properties. The starting interatomic potentials are listed in Table A3.2a, along with the derived potentials (Table A3.2b). The calculated properties for this system are presented in Table A3.3. We note that during the fitting procedure over two hundred calculations were performed, which is indicative of the complex structure of this material.

Table A3.3 - Calculated properties for γ-Bi₄V₂O₁₁

(i) Unit cell parameters

|                | Experimental | Calculated | \(|\Delta|\) (%) |
|----------------|--------------|------------|---------------|
| \(a = b\) (Å)  | 3.922        | 3.941      | 0.019 (0.48)  |
| \(c\) (Å)      | 15.447       | 16.193     | 0.746 (4.83)  |
| \(\alpha = \beta = \gamma\) | 90.000       | 90.000     | 0.000 (0.00)  |
| Volume (Å³)    | 237.668      | 251.559    | 13.891 (5.84) |

(ii) Separation

|                | Experimental (Å) | Calculated (Å) | \(|\Delta|\) (Å) |
|----------------|------------------|----------------|--------------|
| Bi - O(1)      | 2.329            | 2.356          | 0.027        |
| V - O(2)       | 1.627            | 1.656          | 0.029        |
| V - O(3)       | 2.010            | 1.988          | 0.022        |
| O(1) - O(2)    | 2.974            | 3.232          | 0.258        |

Examining Table A3.3 we can see that the derived potentials have reproduced the cell parameters fairly well, although the \(c\)-parameter is still larger than the expected value. We note that this problem has also occurred in similar studies of Bi₃WO₆ [202]. The largest discrepancy arises on comparing the initial and final cell volumes; this clearly has to be minimised before proceeding with further calculations. However, on examination of the cation-anion separations we find good agreement between the calculated and experimental values. The calculated O(1)-O(2) separation is larger than expected and this is probably the
cause of the cell expansion along the c-axis. In an attempt to further refine our potential model three-body terms were also employed between O(2)-V-O(3). Unfortunately the incorporation of the three-body term did not reproduce the structure, with the cell volume differing from the experimental value by as much as 98%.

A3.4 Summary

This study has shown that it is difficult to derive potentials that accurately reproduce the complex structure of $\gamma$-$\text{Bi}_4\text{V}_2\text{O}_{11}$. Nevertheless, our derived potentials have been fairly successful in modelling the properties and reproducing the bond lengths in this structure. It is clear that further work will have to be performed on refining the potential model before undertaking defect calculations.
Appendix 4: *Internet Fuel Cell Resources*
Appendix 4: Fuel Cell Resources on the Internet

Increasingly, academics are turning to the Internet to gather information and exchange ideas. Therefore, it seems appropriate to outline some of the resources available relevant to fuel cell technology.

Listed below are three sites on the World Wide Web which provide a range of information related to fuel cell technology.

1. http://www.fuelcells.org “Fuel Cells 2000 is an activity of the Breakthrough Technologies Institute. Fuel Cells 2000 provides information to policy makers and the public; supports the early utilization of fuel cells by such means as pilot projects and government purchases; conducts activities designed to foster education, training and as supportive; legal and regulatory environment for fuel cells and related technologies.”


Usenet News provides a ‘bulletin board’ for over 26,000 different subjects. It acts as worldwide knowledge base, and is useful for exchanging ideas with other academics. Fuel cell and related topics are usually discussed at sci.chem.electrochem
Appendix 5: Presentations and Publications
Appendix 5: Presentations and Publications

A5.1 Conference Presentations

RSC Polar Solids Discussion Group, Easter Meeting, Oxford University (1995)
“Dopant Effects in Zirconia” (poster)

RSC Polar Solids Discussion Group, Christmas Meeting, Sussex University (1996)
“Lanthanum Gallate: A New Oxygen-Ion Conductor” (talk)

Departmental Colloquium, University of Surrey (1997)
“Atomistic Simulation Studies of Fast Oxygen Ion Conductors” (talk)

RSC Faraday Discussions 106, University College London (1997)
“Dopant Substitution and Ion Migration in the LaGaO$_3$-based Oxygen Ion Conductor” (poster)

VI$^{th}$ European Conference on Solid State Chemistry, ETH, Zurich, Switzerland (1997)
“Dopant Substitution and Ion Migration in the LaGaO$_3$-based Oxygen Ion Conductor” (poster)

A5.2 Publications and Patents

M. S. Khan, M. S. Islam and D. R. Bates, “Dopant Substitution and Ion Migration in the
LaGaO$_3$-based Oxygen Ion Conductor”, *J. Phys. Chem.*, *In Press*

Papers in preparation on the ZrO$_2$ work (Chapters 3 and 4) and the LaGaO$_3$ MD studies
(Chapter 6).

Patent pending in conjunction with BG plc.


[200] D. J. Ilett and M. S. Islam, *unpublished results*


ERRATA

p9     process should read processes
p13    materials properties should read material properties
p16    responsible for should read responsible for the
p20    of a angle should read of an angle
p27    W is the second derivative matrix of the lattice energy function (r ion displacement, E is the symmetric strain matrix)

p28    F is the sum of squares should read F is the sum of squared differences
p34    forces on the ions on their new positions should read forces on the ions in their new positions
p37    Collins et.al should read D. R. Collins, B. Smith, N. M. Harrison and T. R. Forester
p38    Mean Square Displacements should read Mean Square Displacement
p53    function dopant size should read function of dopant size
p58    prefer to be eight-fold co-ordination should read prefer to be eight-fold co-ordinated
p60    Therefore, on comparing should read Therefore, comparing
p68    smaller ionic radii should read smaller ionic radius
p78    introduction oxygen vacancies should read introduction of oxygen vacancies
p109   synergy should read synergic
p112   due hardware should read due to hardware
p130   cell is viewed should read cell is viewed from
p133   Figure 6.11 - La and Mg positions should read Ga and Sr positions