

Cerium-Doped Strontium Titanate Materials for Solid Oxide Fuel Cells

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Abstract

Poor performance arising from high polarisation overpotentials, structural instability under reduction-oxidation (Redox) cycling and long term performance degradation of anodes are three important problems in current SOFC development. These problems can be minimised by appropriate changes to the conventional electrode microstructures and electrode/electrolyte interfaces. Alternatively, new, redox stable, highly conducting ceramic materials can be developed to circumvent these issues. This work focuses on the synthesis, structural and electrical characterisation of cerium-doped strontium titanate, as an all ceramic replacement for the current ceramic - metal (cermet) composite anode materials.

Ceramic samples were prepared with the formula $\text{Sr}_{1-x}\text{Ce}_x\text{TiO}_3$ and $\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_3$. Electrical conductivity was determined using the DC four probe method and AC impedance under a range of temperatures and oxygen partial pressures. In air these materials were found to be very poor conductors, with similar conductivity to un-doped SrTiO_3 . Activation energies in air were found to be between 1.5 and 1.8 eV, typical for SrTiO_3 -based materials. Under reducing conditions the conductivity increases substantially, although the reduction process was found to be relatively slow, even at high temperature. The maximum conductivity of 33 Scm^{-1} at 905°C ($p(\text{O}_2) \sim 10^{-18} \text{ atm}$) increased to 50 Scm^{-1} at 670°C . Re-oxidation was found to be significantly slower than reduction even in relatively porous samples; however, the mechanism for this reaction has not been established.

Thermal expansion coefficients (TEC) in air were found to be in the range of 11-12 p.p.m. K^{-1} over the temperature range $150\text{-}1100^\circ\text{C}$. TEC values changed very little at low oxygen partial pressures ($p(\text{O}_2) \simeq 10^{-20}$), generally decreasing by $\sim 0.5 \text{ p.p.m.K}^{-1}$ compared with the values obtained in air. These thermal expansion coefficients are compatible with common electrolyte materials.

Cerium-doped strontium titanate is therefore a promising candidate as an alternative SOFC anode material. It possesses both high electronic conductivity and good dimensional stability under thermal and redox cycling.

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Originality

This thesis is a record of the work that I carried out in the Department of Materials at Imperial College London and in the laboratories of Ceres Power Ltd. between August 2003 - September 2007.

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Chapter 1

Introduction

1.1 Overview

State-of-the-art anode materials for solid oxide fuel cells (SOFCs) are composed of a mixture of nickel and an ion-conducting material, such as yttria-stabilised zirconia (YSZ) or cerium gadolinium oxide (CGO). These composite materials were developed almost 40 years ago and have seen very few changes in that period. The original patent [1] covered nickel and cobalt composites for solid oxide fuel cells and it highlights many of the problems at that time. Many of the issues which were identified then are still highly relevant to electrode materials today. Ceramic-metal (cermet) composites are capable of very good performance when run on H_2 or reformed natural gas. Ni-cermets, however, do come with some limitations: They are sensitive to sulfur [2,3], they do not tolerate repeated oxidation and reduction (redox) cycles [4,5] and are damaged by exposure to dry hydrocarbons, such as methane. These cause carbon formation and block porosity and inhibit the electrochemical electrode reactions.

There has been significant progress toward alternative materials and electrode structures to try and overcome some of the problems outlined above. However, there have been very few alternative materials that can surpass the performance of the cermet structure and to the authors knowledge there has been no commercial implementation of an alternative material.

1.2 Thesis aims and outline

This research was initially undertaken to find alternative anode materials for SOFCs. This research was not limited to materials for operation in any particular temperature range. As the project progressed, and one particular system was identified, the focus of the research shifted toward characterisation of the new material rather than empirical cell testing. The remainder of the time was used trying to characterise Ce-doped SrTiO_3 . The aims of this work were, broadly:

- To identify a novel compound as a potential anode material for SOFC.
- To identify a material which shows reasonable stability in air and stability under reducing conditions similar to a fuel-cell anode environment (Redox tolerance).
- To identify a material which shows resistance to sulfur poisoning.

Chapter 2

Background

Solid oxide fuel cells (SOFC) are currently at the forefront of research into new electricity generation methods to meet the world's energy demands. This is primarily due to their efficient operation and their environmentally friendly nature when fuelled on hydrogen. There are still a wide range of research and development activities that continue today. These range from investigation of fundamental cell materials to manufacturing processes and system optimisation.

All SOFCs have common components. Generally, there are slight variations in the number or composition of the layers, but their functions remain the same. Figure 2.1 shows the basic schematic of a SOFC and the three basic components that make up all fuel cells; that is, the electrolyte, fuel electrode (anode) and the air electrode (cathode). Not shown is the interconnect which connects cells placed together in a stack, allowing electrical contact between layers while separating the fuel and air streams. Typically the electrolyte is either yttria-stabilised zirconia (YSZ), gadolinia-doped ceria (CGO) or $(\text{La,Sr})(\text{Ga,Mg})\text{O}_3$ (LSGM). The latter two materials have a significantly higher oxygen ion conductivity than YSZ and so allow a cell to operate at lower temperatures. This allows them to be used at temperatures in the 500-600°C range whereas YSZ is generally restricted to use at temperatures above 750°C. Cathode materials have, and still are, attracting a great deal of attention (particularly for lower temperature applications where the cathode over-potential still dominates the cell resistance, due to the increased

difficulty of reducing oxygen at lower temperatures). In general, however, there are two recognised materials in common use; these are strontium-doped lanthanum manganite (LSM) and lanthanum-doped strontium ferrite cobaltite (LSCF).

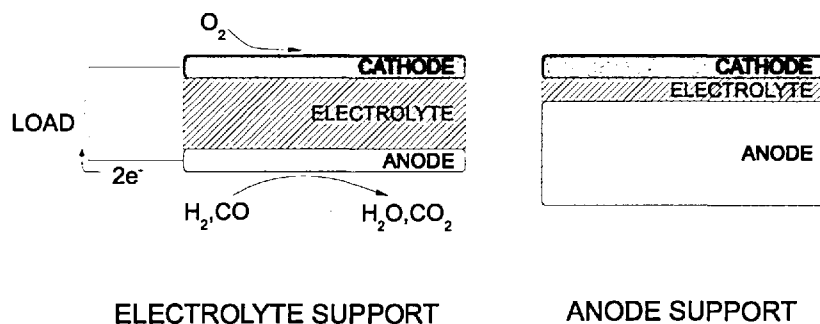


Figure 2.1: Simplified schematic of an electrolyte supported and an anode supported cell

Importantly, the anode material set, with the exception of some microstructural modifications, has remained unchanged since the metal-ceramic (cermet) structure was developed more than 40 years ago. In the 1971 patent by Spacil [1] the description of nickel or cobalt/YSZ anode and the challenges facing anode materials in a SOFC are still relevant today.

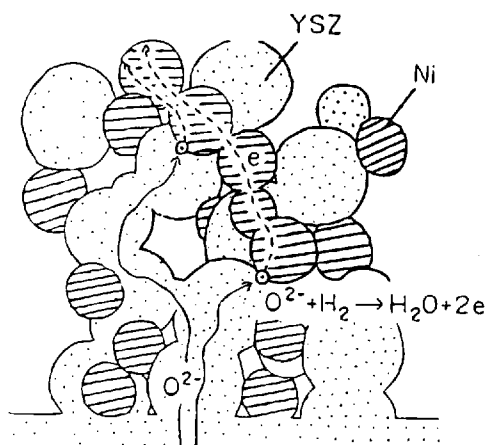


Figure 2.2: A schematic of the anode microstructure showing the paths of oxygen ions and electrons. (After ref. [6])

Anode development up until now has remained largely empirical. Attention has been focused on: Material specification; powder grain size and grain size distribution; powder morphology and nickel to ceramic ratio. The aim is to arrive at a material with

suitable conductivity and expansivity to allow sufficiently high performance while still maintaining an acceptable degradation rate during extended operation [7, 8]. Given that the anode over-potential and polarisation resistances have historically been small by comparison to the cathode [6], it was logical to concentrate research activities on the immediate issues that caused the largest cell resistances. It has only been in the last decade that more detailed computer modelling [9–11] and experimentation has begun to determine the fundamental mechanistic and kinetic understanding of the anode processes [12, 13]. Recently, several groups have been using serial sectioning, imaging and computer reconstruction to characterise the Ni-cermet anode microstructure in three dimensions [14, 15]. From the reconstruction, quantitative analysis of the contact points between the nickel and the ceramic component, the so-called 'triple phase boundary' (TPB), can be performed. It is at these TPB sites where much of the anode reaction takes place. By characterising the relationship between the TPBs, the electrolyte and the current collector, it is hoped that more accurate performance models can be developed. Analysis of real cell microstructures will also lead to a better understanding of the reactions occurring in the anode. This technique has also been applied to composite cathodes [16].

Ni-cermets have operated successfully as fuel cell anodes. However, these materials do present some problems. Firstly, the nickel metal sinters during prolonged operation, reducing surface area. This results in lower catalytic activity and increased cell resistance. Secondly, the cermet suffers from thermal mismatch with the electrolyte material which can result in stresses that cause failure. When using commercially available fuels such as natural gas, the cermet material shows additional problems. Nickel is known to be susceptible to sulfur poisoning at relatively low sulfur concentrations in the gas stream [17]. It is also susceptible to carbon formation (coking) from catalytic cracking during internal reforming [18].

2.1 Motivation

As we have established, there are three main areas (other than outright performance) where one would like to improve the anode's properties. These have been mentioned

above and are summarised below:

- Redox stability: the propensity for nickel to oxidise and cause electrochemical and mechanical damage to the anode.
- Sulfur tolerance: H_2S and other sulfur species can severely impair cell activity, even at low concentrations. In high concentrations the damage can be irreversible.
- Carbon tolerance: under the wrong conditions hydrocarbon fuels will crack on the active nickel surface which may block porosity and damage the cermet structure.

2.1.1 Redox resistance

Typically, SOFC anodes are fabricated using nickel oxide and YSZ. The nickel oxide is reduced to nickel when exposed to a reducing atmosphere under operating conditions. A volume reduction of $\sim 40\%$ occurs during the reduction process. Nickel oxide reduction and nickel oxidation are completely reversible at typical SOFC operating temperatures. If air is allowed to leak into the anode side of the fuel cell through a fuel supply interruption, an emergency stop, seal leakage, or other event, then the nickel will oxidise to nickel oxide with an associated volume expansion of $\sim 70\%$. Porous NiO/YSZ SOFC anodes are unlikely to experience such a drastic volume change during reduction or re-oxidation due to space available by expansion into pores. However, any volume change that does occur may have a significant effect on the integrity of interfaces within a fuel cell and may result in significant degradation in cell activity. This reduction and oxidation process is termed '*redox cycling*'. Although the nickel oxidation reaction is completely reversible, when the oxygen partial pressure returns to low levels it has been found in practice that degradation of cell performance still occurs. Most likely this is due to mechanical damage from the volume changes on redox cycling.

Wood *et al.* [19] and Waldbillig *et al.* [20–22] worked closely with industry to establish the cause of many of the microstructural mechanisms that govern degradation during the redox cycling process. They suggested useful guidelines on how to minimise the effect of redox cycling, ranging from a materials-led approach through to system-level

engineering. The materials aspects of these solutions are outlined in Table 2.1 (*adapted from ref. [19]*).

Table 2.1: Materials and component redox solutions broken down into material, microstructural modification, and kinetic concepts.

Materials	Microstructural modification	Engineered modification
Nickel replacement	Graded nickel content	Improved sealing
Ceramic anode	Anode functional layer	Oxidation barrier
	Increased porosity	Lower operating temperature

- **Nickel replacement:** This involves substituting Ni with another appropriate metal such as cobalt or copper which will not oxidise as readily as nickel. This will have various implications on cost and performance.
- **Ceramic anode:** This involves complete replacement of the Ni-cermet structure with an electrically conductive, catalytically active, ceramic material. Alternatively a ceramic electronic conductor and an oxygen ion conductor can be combined to form an all-ceramic composite.
- **Graded nickel content:** By grading the Ni content from a higher concentration at the current collector to a lower concentration near to the electrolyte, damage due to Ni oxidation near the electrolyte is thought to be minimised.
- **Anode functional layer:** This gives similar results to a graded nickel content electrode. The functional layer contains less nickel and has a finer distribution of porosity to minimise damage caused by re-oxidation near the anode-electrolyte interface.
- **Increased anode porosity:** By increasing the porosity, there is more space for expansion during oxidation.
- **Oxidation barrier:** A sacrificial layer is placed close to the anode that will oxidise before the anode itself is exposed to oxidising conditions. The barrier layer can act as a getter, removing any oxygen from the gas stream. Alternatively, the oxidation of the barrier layer will physically block any further gas access to the anode, sealing it off from further damage.

- Lower operational temperature: This would attempt to slow the kinetics of nickel oxidation, allowing more time to restore the fuel supply or shut the system down before too much oxidation, and potential damage, occurs.

2.1.2 Carbon tolerance

Until the introduction of a viable hydrogen economy and to take advantage of the higher efficiencies offered by fuel cells, fuels such as natural gas and methane would be preferable since these are commercially available. A majority of commercial, high-temperature, fuel cell companies are focusing on the use of natural gas as it is widely available in many western countries and can be piped directly into the home. More complex hydrocarbons, such as liquified petroleum gas (LPG) [23], coal gas [24] and gasified biomass [25, 26] have also been shown as viable fuels. There is a conflict, however, between the chemistry of these fuels (i.e. fuels rich in carbon) and the highly catalytic nature of the Ni-cermet anode. The nickel surface tends to catalyse the pyrolysis of hydrocarbons, leading to the deposition of carbon in the open porosity of the anode microstructure. This results in blocking of the triple phase boundaries, and prevents fuel entering and reactants escaping the anode compartment. Continued and excessive carbon deposition can also lead to mechanical damage of the anode, which leads to catastrophic anode failure.

Fuels and reforming reaction

Another advantage of operating cells at high temperature is that there is no requirement for noble metal catalysts because many of the reactions are thermally activated. High temperatures are utilised in the SOFC to facilitate many reforming reactions which, when appropriately controlled, can be used to prevent carbon deposition. Table 2.2 outlines some of the main reforming reactions that can be performed at high temperatures in the cell or in a pre-reactor connected to the fuel cell assembly. Reforming is the reaction of the hydrocarbon fuel with steam or carbon dioxide. Steam and carbon dioxide are usually recycled from the anode exhaust system or can be introduced upstream from the cell or stack. In practice, a majority of the reforming processes are performed externally in a designated reforming reactor. While so-called 'complete

internal reforming' is possible, the process is endothermic and this complicates the thermal management of the cell, reduces cell activity (due to a lowering of the local cell temperature), and potentially introduces thermal gradients across the cell and stack assembly, which in turn introduces unwanted mechanical stresses.

Table 2.2: Reaction of hydrocarbon fuels.

1.	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO}$	Steam reforming
2.	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{H}_2 + 2\text{CO}$	Carbon dioxide reforming
3.	$2\text{CH}_4 + \text{O}_2 \rightleftharpoons 4\text{H}_2 + 2\text{CO}_2$	Partial oxidation
4.	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$	Water/gas shift
5.	$\text{CH}_4 \rightleftharpoons 2\text{H}_2 + \text{C}$	Hydrocarbon pyrolysis
6.	$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	Boudouard coking
7.	$\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}$	Steam decoking

Carbon tolerant anode materials

Several materials-based alternatives, rather than chemical engineering alternatives, have been proposed to avoid carbon deposition. To overcome the limitations of nickel-based systems, research has focused on materials which are still active for catalytic oxidation of methane (and higher hydrocarbons) yet suppress the cracking reaction and subsequent carbon deposition. Oxide materials have also proved to be very good oxidation catalysts and do not promote the pyrolysis reaction. Ceria has been added as an inter-layer in Ni-YSZ anodes with promising results when run on dry hydrocarbons at 650°C [27]. Further details of other ceramic-based materials will be presented in Chapter 4. The aim of research into direct oxidation is to alleviate the additional complexity introduced when using a fuel processing system. This would simplify the system and reduce its cost significantly.

Unfortunately, many of the first row transition metals, with the exception of Cu, still promote the formation of carbon when the cell is fuelled with dry hydrocarbons. Other metals such as Ag and Au are good conductors but show very little activity toward hydrocarbon oxidation, and are expensive. Copper, gold and silver also have relatively low melting points (1083°C, 1064°C and 962°C respectively) which limits the upper operational temperature range of cells that contain these materials. It also complicates the manufacturing process where sintering temperatures of ceramic components often

exceed 1000°C. Copper-ceria cermet systems have attracted significant attention [28–30]. Copper was found to be inactive as an oxidation catalyst but did not show any signs of significant carbon deposition. Ceria was found to improve the catalytic activity toward the fuel oxidation [31]. These materials showed satisfactory performance when operating on dry hydrocarbon fuels [32].

2.1.3 Sulfur tolerance and other impurities

Another major issue surrounding the use of commercial fuel is the tolerance of cell operation to impurities often present in commercially available fuel supplies. McEvoy [6] commented on impurities such as ammonia and hydrochloric acid which are sometimes present depending on the source of the fuel; such as from biomass or fermentation processes. High temperature studies have shown cells to be tolerant to HCl over several hundred hours [33]. Ammonia seems to pose very few problems, even at high concentrations, and some authors have even proposed running fuel cells entirely on ammonia [34, 35].

Sulfur, whether added as a safety measure in the form of thiols, or as H₂S from impurities, causes serious degradation of cell activity. Much of the research in this area has focused on the understanding of the mechanism of sulfur poisoning. The overriding consensus is that sulfur strongly chemisorbs on the nickel surface, blocking the active sites for hydrogen oxidation [17]. Even at very low concentrations, in the order of part-per-billion, significant loss of activity occurs, particularly at lower temperatures [36]. Ni-cermet containing ceria are also thought to be susceptible to an additional deleterious poisoning reaction whereby, at high sulfur contents, there is a reaction with CeO₂ to form Ce₂O₂S [32].

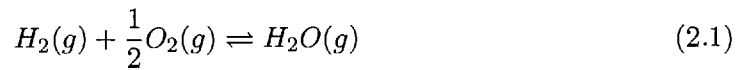
Cu-based anodes do not suffer as badly as their Ni-based counterparts. Gorte [32] has shown that Cu-CeO₂-YSZ anodes can operate at relatively high sulfur concentrations. This is thought to be partially due to a lower stability of copper sulfides compared to nickel sulfides. More importantly, copper shows very low catalytic activity toward fuel oxidation and so sulfur adsorption seems to have very little effect on the cell activity. It is the catalytic activity of CeO₂ that has been responsible for the enhanced activity

when using these materials. However, the same group found a drop in performance corresponding to operation at a sulfur partial pressure where $\text{Ce}_2\text{O}_2\text{S}$ was stable [32].

Using commercial fuels is imperative for the initial penetration of fuel cells into the market place. Minimising or eliminating the deleterious reaction of sulfur with Ni-cermet anodes is very important for commercial exploitation. Significant progress has been made in the understanding of the sulfur poisoning mechanism. However, the crux of the problem is nickel, and removing or pacifying nickel does not appear likely in the near future. Many commercial developers use sulfur traps to completely remove the sulfur from the fuel well before it reaches the fuel cell [36]. But as with the reforming and redox issues outlined above, it adds cost, complexity, size and weight to a system.

2.2 Solid Oxide Fuel Cell Operation

One very attractive benefit of the SOFC is that all of the components are solid from room to operating temperature. This alleviates the electrolyte containment issues that occur in phosphoric acid cells and molten carbonate cells. Precious metal electrocatalysts are not required due to the high operating temperatures at which thermal activation is possible. High temperature operation also allows a SOFC to be operated on a variety of fuels. The basic operational principles of an SOFC were illustrated in Figure 2.1 (page 4). For a SOFC running on hydrogen, the overall oxidative reaction of hydrogen is:



Under open circuit conditions, there is an electrochemical potential due to the oxygen partial pressure gradient across the electrolyte membrane. This potential is referred to as the open circuit voltage (OCV). It is related to the net change in Gibb's free energy, $\Delta\overline{G}_f$, of equation 2.1 by the following:

$$\Delta\overline{G}_f = -nFE \quad (2.2)$$

where n is the number of electrons participating in the reaction, F is Faraday's constant and E is the Nernst potential or OCV and can be related in terms of reactant partial pressure by:

$$E = -\frac{\Delta\bar{G}_f}{2F} = -\frac{\Delta\bar{G}_f^0}{2F} - \frac{RT}{2F} \ln \left(\frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{\frac{1}{2}}} \right) = E^0 + \frac{RT}{4F} \ln \left(\frac{p_{H_2}^2 \cdot p_{O_2}}{p_{H_2O}^2} \right) \quad (2.3)$$

Equation 2.3 is a form of the Nernst equation where E^0 is the theoretical open circuit voltage of a single cell and $\Delta\bar{G}_f$ is the Gibbs free energy of the reaction.

2.2.1 Cell losses

Once a cell is connected to an external circuit, current begins to flow and the OCV decreases. There are a number of processes that lead to a drop in OCV and all of these process are irreversible. One of the most straight forward reasons for a voltage drop is that the circuit will have a finite resistance and therefore the voltage will decrease in accordance with Ohm's law. Other factors that affect the voltage in a working fuel cell are illustrated schematically in Figure 2.3 and 2.4. Other than ohmic losses, the other main contributors are so-called polarisation losses. These can be split into two types:

Activation Polarisation: This occurs at low current densities and is a symptom of slow electrode reactions (either cathode or anode, or both). Part of the open circuit voltage is lost driving the chemical reaction that transfers the electrons to or from the electrode.

Concentration Polarisation: Concentration polarisation is concerned with the relationship of OCV and the concentrations of reactants and products in the electrode compartments, as defined by Eq. 2.3. If the microstructure of the electrodes is poor or current density high, then reactants cannot reach the reaction zone quickly enough. This results in depletion of fuel or air near the active regions of the cell and leads to a reduction in the OCV in accordance with Equation 2.3. Because of this failure to transport enough reactant to the electrode surface, this type of loss is often referred to a 'mass transport loss'.

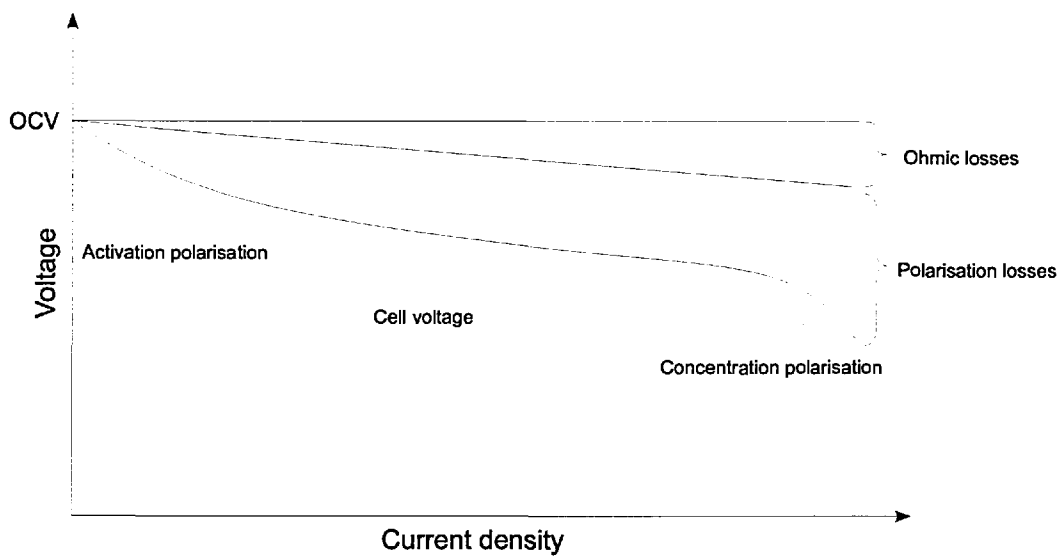


Figure 2.3: Schematic V-I curve displaying different types of irreversible voltage losses in an operational fuel cell.

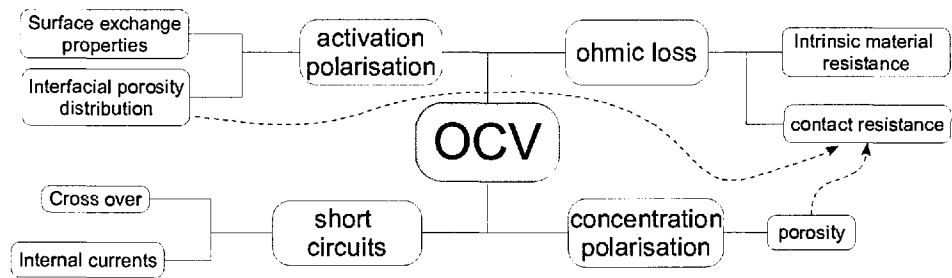


Figure 2.4: Representation of irreversible resistances and their relationships in a fuel cell

Reduction in OCV can also be caused by gas leakage between the air and the fuel compartments, commonly referred to as 'cross-over'. Fuel (or air) leakage occurs when the electrolyte membrane is not entirely gas-tight due to low density, sintering defects or cracking caused by excessive mechanical stresses. Gas cross-over results in a lowering of the chemical potential gradient, as described in equation 2.2. This also typically has a detrimental physical effect on the fuel cell, due to uncontrolled burning of the fuel on the air-side of the cell. Internal leakage currents can be caused by electronic conduction in the electrolyte layer instead of purely ionic conduction. This is one of the reasons why doped ceria is often cited as unsuitable for cell operation above 600°C [37].

2.2.2 Anode operation

Understanding the fundamental operation of the anode is an obvious, but difficult goal for anyone working the SOFC electrode area. There have been several comprehensive studies on Ni-cermet anode operation and characterisation. Two key factors are needed for basic anode operation: electrical conductivity and a highly porous microstructure. Good electrical conductivity is needed because, in many cases, the anode doubles as an electrode for fuel oxidation and is also the current collector. The minimum electrical conductivity required for efficient cell operation is often considered to be around 100 Scm^{-1} [38]. This value is, in part, derived from the requirement of each cell component (anode, cathode and electrolyte) to have an area-specific resistance (ASR) at or below 0.15 Ωcm^2 to ensure optimal cell performance [39].

ASR is a material property often quoted in fuel cell literature. It is simply the cell resistance normalised by the cell area and is expressed in units of Ωcm^2 . ASR can be related to the conductivity and thickness of a layer by the following equation:

$$ASR = R \times A = L/\sigma \quad (2.4)$$

where R is the resistance (in Ω), A is the cell area (in cm^2), σ is the conductivity (in Scm^{-1}) and L is the layer thickness. It should be noted that the ASR represents the resistive contribution from all parts of the cell. Further to this, when the ASR is broken down into anode, electrolyte and cathode components, each of these is the sum of the

ohmic, polarisation, contact and, in the case of electrodes, mass transport resistances. For example:

$$ASR_{anode} = R_{anode} + R_{cont} + R_p + R_{mass} \quad (2.5)$$

where R_{anode} is the material resistance of the anode material itself, R_{cont} is the contact resistance caused by non-ideal contact between cell layer ($R_{anode} + R_{cont} = R_s$), R_p is the polarisation resistance and R_{mass} is the mass transport resistance.

Porosity is the other key parameter that needs to be optimised. The term 'porosity' is often used relatively loosely to mean the open space in an anode microstructure. Details of the microstructure of the porosity is often more important than just the volume of voids in a microstructure. There is obviously a clear difference between open and closed porosity; the latter is ineffective during cell operation. But there are factors such as pore size, porosity distribution and tortuosity of the pores that have all been shown to be important factors. Unsurprisingly, these factors are highly dependent on the microstructure and hence there is a significant correlation between electrode microstructure and performance. Unfortunately, many of these parameters are difficult to measure directly. Performance is empirically observed and related to the variation in, for example, starting particle size of the component materials.

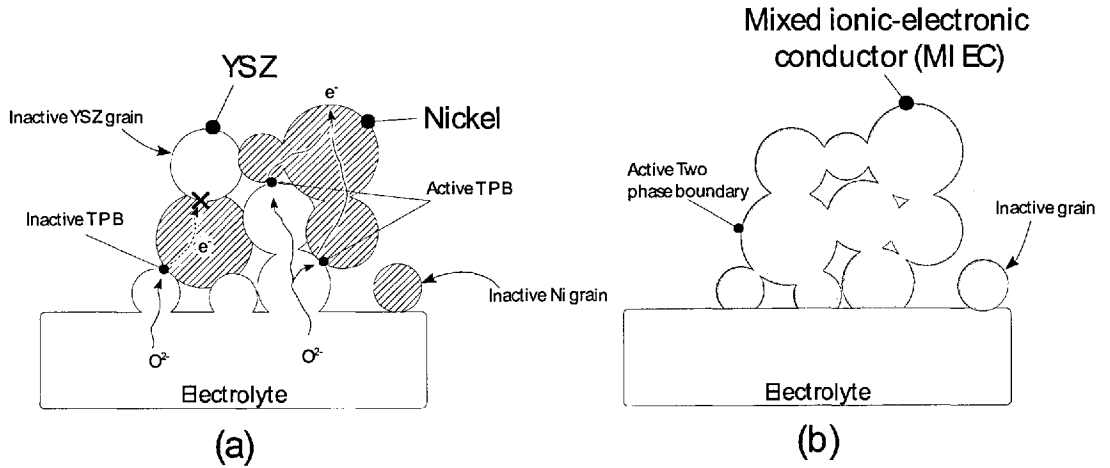


Figure 2.5: Schematic representation of a composite anode structure (a) and a mixed conducting structure (b). Active regions of the composite structure are where, not only is there a TPB, but one which is in contact with the current collector and electrolyte. TPBs in contact with only one of these become inactive. A mixed conductor, that is, a material which can simultaneously conduct electrons and oxygen ions, only has double phase boundaries and so the active region can be significantly increased.

Also recognised as important, particularly in composite electrodes, is the role of the triple phase boundary (TPB). The TPB is the region of the anode (or cathode) where there is a contact point between electronic conductor, ionic conductor and a porous region. This is where oxide ion, fuel and electrons meet to complete the anode reaction. There are several steps in this reaction but a simple schematic (Figure 2.5) shows the process. It has been shown that the TPB length is a critical factor determining the cell performance [40].

Example calculation - Target anode conductivity

Assume we want to estimate the conductivity required for an anode material. In this example we will consider an anode supported design where the anode substrate is 1.5mm thick and we want to achieve an anode ASR of $0.15 \Omega \text{ cm}^2$. From Equation 2.4 we get:

$$\sigma = L/ASR = 0.15 \text{ cm}/0.15 \Omega \text{ cm}^2 = 1 \Omega^{-1}\text{cm}^{-1} = 1 \text{ Scm}^{-1} \quad (2.6)$$

This assumes ideal current collection and does not take into account the other resistances (such as those in Eq. 2.5) that also contribute to the ASR. Nevertheless, it can be used to estimate the required electronic conductivity needed for an anode material. Atkinson *et al.* [38] confirm that, given good current collection, anode conductivity could be as low as 10 Scm^{-1} .

Although it has been identified as a critical area of the anode, actually relating the triple phase boundary area to performance has proved difficult to quantify, let alone control. It was mentioned above that there are several groups presently working on reconstruction techniques with the aim of directly linking the microstructure to cell performance (see page 5). There is very little published work in the area but the existing results are interesting. What is clear is that there is a distinction between active and inactive TPBs. Active triple phase boundaries are those where all three phases connect to their respective sources. That is to say there is a percolating network of three phases: electronic conductor, ionic conductor and connected porosity. If any one of these three networks is broken, the TPB will become inactive.

To briefly summarise, the three main resistances contributing to anode ASR are (very

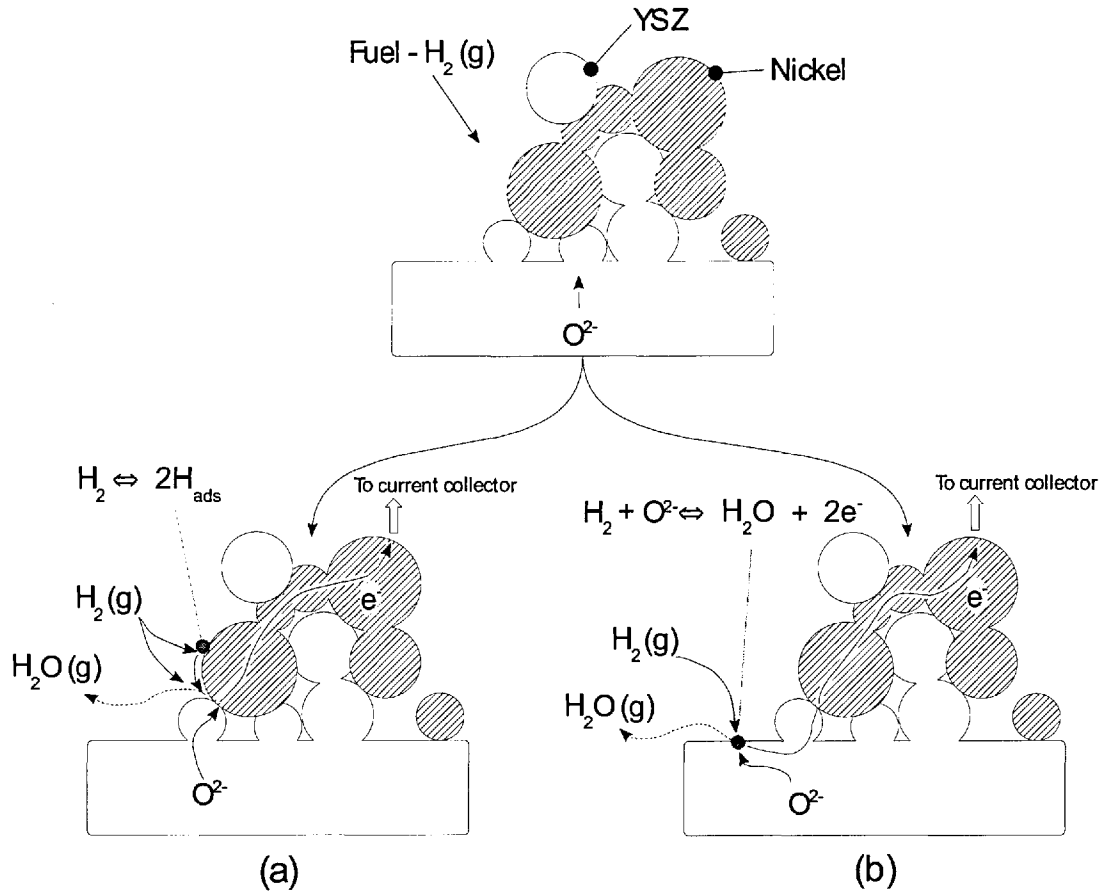


Figure 2.6: Two possible reactions in a composite anode structure. Fig 2.6(a) shows the typical reaction mechanism whereby H_2 adsorbs onto the nickel surface. The adsorbed H_2 can then easily react at an active TPB site, forming steam and two electrons. The steam flows out as an exhaust gas and the electrons travel out through the nickel network to the current collector where they travel around the external circuit. In 2.6(b) an alternative, direct reaction, is shown. This mechanism has been suggested if there is some electronic conductivity in the YSZ. If the pathway to the nearest nickel grain is short the oxidation and direct combination with an oxygen ion is possible. This is not considered a likely reaction, but it does not require active TPBs.

simplistically):

- Series or ohmic resistance (R_s): This is caused by the finite resistance of the material and the contact resistance between the interconnect-anode-electrolyte assembly. This can be minimised by selecting a material with adequate electronic conductivity.
- Mass transport resistance: This is related to gas transport into and out of the anode structure. Resistances are minimised by increasing the volume fraction of open porosity and structuring of that porosity (e.g. porosity distribution etc.).
- Polarisation resistance (R_p): This essentially determines the efficiency of the electrochemical processes occurring and has been found to be highly dependent on the length of active TPB.

Very often it is possible to achieve one or two of these objectives but the challenge of producing a three-phase network is difficult in practice. Because of this there is interest in using mixed ionic and electronic conductors (MIEC) where the stringent requirement for three percolating phases is reduced.

2.2.3 Mixed Conductors

In theory, mixed conductors should perform significantly better than their composite counterparts. Assuming there is sufficient electronic and ionic conductivity so that the ohmic resistance is not too large, mixed conductors effectively spread the active anode area throughout the whole structure as demonstrated in Figure 2.5b.

Another reason for interest in single-phase ceramic materials is that many show some degree of mixed conduction. The problem lies in that, particularly under the reducing conditions found in the anode compartment, it has been difficult to identify a material with the appropriate stability and transport properties to effectively satisfy the demands of an entirely single-phase anode material.

Generally, once a stable material has been identified, electronic conductivity is traded

off against ionic conductivity or vice versa. This ultimately leads back to the original problem of managing the polarisation resistances against the ohmic resistances.

2.3 Material property requirements of a ceramic anode material

Given many of the attractive benefits of replacing nickel in the anode structure, all ceramic anodes (even single phase anode materials) are worthy of research. Chapter 4 (beginning on pg. 31) details some of the most promising developments in this area so far. However, for this research project, the desired properties for a new anode material were as follow:

Firstly, the material must be stable, both dimensionally and chemically in a reducing atmosphere and under oxidising conditions. Secondly, minimum electronic conductivity must be high enough to function at least as a thin active layer (i.e. $\sim 10\text{-}15\mu\text{m}$) which would mean a conductivity of at least 10 Scm^{-1} , preferably higher, so that it may also operate effectively as a current collector. Thirdly, the thermal expansion coefficient (TEC) should match the state-of-the-art electrolyte materials such as YSZ and CGO. This requires a TEC in the region of $10\text{-}13\times 10^{-6}\text{K}^{-1}$. Fourthly, the electrical properties should be recoverable after going from a reducing environment to oxidising and back to a reducing environment without significant deterioration. Other properties such as ionic conductivity would be an advantage; however, such materials are rare and can be substituted by making an appropriate composite structure. These properties have been summarised in Table 2.3 below:

Property	Ni-Cermet	Ceramic anode	(Units)
Mandatory properties			
Electrical conductivity	300-1000	<10	Scm^{-1}
Thermal expansivity	13-15	10-12	p.p.mK^{-1}
Chemically stable in reducing atm.	✓	✓	
Recoverable properties after redox cycle	Partially	✓	
Dimensionally stable during redox cycle	×	✓	
Desirable properties			
Ionic conductivity	$\sim 10^{-3}$	$\sim 10^{-2}$	Scm^{-1}
Catalytic activity toward fuel oxidation	✓	✓	
Resistance toward carbon deposition	×	✓	
Resistance to sulfur poisoning	×	✓	

Table 2.3: Classification of properties for a potential ceramic anode material compared with the state-of-the-art Ni-cermet anode material.

Chapter 3

Defect Model of Donor-doped SrTiO_3

3.1 Introduction

The importance of defects in understanding the properties of ceramics cannot be underestimated. Point defects in particular have a large impact on the properties of oxide ceramics; especially on their electrical, transport and structural properties. Defect chemistry covers a very wide area and this chapter is not intended as a complete review of defect chemistry in SrTiO_3 .

There are many excellent reviews on the defect chemistry of doped and un-doped titanates. Smyth in ref. [41] has a very good section on BaTiO_3 . References [42–50] and the references therein cover many of the important details of donor-doped titanates and the effect of defects on the electrical properties. For an excellent introduction to general defect chemistry in oxides the text by Barsoum [51] contains clear explanations and worked examples.

3.1.1 Some General Defect Concepts and Definitions

Point defects can be broadly classed as either intrinsic or extrinsic. Intrinsic defects can be due to thermally activation which allows new defects to form or existing defects to become mobile. Higher temperatures can also cause a deviation from stoichiometry to form a non-stoichiometric compound. For example, in metal oxides at high temperatures that start out as stoichiometric, the deviation to non-stoichiometric is usually caused by a change in the oxygen content. Extrinsic defects are created when there is an impurity in the crystal. This may be because of unwanted contamination or it may be due to intentional doping. Defects can be further classified into 'lattice' defects and 'electronic' defects; these are summarised in Table 3.1

Table 3.1: Summary and examples of the main defects in metal oxides.

Defect	Example	Kröger-Vink Symbol ¹
Lattice defects		
Vacancy	Oxygen vacancy	$V_O^{\bullet\bullet}$
	Divalent cation vacancy	$V_M^{\prime\prime}$
Interstitial	Oxygen interstitial	$O_i^{\prime\prime}$
	Divalent cation interstitial	$M_i^{\bullet\bullet}$
Substitutional	Oxygen for Fluorine	F'_O
	Iron (III) for Titanium (IV)	$Fe_{Ti}^{\bullet}$
Electronic defects		
Electron		e'
Hole		$h^{\cdot}$

¹ Defect notation used throughout this thesis is the system devised by Kröger and Vink [52]

3.1.2 Defect reactions

There are some basic rules which govern the chemistry of defects, which are very similar to those that govern normal chemical reactions:

1. Electroneutrality: Sometimes referred to as the electroneutrality condition (ENC) which states that all charges must stay balanced. Charges may not be created or destroyed.
2. Mass balance: Just as in a typical chemical reaction, one side of the equation

must balance the other. Vacancies are considered to have zero mass.

3. Site ratios: The ratio of normal lattice sites (both cation and anion) must stay the same. Interstitial sites are not considered to be normal sites.

Intrinsic Schottky and Frenkel Disorder

In a stoichiometric crystal there are two main types of intrinsic disorder that can occur: Schottky and Frenkel. Generally, depending on the crystal structure and the elements that make up the crystal, one of these defect types will always dominate. Schottky disorder occurs when there is the simultaneous formation of an anion and cation vacancy in the crystal and the atoms move to the surface (Shown in Figure 3.1a). A good example of this is in MgO:

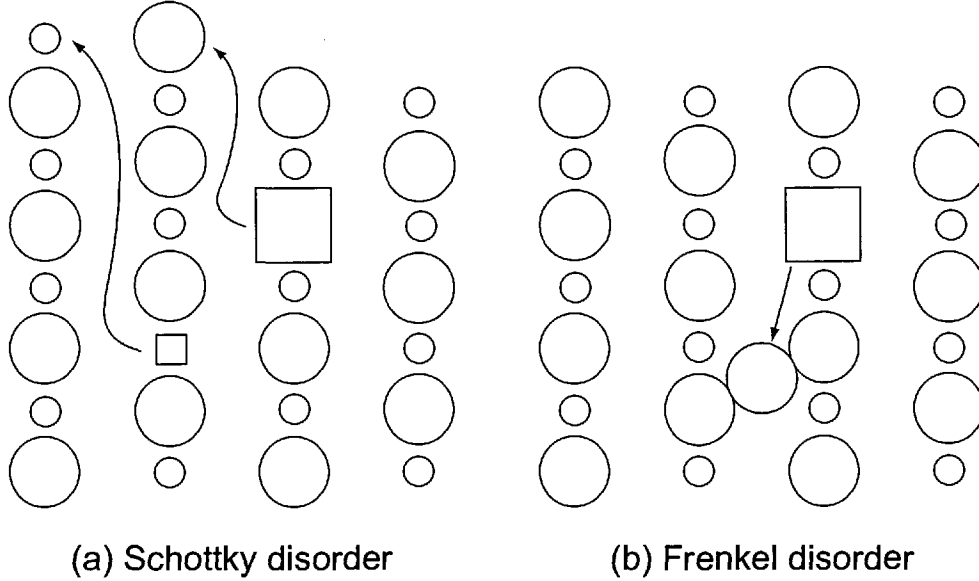
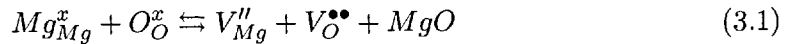


Figure 3.1: Shows a schematic representation of Schottky (a) and Frenkel (b) disorder. The small circles represent cations and the large represent anions. The small square and the large square represents cation and anion vacancies respectively. The large circle in (b) represents an anion interstitial (Frenkel defect).



This is often rewritten as:



where *nil* represents the perfect lattice so there is no need to explicitly state that Mg was on the Mg site etc. It is also implicit in Schottky disorder that the formation of the vacancy pair means that the two cations have migrated to the surface (and therefore MgO is removed from the right hand side of the equation).

Frenkel disorder (Fig. 3.1b) occurs when an ion moves from a normal site to an interstitial position leaving behind a vacancy. There can be either cation or anion Frenkel defects. An example of the formation of divalent cation Frenkel defect is shown below in Eq. 3.3:



3.1.3 Defect Equilibrium and Kröger-Vink Diagrams

Even though the defects described above can all theoretically exist, there will be some defects that will be more favourable, depending on the prevailing conditions, such as temperature or $p(O_2)$. To understand how defects affect the transport properties, particularly the electronic conductivity, it is important to understand how the defect equilibrium will change under certain circumstances. As with any other chemical reaction it is possible to write the equilibrium constant, or in the case of defect chemistry, the mass action expression. Consider the following hypothetical reaction shown in Equation 3.4:

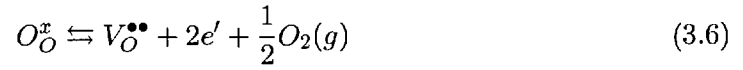


Equation 3.4 will have the following mass action expression:

$$\frac{x_C^c x_D^d}{x_A^a x_B^b} = \exp\left(-\frac{\Delta G^0}{kT}\right) = K_{eq} \quad (3.5)$$

where x_A^a , x_B^b , x_C^c , x_D^d are the activity of elements A, B, C and D respectively and ΔG^0 is the Gibbs free energy of the reaction, K_{eq} is the equilibrium constant, k is the Boltzmann constant and T is the temperature.

To demonstrate how this equilibrium works in practice, consider the metal oxide (MO) under three oxygen partial pressures: At low $p(O_2)$, oxygen could be lost from the oxide and lead to the following reaction:



The corresponding mass action expression is:

$$\frac{[V_O^{\bullet\bullet}][n]^2 p(O_2)^{1/2}}{[O_O^x]} = K_{red} \quad (3.7)$$

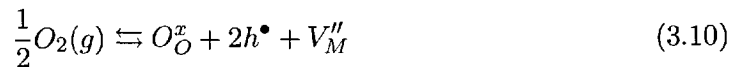
At intermediate oxygen partial pressure where Schottky disorder tends to dominate:



The corresponding mass action expression is:

$$\frac{[V_O^{\bullet\bullet}][V_M'']}{[O_O^x][M_M^x]} = K_s \quad (3.9)$$

At high oxygen partial pressure where cation vacancies will form:



The corresponding mass action expression is:

$$\frac{[V_M''] [O_O^x] [p]^2}{p(O_2)^{1/2}} = K_{ox} \quad (3.11)$$

In addition to these equations, the following electronic defect reaction is also possible:

$$nil \rightleftharpoons e' + h^\bullet \quad (3.12)$$

with the mass action equation:

$$[n][p] = K_i \quad (3.13)$$

At equilibrium, the concentrations of all defects must simultaneously satisfy Equations 3.7 - 3.13. The crystal must also remain electrically neutral. There are probably more reactions one could conceive and the mass action expression for these reactions could be derived. However, the key to practical application of defect chemistry is to understand that while there is a huge range of possible defect reactions, all of these occur simultaneously. However, there will generally be only one reaction that dominates under a certain set of circumstances. It is then possible to divide the existence regime of a compound into subregimes where each region has a dominant defect reaction. When this is established different approximations to the electroneutrality equation can be derived. This is often referred to as the 'Brouwer approximation'. The results of the Brouwer approximation are often plotted on a log-log plot, an example of which is shown in Fig. 3.2.

3.2 Defect Chemistry in Titanates

Due to the close packed nature of the perovskite structure, Frenkel disorder is generally considered unlikely, due to large enthalpies for all three Frenkel defects. Theoretical calculation for intrinsic disorder give values of 3.94, 7.10 and 2.57eV (380, 685 and 248

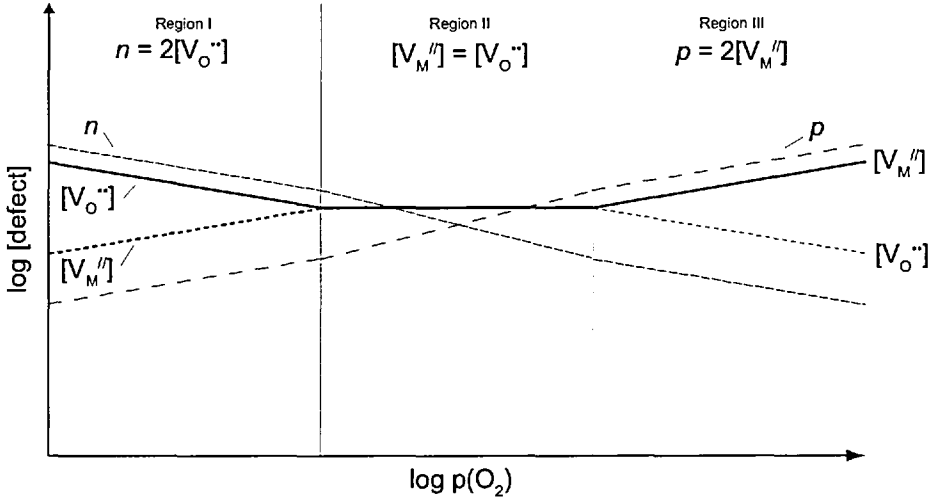


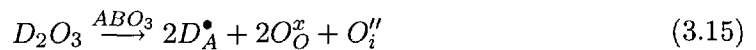
Figure 3.2: Example of a Brouwer diagram showing the concentration of various defects as a function of $p(\text{O}_2)$.

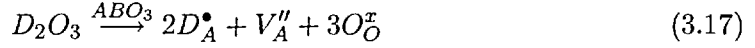
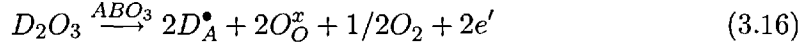
kJ/mol) for strontium, titanium and oxygen Frenkel defects respectively [53]. These values for Frenkel disorder are comparable to BaTiO₃ where the enthalpies of $\text{Ba}_i^{\bullet\bullet}$, $\text{Ti}_i^{4\bullet}$, and O_i'' are 5.94, 7.56 and 4.49 eV (572, 728 and 432 kJ/mol) respectively [54]. It would therefore be expected that intrinsic ionic disorder would be Schottky disorder.

$$\text{nil} \rightleftharpoons V_{\text{Sr}}'' + V_{\text{Ti}}''' + V_{\text{O}}^{\bullet\bullet} \quad (3.14)$$

where *nil* represents the perfect lattice.

Donor-doping can be achieved with large donors such as La on the A-site and small donors, such as Nb, on the B-site. Donor compensation can occur via the following mechanisms (shown in Equations 3.15 - 3.17) and assumes large trivalent dopants on the A-site. Incorporation can occur as a result of the following: an increase in oxygen content (Eq. 3.15), electronic compensation (Eq. 3.16), or via the formation of cation vacancies (Eq. 3.17).





Incorporation of the additional oxygen (Eq. 3.15) is unlikely since it would require the formation of oxygen interstitials (oxygen Frenkel defect). It is generally accepted that donor compensation under oxidising conditions in SrTiO₃ occurs by the formation of Sr vacancies and by electronic compensation under reducing conditions [44].

At low donor levels ($\sim 0.6\text{wt}\%$) samples fired in air turn out to be dark semiconductors; this is thought to be due to incorporation via Eq.3.16. When the donor level is increased, the material becomes a light-coloured insulator due a change in incorporation mechanism where Sr vacancies dominate (Eq.3.17). In addition to a change in defect compensation, increasing the donor content induces grain refinement resulting in the grain size dropping from tens of microns for the un-doped material down to $\sim 1\mu\text{m}$ for $\sim 1\text{wt}\%$ donor doping. The reasons for this shift in compensation mechanism and grain-size effect are unclear [54].

With the exception of the anomaly described above for very low dopant concentrations, donor doped titanates show two defect regimes which operate depending on the oxygen partial pressure. That is, cation vacancy compensation at high $p(\text{O}_2)$ and electronic compensation at low $p(\text{O}_2)$. This has ramifications for the preparation of a particular phase depending on the oxygen partial pressure.

3.2.1 Example from the literature - La-doped SrTiO₃

According to the defect model for SrTiO₃ compensation at low $p(\text{O}_2)$ occurs due to the loss of oxygen and the formation of electrons. At higher $p(\text{O}_2)$, compensation occurs due to the incorporation of additional oxygen. As already mentioned, it is unlikely additional oxygen can be accommodated by the formation of oxygen interstitials. This leaves only the formation of cation vacancies along with the precipitation of a second

phase or structural incorporation in the form of ordered layered structures.

Formation of shear structure represented by the homologous series $A_nB_nO_{3n-1}$ is sometimes argued not to be a true second phase [55] but a crystallographic shear. Similar layered phases such as the Ruddlesden-Popper (R-P) series ($A_{n+1}B_nO_{3n+1}$) have also been proposed to explain the layered defects observed in TEM studies of La-doped SrTiO₃. The significant differences between shear structures and R-P phases is that the R-P phase contains perovskite blocks interleaved with rock salt, SrO layers, resulting in an $A/B > 1$. Shear structures, however, are composed of perovskite blocks that have sheared along the [110] plane by a half the width of one titania octahedra, leaving the A/B ratio at unity (an example of this is shown in Fig. 4.1 on page 35).

When samples are prepared using a stoichiometry that assumes electronic compensation (Eq. 3.16),

$$Sr_{1-x}D_x^{3+}TiO_{3-x/2} \quad (3.18)$$

firing in an oxidising atmosphere should result in a two-phase material due to the preferred self-compensation by the formation of V''_{Sr} at high donor levels (Eq. 3.17). This has been observed in the form of SrO-rich surface phases and extended, layered, defects. Canales-Vazquez [56] suggested the formation of oxygen-rich shear structures (or disorder variations thereof) are the only compensation mechanism capable of operating at high oxygen partial pressure in $La_4Sr_8Ti_{12}O_{38}$. This is in support of earlier work by Bowden *et al.* [57]. They showed significant evidence to indicate the formation of $A_nB_nO_{3n-1}$ shear structures in $A_{1-x}D_xBO_{3+d}$ compounds. However, all of the studies have been performed at relatively high doping levels ($x > 0.2$). TEM observation of intergrowth layers becomes less frequent when the doping level approaches $x = 0.2$. Bowden [57] has suggested that lack of layers around $x = 0.2$ was due to lack of suitably oriented thin crystals; Smyth [58], on the other hand, has pointed out it may also be that these layered structures do not exist below a critical dopant concentration ($0.2 < x < 0.33$). Instead there is cation vacancy compensation operating at donor contents less than $x=0.2$ and that layered intergrowths form at higher donor concentrations. It seems there may be interesting behaviour around this transition [59, 60] from ordered layered defects to disordered point defects. The exact nature of the point de-

fects in this region is not clear but these materials appear to have promising attributes for SOFC anode applications.

If the formation of V''_{Sr} is taken into account using Eq 3.17,



the material forms a single-phase when fired under oxidising atmospheres but when heated under reducing atmospheres there is a shift toward electronic compensation and the material adopts the preferred stoichiometry as shown in Eq. 3.18. This results in the formation of a Ti-rich second phase [61].

3.3 Conclusions

The debate as to the nature of the precise defect chemistry in donor-doped titanates is ongoing and we have not gained any significant new data or insights to allow us to quantitatively comment on this problem. The most interesting and important result from this chapter is that, in donor-doped titanates, the key to understanding their behaviour lies in the fact that there are two defect regimes depending on the oxygen partial pressure.

Chapter 4

Review of Ceramic Anode Materials

4.1 Introduction

There have been a number of proposed replacements for Ni-cermet anode materials. These can be divided into two main groups: alternative cermet materials, such as Cu-ceria [29], and ceramic anode materials. Although there has been significant progress in the area of alternative cermet structures and compositions, this chapter will deal exclusively with all-ceramic anode compounds.

The main disadvantages to using Ni-based materials are their poor redox resistance, poor sulfur tolerance and carbon deposition when operating on dry hydrocarbon fuels. Many of the ceramic anode materials that have been tested to date tend to show excellent resistance to redox cycling, prevent excessive carbon deposition, and are resistant to sulfur poisoning. Unfortunately, the performance of ceramic anode materials has, in many cases, not matched Ni-based cermets.

Classification of potential anode materials is best achieved by splitting the candidates into crystallographic classes. Perovskite materials are by far the most prolific materials presently under investigation. There have also been some interesting developments

using fluorite, pyrochlore and spinel compounds. This chapter aims to examine the most prominent developments in the area.

4.2 Perovskite and perovskite related materials

There are many materials with the formula ABO_3 that assume the perovskite structure [62]. Perovskite compounds are often designated according to the oxidation state of the constituent elements. For example, $CaTiO_3$ (the naturally occurring mineral titanate) would be designated a 2,4 perovskite, whereas $LaCrO_3$ would be a 3,3 perovskite.

4.2.1 Titanates

Titanate perovskites have a wide range of applications. They show many structural variations. Electrical properties range from insulating to highly conductive, there are some examples that show superconduction. The alkaline earth titanates $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ all found technical applications; ranging from capacitors to resistive oxygen sensors. With the increasing interest surrounding SOFC three important donor-doped titanates have been identified as potential anode materials:

- La-doped $SrTiO_3$
- Y-doped $SrTiO_3$
- Nb-doped $SrTiO_3$

Lanthanum (III) and yttrium (III) both substitute for strontium on the A-site. Niobium (V) substitutes for titanium (IV) on the B-site. Lanthanum and niobium-doped $SrTiO_3$ have been of interest to solid-state chemists for many years as model materials for the understanding of donor doped materials [42, 48, 63, 64].

Lanthanum-doped strontium titanate

As covered in Section 3.2, there are two possible defect regimes that operate in donor-doped $SrTiO_3$ depending on the $p(O_2)$. At high $p(O_2)$, Sr-vacancies are the preferred defect, while at low $p(O_2)$ there is a shift toward electronic compensation. Depending on

the choice of synthesis atmosphere, samples can be prepared where the stoichiometry is matched to the preferred defect regime and synthesis $p(\text{O}_2)$ range. For example, if we were to prepare a sample in air an A-site deficient stoichiometry (such as in 4.1) would be appropriate if a single phase product was desired. Alternatively, if the synthesis were to proceed under reducing conditions, a stoichiometric composition (such as in 4.2) could be used. La-doped SrTiO_3 was first identified and investigated as a potential anode material by Slater [65]. The approach of Slater *et al.* was to use an A-site deficient composition:



A-site deficient compositions prepared by Slater assume compensation by strontium vacancies. These compositions formed a single phase when prepared in air. They were also found to be stable in reducing atmospheres, with no evidence of second phase after treatment in a reducing atmosphere. It was suggested that the changes in the specimen's electrical properties between low and high $p(\text{O}_2)$ was due to variation in oxygen stoichiometry. The issues surrounding the phase stability under differing defect regimes may have been suppressed due to sluggish equilibrium kinetics at the measurement temperatures (i.e. $\sim 1000^\circ\text{C}$). Nevertheless, a conductivity of $\sim 7 \text{ Scm}^{-1}$ at 930° and 10^{-18} atm. was reported for samples that had been reduced for 24hrs at 930°C in $5\%\text{H}_2/\text{Ar}$.

Later Marina *et al.* [66] prepared the stoichiometric composition:



Stoichiometric samples were prepared and sintered in air and then reduced at high temperature (1650°C for 8hrs in $2\%\text{H}_2/\text{Ar}$). After this treatment the samples were found to have very high conductivity ($500\text{-}5000 \text{ Scm}^{-1}$); the conductivity decreased as the temperature increased. This was attributed to a metallic conductivity mechanism

[66]. Slow equilibrium kinetics were also identified in $p(\text{O}_2)$ dependent measurements but not discussed in detail. No microstructural data was presented in relation to the occurrence of second-phases such as SrO or other planar defects which would be predicted if a stoichiometry such as that in Eq 4.2 had been prepared in air. There was a suggestion that if these phases were present they would have re-dissolved under reducing conditions. Despite potential questions over the true nature of the phase relationships in these compositions, they did however display excellent dimensional stability, chemical stability and good fuel cell performance.

Later, a cerium-modified SrTiO_3 was also developed [67]. This was ultimately shown to be a composite of $(\text{La},\text{Sr})\text{TiO}_3$ and La-modified CeO_2 . Nevertheless these materials showed polarisation resistances of $0.2 \Omega\text{cm}^2$ and $1.3 \Omega\text{cm}^2$ at 1000°C and 700°C respectively. It was also shown that this material did not promote carbon formation and was resistant to sulfur poisoning.

The questions regarding the fate of excess oxygen/SrO in the literature led to the suggestion that segregated SrO formed a layered phase within grains or at the grain boundaries. These intergrowth compounds are not easily detected by typical laboratory X-Ray diffraction instruments and so this would explain why in reference [66] no unusual second phases were detected when preparing a stoichiometric composition in air. Originally the intergrowth compounds were thought to have the stoichiometry shown in Eq.4.3 [68, 69]:

$$A_{n+1}B_nO_{3n+1} \tag{4.3}$$

This phase belongs to the Ruddlesden-Popper (RP) series [69]. It consists of SrTiO_3 perovskite slabs, n layers thick, interleaved with SrO rocksalt-type layers.

High resolution transmission electron microscopy (HRTEM) confirmed the presence of layered intergrowths in these materials [68]. However, closer examination showed that the layered phases were members of the homologous series with the general formula [56, 57]:

$$A_nB_nO_{3n+2} \quad (4.4)$$

In the La-Sr-Ti-O system, $\text{La}_4\text{Ti}_4\text{O}_{14}$, represents the $n = 4$ member of the homologous series. As the value of n increases, so the thickness of the perovskite slabs increase until $n = \infty$, which corresponds to the typical, undistorted, perovskite. Figure 4.1 shows the crystal structure of $\text{La}_4\text{Ti}_4\text{O}_{14}$. Perovskite sections show significant octahedral tilting within each slab. However, it is at the interface, between these perovskite-type slabs, where excess oxygen is thought to be accommodated. The location of excess oxygen is one of the key differences between a RP phase and the $A_nB_nO_{3n+2}$ phase. In a R-P phase, additional oxygen resides as SrO in a rocksalt-type layer between the perovskite slabs.

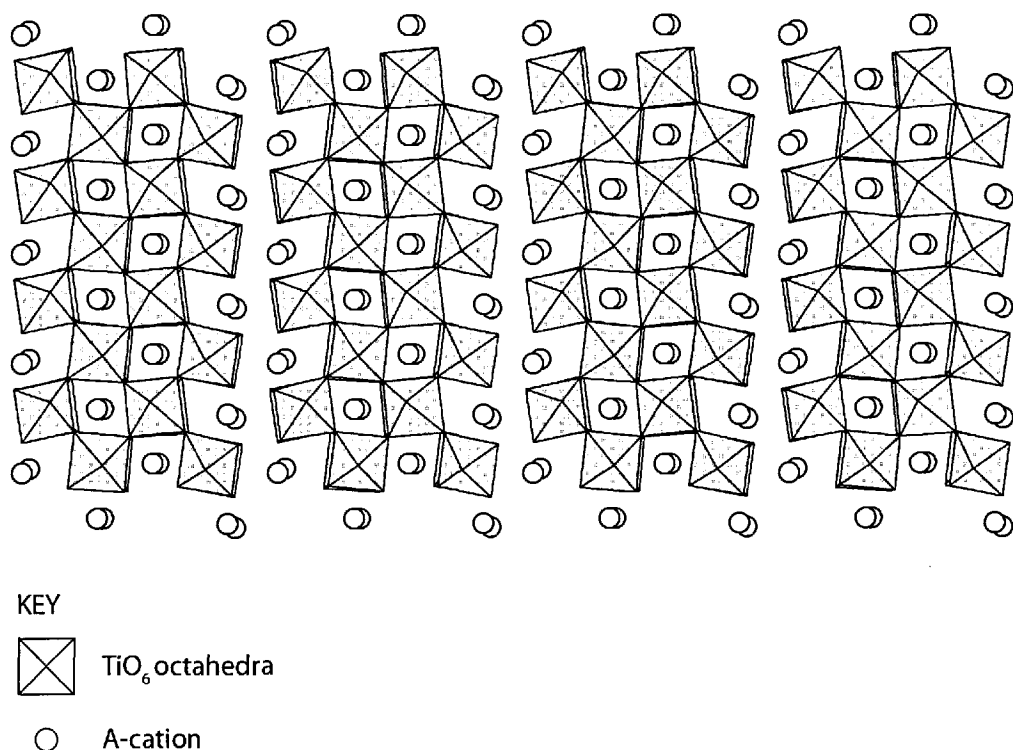


Figure 4.1: Structure of $\text{La}_4\text{Ti}_4\text{O}_{14}$ showing perovskite-type blocks and sheared regions between perovskite slabs, where it is thought that additional oxygen (introduced by a donor dopant) may reside.

As outlined above, stoichiometric compositions prepared in air are probably a mixture of two phases: an A-site deficient compound (as in Eq. 4.1) and a member of the layered

perovskite series shown in equation 4.4. A better approach was described by Canales-Vazquez *et al.* when they investigated the $n = 12$ composition of the homologous series, $La_4Sr_8Ti_{12}O_{38-\delta}$ [70].

Based on XRD evidence, at values of $n \geq 12$, the crystal structure of this material appears to be a simple perovskite (S.G. $Pm\bar{3}m$) [56]. A model has been proposed, based on careful examination in the TEM, which explains the structure in terms of oxygen-rich, crystallographic shear structures, similar to $La_4Ti_4O_{14}$, that are randomly distributed in a perovskite matrix [56, 68]. Some aspects of the defect chemistry of this material were presented in Section 3.2.1 on page 28 (Chapter 3)

In air, this material displays very low electronic conductivity, similar to un-doped strontium titanate. Grain boundary resistivity tends to dominate the overall conductivity of these materials. Figure 4.2 shows a Nyquist plot of $La_4Sr_8Ti_{12}O_{38-\delta}$ measured in argon which shows the dominant contribution from the grain boundary.

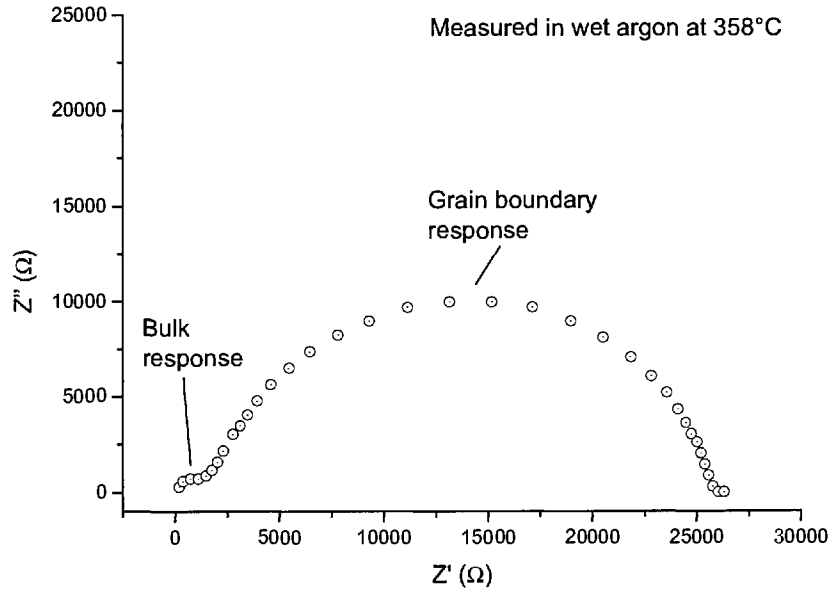


Figure 4.2: Impedance plot of $La_4Sr_8Ti_{12}O_{38-\delta}$, measured in argon, which highlights the grain boundary dominated conductivity typical of this and other titanate materials (After [70]).

Figure 4.3 compares the temperature-dependent total conductivity in air of $La_4Sr_8Ti_{12}O_{38-\delta}$ and a range of doped $La_4Sr_8Ti_{1-x}M_xO_{38-\delta}$ compounds, where $M = Sc, Mn, Ga$. As the La-doped parent compound is doped with Sc, Mn, or Ga on the Ti-site, there is an increase in the p-type contribution which results in an increase in the observed

conductivity in air.

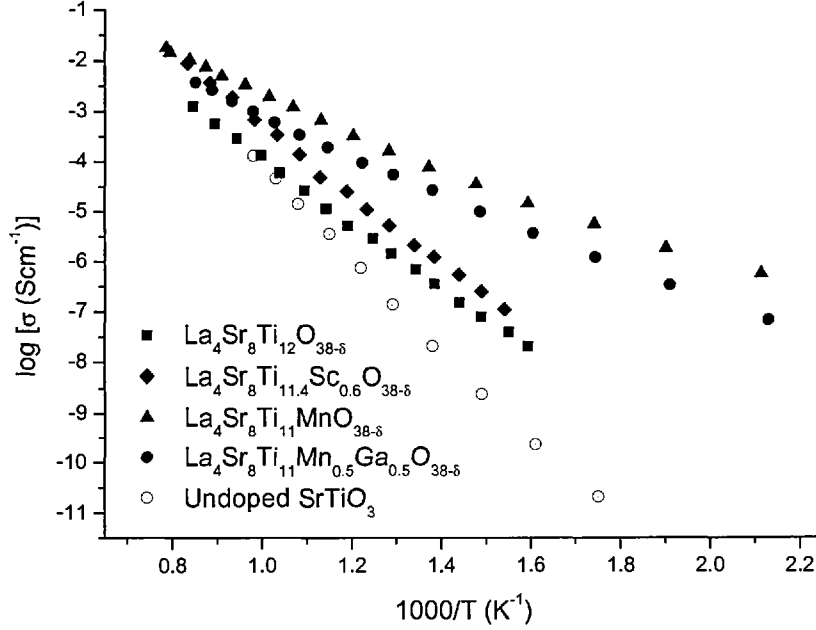


Figure 4.3: Total conductivity in air as a function of temperature for doped and un-doped $\text{La}_4\text{Sr}_8\text{Ti}_{12-x}\text{M}_x\text{O}_{38-\delta}$ (SrTiO_3 is added for comparison).

Under reducing conditions oxygen is thought to be lost from oxygen rich shear regions [70], leading to the formation of Ti^{3+} to maintain charge neutrality. This significantly increases the electronic conductivity. Un-doped $\text{La}_4\text{Sr}_8\text{Ti}_{12}\text{O}_{38-\delta}$ has shown excellent electronic conductivity: $\sim 60 \text{ Scm}^{-1}$ in dry hydrogen-noble gas atmospheres (see figure 4.4). In wet hydrogen atmospheres, the $p(\text{O}_2)$ is slightly higher which reduces the conductivity slightly (as these materials are n-type compounds). Polarisation resistances for $\text{La}_4\text{Sr}_8\text{Ti}_{12}\text{O}_{38-\delta}$ of $2.97 \text{ } \Omega\text{cm}^2$ and $8.93 \text{ } \Omega\text{cm}^2$ were observed operating at 900°C under wet H_2 and wet CH_4 respectively. The maximum observed power density in fuel cell testing was 76 mWcm^2 at 900°C .

Doped variants of $\text{La}_4\text{Sr}_8\text{Ti}_{12}\text{O}_{38-\delta}$ mentioned above have also been investigated as fuel cell materials. Sc [59], Mn [71] and co-doped Ga,Mn [72] have all shown successive improvement in fuel cell performance (summarised in table 4.1).

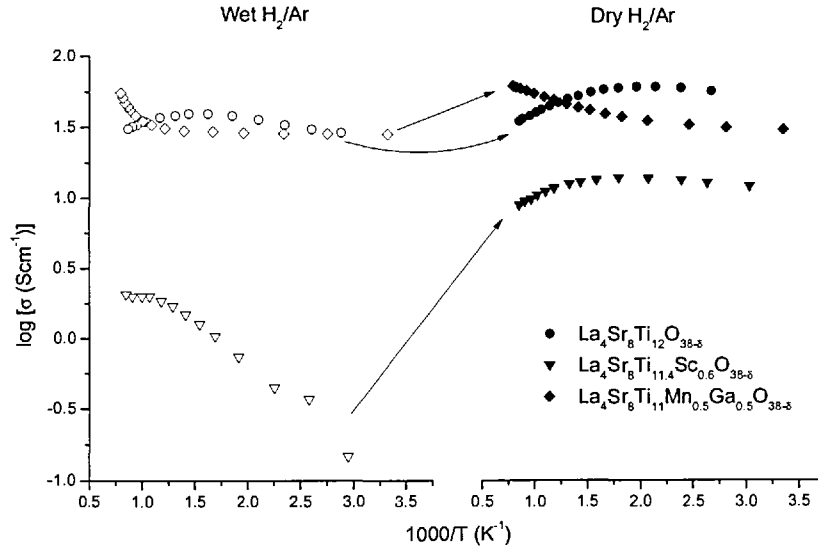


Figure 4.4: Total conductivity of $\text{La}_4\text{Sr}_8\text{Ti}_{1-x}\text{M}_x\text{O}_{38-\delta}$ in wet and dry hydrogen-argon atmospheres as a function of temperature. The conductivity of $\text{La}_4\text{Sr}_8\text{Ti}_{12}\text{O}_{38-\delta}$ and the Ga,Mn-doped compound ($\text{La}_4\text{Sr}_8\text{Ti}_{11}\text{Mn}_{0.5}\text{Ga}_{0.5}\text{O}_{38-\delta}$) change very little between dry and wet atmospheres, whereas the conductivity of $\text{La}_4\text{Sr}_8\text{Ti}_{11.4}\text{Sc}_{0.6}\text{O}_{38-\delta}$ increases significantly (Data from references [59, 70, 72]).

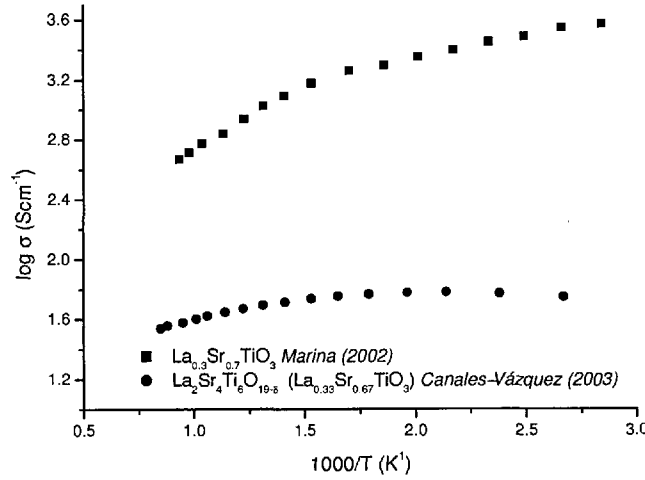


Figure 4.5: Total conductivity in dry hydrogen of two nominally identical compositions, showing the large differences in reported conductivities. This is thought to be partly due to different thermal history between samples (Data from Marina [66] and Canales-Vázquez [70]).

Compound	R_p (Ωcm^2)		OCV (V)
	H_2	CH_4	97% H_2
$\text{La}_4\text{Sr}_8\text{Ti}_{12}\text{O}_{38-\delta}$	2.97	8.93	0.98
$\text{La}_4\text{Sr}_8\text{Ti}_{11.4}\text{Sc}_{0.6}\text{O}_{38-\delta}$	0.50	1.20	1.10
$\text{La}_4\text{Sr}_8\text{Ti}_{11}\text{MnO}_{38-\delta}$	0.43	1.14	0.98
$\text{La}_4\text{Sr}_8\text{Ti}_{11}\text{Mn}_{0.5}\text{Ga}_{0.5}\text{O}_{38-\delta}$	0.20	0.57	1.25

Table 4.1: Polarisation resistances of $\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ compounds, demonstrating improved performance with successive doping strategies (after ref. [60]).

Yttrium-doped strontium titanate (YST)

Yttrium-doped strontium titanate has been identified as another promising anode material. The A-site deficient composition was first suggested by Hui and Petric [73]. High electrical conductivity of 64 Scm^{-1} was reported. Initially, the solid solubility of yttria was thought to be $\sim 8\text{at}\%$ (which also coincided with a maximum in the electrical conductivity). However, the solubility limit was shown in a later publication to be closer to $4\text{at}\%$ [74]. Nevertheless, there have been several other authors who have also found that maximum electrical conductivity occurs at $8\text{at}\% \text{YO}_{1.5}$ [75, 76].

Y-doped SrTiO_3 displays properties very similar to other donor-doped titanates: high, n-type, electrical conductivity at low $p(\text{O}_2)$ which is highly dependent on the thermal history of the sample [61]. This is clearly demonstrated in Figure 4.6 which shows samples with an identical composition treated at different temperatures or in different atmospheres. One set of samples was sintered at 1400°C in air and subsequently treated in a reducing atmosphere, while the other set were sintered in a reducing atmosphere only. Peak temperature during the reducing treatment would seem to determine the overall electrical conductivity, although the sample porosity may also have an effect. Clearly the samples in Fig. 4.6 with higher percentage of porosity showed the lowest conductivity values.

Simultaneous doping of SrTiO_3 with yttrium and cobalt on the A and B-site respectively was found to significantly improve the electrochemical performance in this system [77, 78]. Doping with cobalt on the B-site acts as an acceptor and results in an increased oxygen vacancy concentration. This reduces the electronic conductivity, under reducing conditions, due to a shift towards a p-type regime. An increase in the oxygen vacancy concentration, and therefore improved oxygen ion conductivity, has also been observed to improve the catalytic activity. The combination of increased mixed conduction and an increased activity towards fuel oxidation reduces the polarisation resistance in fuel cell tests.

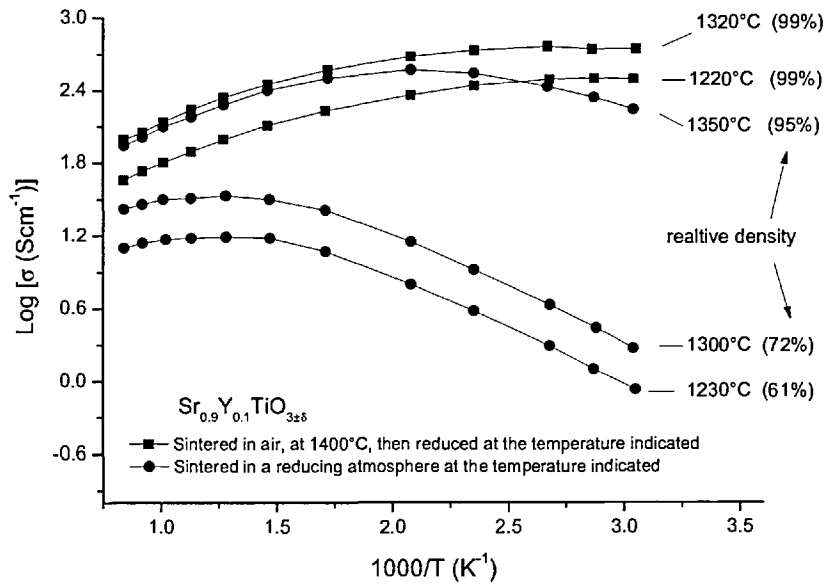


Figure 4.6: Total conductivity of Y-doped SrTiO_3 with different thermal histories. Measured under low $p\text{O}_2$. See text for more details (After [77]).

Niobium-doped SrTiO_3

Niobium-doped strontium titanate differs from the previous two cases because the donor dopant substitutes for titanium on the B-site. Kolodiazhnyi [61] found the A-site deficient composition $(\text{Sr}_{1-x/2}\text{Nb}_x\text{Ti}_{1-x}\text{O}_3)$ stable up to $x=0.3$ when prepared in air which was also in agreement with earlier work of Slater [65]. X-Ray diffraction suggests simple cubic symmetry up to the solubility limit. The lattice parameter increases with increasing Nb content, in agreement with cation substitution on the B-site [79]. Under reducing conditions X-Ray diffraction suggest the simple cubic symmetry remains in the A-site deficient material. However, as we have seen with the other titanates above, the compensation mechanism should shift toward electronic compensation at low $p(\text{O}_2)$. SEM examination showed that A-site deficient Nb-doped SrTiO_3 contained a significant amount of TiO_2 second phase which would be consistent with a shift in compensation mechanism at low $p(\text{O}_2)$.

Once again, these materials show relatively high conductivity (up to 500Scm^{-1}) when sintered or calcined at high temperature under reducing environments [61,79]. Gross [80] has reported promising fuel cell performance of 415 mWcm^2 at 700°C and 640 mW/cm^2 at 800°C for a $\text{SrNb}_{0.01}\text{Ti}_{0.99}\text{O}_3\text{YSZ}$ composite infiltrated with 1 wt% Pd and

3 wt% CeO₂. The Pd and CeO₂ were added to improve the catalytic activity. Such small additions would not be considered to contribute to the electronic conductivity as they are well below the percolation threshold. However, it is another example of the poor catalytic activity seen in the donor-doped titanates. Interestingly, Gross also demonstrated that the best redox tolerance was found at lower dopant concentrations, as demonstrated by 1mol% doping in the composition above.

Blennow *et.al* [81] have also demonstrated very low polarisation resistances in symmetric cell tests using Nb-doped SrTiO₃ infiltrated with Gd-doped ceria (CGO). Using a vacancy-compensated composition (Sr_{0.94}Ti_{0.9}Nb_{0.1}O₃ on a 200μm thick YSZ electrolyte they reported polarisation resistances of 0.12 Ωcm² and 0.44 Ωcm² in humidified H₂ at 850 °C and 650 °C, respectively. The material also performed well after repeated redox cycles. However it should be noted that platinum paste current collectors were used.

Nb-doped SrTiO₃ shows many of the desired properties such as high electronic conductivity and dimensional stability. It has also shown promising performance in fuel cell tests. However, as with the other titanates, the electronic conductivity is highly dependent on the thermal history. In addition to this, the fuel cell trials have used noble metal current collector paste which significantly improve the current collection in the laboratory but will not be suitable for use in a commercial environment. More work is needed to optimise the current collection between the electrode and external circuit, without having to resort to noble metal pastes, maybe with the use of a fine mesh for example.

Summary

Titanate materials show exceptional stability and performance under certain conditions. They show conductivity and polarisation values that can rival Ni-cermet composition. However, many aspects of donor-doped titanate defect chemistry are not completely understood. Very slow reduction-oxidation kinetics, even at high temperatures, are a hallmark of these materials in general, irrespective of the dopants. This tends to make electrical measurements on these materials quite difficult as the equilibrium times are

often not achievable in practice. The general consensus seems to be that slow equilibration kinetics are related to the low oxygen mobility in many of these compounds. This in turn results in low ionic conductivity and low catalytic activity. These factors can lead to higher polarisation resistances in cell testing or the requirement to add other materials, such as CGO or YSZ, to form composites to improve the performance.

Along with their complex defect chemistry, titanate materials also display subtle variations in their phase relationships and microstructures. For example, samples that appear single-phase in an XRD instrument present complex relationships when examined in more detail, such as those found in La-doped SrTiO_3 . Layered compounds, such as $\text{La}_4\text{Sr}_8\text{Ti}_{12}\text{O}_{38-\delta}$, or partially disordered layered materials would appear to hold a great deal of promise as they can more easily form oxygen rich intermediates which are easier to reduce and do not require the same length equilibrium times as the more traditional titanate compounds.

4.2.2 Doubly substituted perovskites ($\text{AB}_{0.5}\text{B}_{0.5}\text{O}_3$)

LaCrO_3 has been of interest to fuel cell scientists and engineers for many years mainly for use as an interconnect material [18]. Compositions based around the lanthanum-rich composition $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{M}_y\text{O}_{3-\delta}$ (where $M = \text{Mn, Fe, Co and Ni}$) have been trialled with some success [82]. Above all other double perovskites, there is one composition that has attracted significant attention: $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM).

Structural Properties of LSCM

At room temperature LSCM has a rhombohedral structure (space group $R\bar{3}C$ (167)) and lattice parameters $a = 5.4479(1) \text{ \AA}$, $\beta = 60.477(1)^\circ$ and $V = 115.563 \text{ \AA}^3$. High temperature neutron diffraction has shown that there is a rhombohedral to cubic ($Pm\bar{3}m$ (223)) phase change which begins at around 400°C . There is a gradual transition from rhombohedral to cubic symmetry between 400°C - 1000°C . The phase change is not thought to be displacive or kinetically controlled. At 1000°C there was estimated to be 85% cubic phase with the remainder being rhombohedral. Although not observed directly, it was estimated that the phase transition was completed by 1100°C [83].

In addition to the discovery of the rhombohedral to cubic phase change, neutron diffraction identified a small amount of spinel material (ca. 0.26%) which was below the detection limit of laboratory XRD. In an attempt to avoid deleterious reactions with other cell components, the study in ref. [83] had prepared a slightly A-site deficient composition $((\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta})$. They suggest the compound that actually formed was not A-site deficient (i.e. $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$) and that the residual Cr and Mn formed the spinel compound with the formula: MnCr_2O_4 .

Electrical Properties of LSCM

LSCM behaves as a semiconductor with high, p-type, electronic conductivity in air. The conductivity decreases significantly under reducing atmospheres (see fig. 4.7). This is due to the loss of p-type carriers as oxygen is lost from the structure [84]. The $p\text{O}_2$ dependent conductivity is shown in figure 4.8 and this figure highlights the hole-dominated, p-type behaviour, observed in LSCM. The temperature dependent conductivity shows an activation energy (E_a) of 0.23 eV below 600°C and a slightly higher value, 0.31 eV, above 600°C.

Under fuel cell conditions ($p(\text{O}_2) \approx 10^{-14}$ atm.) the total conductivity is in the order of 2.5 Scm^{-1} which is relatively low. If the current collection is not ideal this will lead to increased ohmic losses in the cell¹. Although the total conductivity is lowered under reducing conditions, loss of oxygen is thought to increase the oxygen ion conductivity and this, in turn, is thought to improve the catalytic activity [84]. In addition to this, when a cell operates at high fuel utilisation, the $p(\text{O}_2)$ in the anode compartment can increase significantly which should lead to a higher electronic conductivity and improved cell performance.

The thermal expansion coefficient in air was determined to be 10.8 p.p.mK^{-1} between 100-600°C and 14.1 p.p.mK^{-1} between 600-1250°C. This variation, along with the change in activation energy and is thought to be related to the phase change that begins around 400°C.

¹See Atkinson *et al.* ref. [38] pp.22 for a brief discussion of minimum conductivity requirements of an anode material.

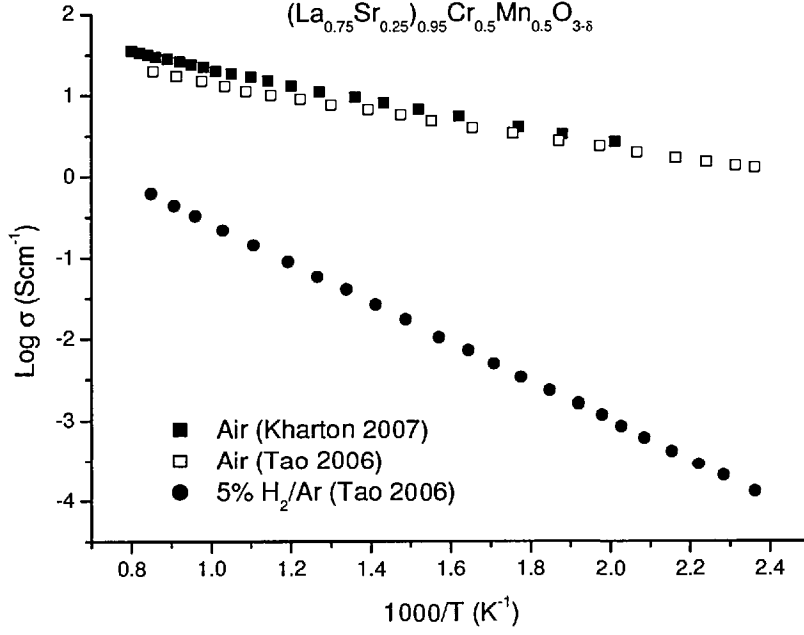


Figure 4.7: Comparison of total conductivity of LSCM samples in air from two authors that shows agreement between samples measured in air. A significant drop in conductivity is seen under reducing atmospheres (Data from Tao [85] and Kharton [84]).

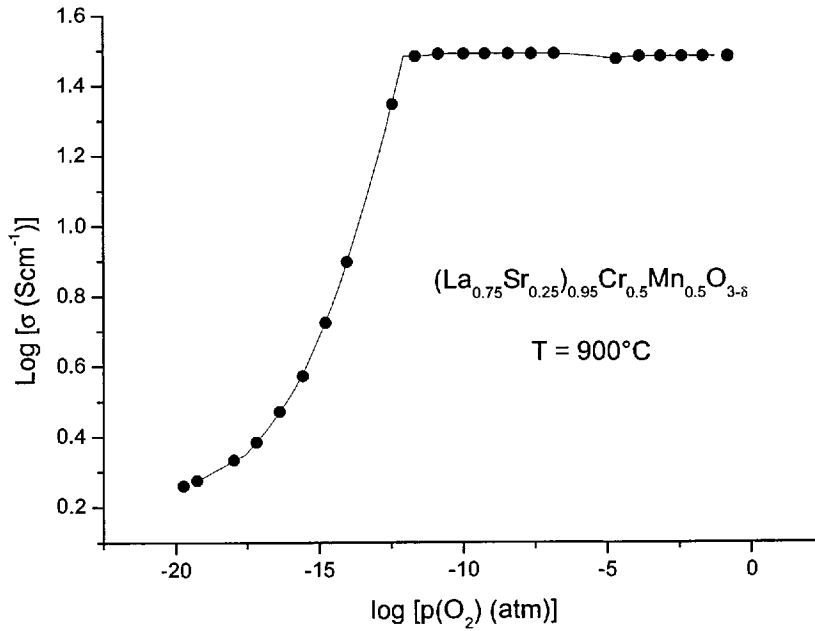


Figure 4.8: Oxygen partial pressure dependencies of the total conductivity of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ at 900°C . This shows the p -type conductivity typical of this material (Data from reference [84]).

Published cell performance seems to vary considerably for these materials. Variation seems to depend on the cell setup and measurement conditions. However, there may be other factors, such as undetected secondary phases as highlighted by the study above, which could improve or retard cell performance. Figure 4.9 summarises the polarisation resistances of LSCM and LSCM-CGO composites. Cell performance close to that of a Ni-cermet is obtained when running a LSCM-CGO composite anode on both hydrogen and weakly humidified methane. Clearly the difference between results decreases with increasing temperature which suggests subtle variations in the phase relationships that are borne out at lower temperatures. Unfortunately, these results only show half of the story; they do not include the ohmic resistances, which could be quite large. In LSCM, high ohmic resistance values can be an issue due to the p-type conductivity and associated decrease in conductivity at low oxygen partial pressure. Nevertheless, high power densities have been routinely observed in these materials. Ruiz-Morales and Kharton [84, 86] discuss the issue of diminished electronic conductivity in more detail.

Lay *et al.* has recently reported a new cerium-substituted LSCM ($\text{La}_{0.65}\text{Sr}_{0.25}\text{Ce}_{0.1}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_{3-\delta}$) [87]. It displays similar structural and electronic properties to un-doped LSCM but the fuel cell performance is significantly improved ($R_p = 0.2 \Omega\text{cm}^2$ at 900°C in H_2). There is limited experimental data available in the literature for this material but early indications are promising.

The paradox of LSCM is that, as a p-type conductor, lowering the oxygen partial pressure increases the oxygen vacancy concentration which improves the ionic conductivity and catalytic activity. These factors are thought to reduce the polarisation resistances. However, under operating conditions at low $p(\text{O}_2)$ the electronic conductivity decreases which increases the ohmic resistance. The performance is balanced (even limited) between the series and polarisations resistances. They are linked and complementary meaning only one *or* the other can be optimised at any one time.

In summary, LSCM shows many of the key features needed for successful application as an anode electrode material, such as stability over a wide range of oxygen partial pressure and suitable thermal expansion coefficient. However low electronic conductivity at low $p(\text{O}_2)$ means that efficient current collection or addition of an electronically

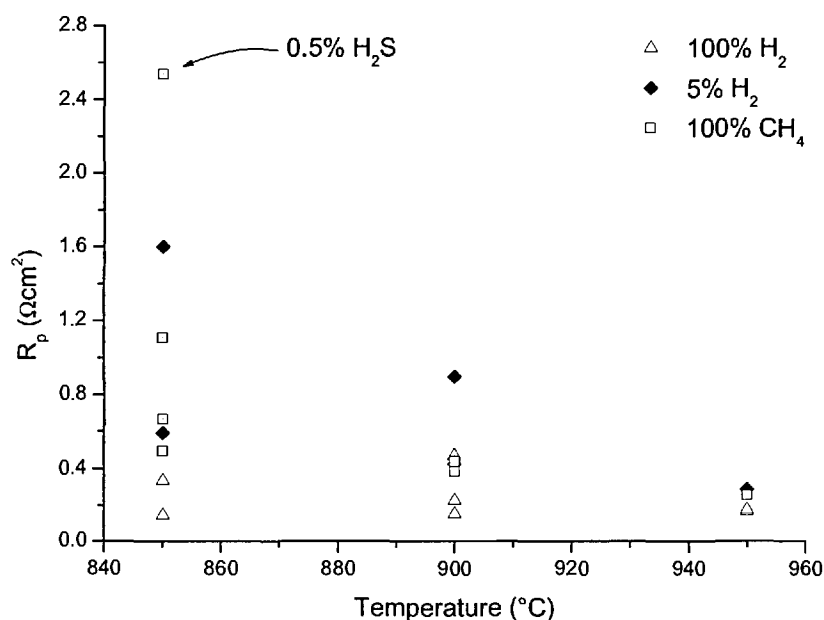


Figure 4.9: Polarisation resistances measured in different laboratories under various fuel atmospheres. Notice that the scatter in results reduces as the operation temperature is increased. (Data from references [86, 88–92])

conductivity phase may be necessary to ensure high performance. Alternatively, optimisation of the composition to achieve increased conductivity at low oxygen partial pressure could be advantageous.

Phases based on Strontium molybdate

Another highly promising double perovskite material is $\text{Sr}_2\text{MgMoO}_{6-\delta}$ (SMMO) first reported by Huang *et al.* [93]. Very promising performance has been published for cells running on hydrogen and methane. High performance can be maintained even when up to 50 p.p.m of H_2S was introduced into the fuel stream [94].

Careful examination of the crystal structure has shown $\text{Sr}_2\text{MgMoO}_{6-\delta}$ adopts the $I\bar{1}$ structure [95]. There is evidence of RP phases which have been linked with improved catalytic activity.

SMMO displays n -type conductivity and is $p(\text{O}_2)$ invariant at low oxygen partial pressure (10^{-12} - 10^{-22} atm.). At 800°C in dry hydrogen the maximum conductivity was 8.6 Scm^{-1} and in 5% H_2/Ar the conductivity dropped to 4.26 Scm^{-1} [94]. Bernuy-

Lopez [95] showed that the degree of reduction was small under fuel conditions because of difficulty lowering the Mo(VI) valence and altering the coordination state of the five-coordinate Mg(II). It was also shown that this material begins to decompose at temperatures above 900°C in reducing atmospheres forming MgO, Mo(0) and lower Mo oxides.

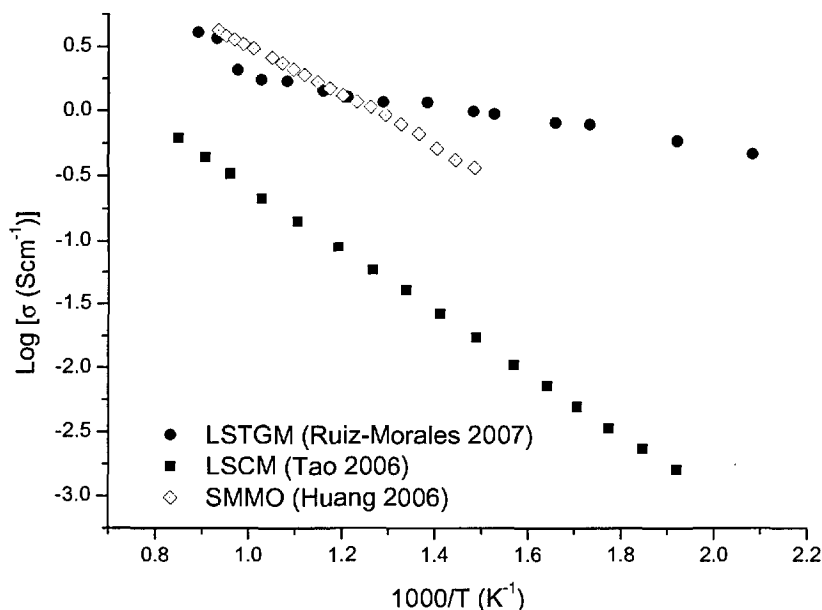


Figure 4.10: Comparison of the temperature dependent total conductivity of SMMO, LSCM and LST under 5%H₂/Ar atmospheres. The conductivity of SMMO is $p(\text{O}_2)$ independent compared with the p -type conductivity seen in LSCM (Data from Ruiz-Morales [72], Tao [88] and Huang [94]).

Cell tests, generally using electrolyte supported LSGM cells, have shown high power densities and stable operation when fuelled using hydrogen or methane [75, 93]. A lanthanum-doped analogue ($\text{Sr}_{2-x}\text{La}_x\text{MgMoO}_{6-\delta}$) has also been prepared which has been found to operate well on wet propane [96]. Lanthanum is thought to improve the catalytic activity because it causes ordering of the Mg and Mo B-site elements.

Other double perovskites

$\text{Sr}_2\text{FeNbO}_{6-\delta}$ (SFN) and $\text{Sr}_2\text{MnNbO}_{6-\delta}$ (SMN) have been investigated by Tao [97] and Irvine [98]. They found the structures to be stable in air and reducing conditions up to 900°C. The key difference between the two is that SFN shows n-type behaviour whereas SMN is p-type. The maximum conductivity of both samples is around $1\text{--}3 \text{ Scm}^{-1}$ (see table 4.2). This means that the conductivity of SMN diminished to $3.1 \times 10^{-2} \text{ Scm}^{-1}$

in reducing atmospheres. Conversely, SFN displays n-type conductivity and chemical stability but the maximum conductivity reaches 2.39 Scm^{-1} . With efficient current collection these materials may find some application but a higher electronic conductivity would be preferable.

Compound	Max. conductivity (Scm^{-1})	type (n, p)	Atmosphere	Ref.
LSCM	38	p	air	[88]
SMM	8.6	n	H_2	[94]
SFN	2.39	n	H_2	[97]
SMN	1.23	p	air	[98]

Table 4.2: Selected electronic conductivities of the double perovskites

($\text{Sr}_2\text{Fe}_{1-x}\text{M}_x\text{NbO}_{6-\delta}$), where $\text{M} = \text{Cu}, \text{Zn}$, has also been reported [99]. Doping caused a shift from predominantly n-type conductivity to a mixed n-p regime. However, in the zinc-doped composition, the conductivity minimum was between $p(\text{O}_2) = 10^{-5}$ and 10^{-10} atm. At temperatures above 700°C the stability limit is reached when the oxygen partial pressure falls below 10^{-10} atm. Given the relatively low electronic conductivity and instability under reducing conditions these materials can be ruled out as potential SOFC anode replacements.

4.2.3 Tungsten bronzes

The tungsten bronze structure is essentially a highly A-site deficient perovskite where the B-site octahedra have been rotated; the general formula can be written $\text{A}_{0.6}\text{BO}_3$. Amongst the numerous compositions synthesised and tested by Slater [100] and later by Kaiser [101], $\text{Sr}_{0.2}\text{Ba}_{0.4}\text{Ti}_{0.2}\text{Nb}_{0.8}\text{O}_{3-\delta}$ exhibits the highest electronic conductivity (10 Scm^{-1} at 930°C under low $p(\text{O}_2)$).

Cell performance figures were low in the samples tested by Kaiser; reaching a maximum current density of $\approx 80 \text{ mAcm}^{-2}$. There has been very little work on these materials as focus appears to have moved on to donor-doped titanates and the Cr-Mn double perovskites. As has been shown with other materials (above), conductivity in the range $1\text{-}10 \text{ Scm}^{-1}$ is high enough to allow good fuel cell performance, especially at high temperature. Perhaps there is merit in revisiting these materials in more detail.

4.3 Fluorite materials

4.3.1 Zirconia-based phases

Tao [102] has presented an extensive survey of zirconia-based materials, showing the range of elements capable of alloying with ZrO_2 . Doping with Sc, Ti, Mn, Fe, Ni, In, W and Nb have been trialled. However the general trend (even at high doping levels) is a minimal increase in electronic conductivity and a reduction in the ionic conductivity.

Ti-doped ScYSZ ($\text{Sc}_{0.15}\text{Y}_{0.05}\text{Zr}_{0.62}\text{Ti}_{0.18}\text{O}_{1.9}$) is the exception. At 900°C , Ti-ScYSZ has an electrical and ionic conductivity of 1.14 Scm^{-1} and $1 \times 10^{-2}\text{ Scm}^{-1}$ respectively [103]. As with many of the double perovskites discussed above, this electronic conductivity is probably too low for use as a SOFC electrode.

4.3.2 Ceria-based phases

Highly-doped ceria was identified early in the search for ceramic anode materials [104]. It has been shown to be resistant to carbon deposition [105] and is highly effective in Ni-cermet electrodes [8]. One of the main advantages of using ceria-based materials is that under low $p(\text{O}_2)$ some Ce(IV) reduces to Ce(III), which increases the electronic conductivity. Unfortunately, the partial reduction of Ce^{4+} causes a volume expansion (also referred to as chemical expansion) which can cause mechanical instability and cracking. With the correct choice of dopants (commonly Gd, Sm or Y), the chemical expansion can be minimised and the ionic conductivity is improved.

As with other fluorite materials, low electronic conductivity is the primary reason why ceria-based materials are not suitable as SOFC anode materials. However, there was a considerable increase in fuel cell performance when ceria was used as an active functional layer [106,107]. These materials have also shown improved catalytic activity towards hydrocarbon fuels, and significantly reduce cell resistance. Use of fluorite materials in composite electrodes, along with a good electronic conductor, shows a great deal of promise.

4.4 Other phases

Pyrochlores

$\text{Gd}_2\text{Ti}_{1-x}\text{Mo}_x\text{O}_7$ was investigated by Porat [108] as an anode material. Under reducing conditions it showed very high electronic conductivity: for $x = 0.7$, $\sigma \sim 70 \text{ Scm}^{-1}$, while for $x = 0.5$, $\sigma \sim 25 \text{ Scm}^{-1}$. At lower doping levels, the electronic conductivity approaches that of un-doped $\text{Gd}_2\text{Mo}_2\text{O}_7$ which is in the order of 10^{-2} Scm^{-1} . Unfortunately, samples with high Mo content were unstable at high $p(\text{O}_2)$. Redox instability makes these materials unsuitable for SOFC application.

$\text{Pr}_2\text{Zr}_2\text{O}_7$ has also been investigated by Holtappels [109]. Samples doped with 5% Mn and 20% Ce showed p-type electronic behaviour. Under reducing atmospheres the electronic conductivity was low, around $2 \times 10^{-3} \text{ Scm}^{-1}$. Once again the electronic conductivity is too low for practical application as an electrode material.

Spinel materials

Flot and Irvine [110] have investigated transition metal doped magnesium titanate (Mg_2TiO_4). Conductivities between $2\text{--}5 \text{ Scm}^{-1}$ were observed at low oxygen partial pressures. However, there was partial decomposition observed at low $p(\text{O}_2)$ at $\sim 900^\circ\text{C}$.

4.5 Conclusions

Promising materials have been identified in the search for alternatives to the cermet structures currently used in SOFCs. Of the proposed alternative materials currently cited in the literature, there are several that perform as well as the state of the art anode materials. These materials also show increased redox tolerance, resistance to sulfur poisoning and the ability to directly reform methane and higher hydrocarbons without carbon deposition.

Materials of note are as follows:

- Ga,Mn doped $\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ and related materials show excellent perfor-

mance and are reasonably well characterised.

- $(\text{La}_{0.65}\text{Sr}_{0.25}\text{Ce}_{0.1}\text{Mn}_{0.5}\text{Cr}_{0.5}\text{O}_{3-\delta})$; even though this material shows relatively low electronic conductivity at low $p(\text{O}_2)$, the cell performance of this material is high. Initial research when doping with cerium has shown promising results.
- $\text{Sr}_2\text{MgMoO}_{6-\delta}$ has also shown the high electronic conductivity and stability required for SOFC operation. High cell performance has also been demonstrated.

One of the major challenges facing all of these materials is the number of constraints placed on them as single phase anode materials. Apart from stability, thermal expansion, and reactivity requirements the fundamental transport properties need special attention. For a material to have high electronic conductivity at low oxygen partial pressure while maintaining high ionic conductivity and catalytic activity is very difficult to achieve in practice.

Materials for which there is a large amount of cell testing data, there is also a large spread in the published results, especially at lower temperatures. This could be due to differing cell testing conditions but there is also the possibility of subtle interactions between minor second phases or impurities. Detailed phase characterisation is important in understanding the spread of experimental results in compositions which are nominally the same.

In the short term, practical application of these materials will have more use as composites or alternative anode arrangements. Many of the materials that have shown the most promising performance have been composites, for example the Ce-modified SrTiO_3 materials prepared by Marina [67].

Gross [106] has successfully shown that it is also possible to use a ceria-based functional layer, the electronic conductivity of which may be too low to use alone. One would then apply a relatively inactive, highly conducting material as a current collector.

Finally, as with Ni-cermet anode materials, performance in SOFC electrodes is highly dependent on the microstructure. Careful control of the anode microstructure, partic-

ularly in composite electrodes, could lead to a large increase in performance.

Chapter 5

Experimental Methods and Synthesis

This chapter identifies and describes, in detail, the experimental techniques used and the conditions under which the experiments were performed. In addition to this, some results are presented in relation to the synthesis and early characterisation of Ce-doped SrTiO_3 and the rationale for the stoichiometries chosen for this research.

Initial work had focussed on the reproduction of earlier work published by Marina and Slater on La-doped SrTiO_3 [65,66]. It was relatively easy to prepare compounds as described in the literature and this was a good introduction to the synthetic techniques. Preparation in our laboratory of Ce-doped $(\text{La,Sr})\text{TiO}_3$ resulted in similar multi-phase mixtures as reported by Marina [67].

Following this result, alternatives were trialled, with the aim of preparing a single phase, Ce-doped SrTiO_3 . Ce-doped BaTiO_3 had been reported in the literature and was successfully prepared using solid-state and glycine-nitrate techniques. Preparation of $\text{Ba}_{0.9}\text{Ce}_{0.1}\text{TiO}_{3\pm\delta}$ was successful. However, the potential deleterious reaction with CO_2 led us to suspend any further work on this material.

Preparation of Ce-doped SrTiO_3 has not been widely reported in the literature. There is

also no reference to its use as a material in SOFCs. Careful examination of the literature found that the compound $\text{Sr}_2\text{Ce}_2\text{Ti}_5\text{O}_{16}$ had been identified and characterised as stable titanate host for the disposal of plutonium. Trials on cerium-containing compounds were preferred because cerium is a non-toxic, non-radioactive substitute for plutonium [111, 112]. It was also investigated as a potential microwave frequency dielectric [113–115]. $\text{Sr}_2\text{Ce}_2\text{Ti}_5\text{O}_{16}$ is a member of the homologous series $\text{Sr}_{2+n}\text{Ce}_2\text{Ti}_{5+n}\text{O}_{15+3n}$ which can also be described as $\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_3$, an A-site deficient perovskite. Throughout this work we have described the compounds using the ABO_3 stoichiometry.

5.1 Solid state synthesis

Samples were prepared using TiO_2 (99.8%, Aldrich), SrCO_3 (99+%, Aldrich) and CeO_2 (99+%, Aldrich). Starting reagents were dried at 600°C before they were weighed, to remove any volatile impurities. Stoichiometric amounts of starting material were weighed to within 1 mg of desired values. Reactant mixtures were ball milled for 10–16 hours under acetone in polypropylene jars using zirconia milling media. Following milling, powders were dried and uniaxially pressed at 600 kgcm^{-2} . Compacts were then fired between 1100°C and 1350°C for 24 hours in alumina crucibles. Synthesis was complete after two cycles including an intermediate milling step for 15 min in a planetary ball mill (PM100, Retsch) operating at 100 rpm. Zirconia-lined milling jars were used during planetary ball milling.

5.2 Milling

Powders were milled during synthesis to improve homogeneity and to reduce the particle size of the fully synthesised powders. A wet roll mill was used for general milling and particle size reduction. Typically this was done in polypropylene jars with CaO-stabilised zirconia media under ethanol or propanol. Milling times ranged from 12 hrs to 1 week.

For significant reduction in particle size, high-speed, planetary ball milling (PBM) was found to be the most effective technique. PBM was performed using a Retsch PM100 operating at 250–300 rpm. Rotation was reversed every 10 mins. The milling jars were

Element	Reagent		
	CeO ₂	TiO ₂	SrCO ₃
Al	100	43.6	-
Ba	-	-	95.2
Ca	12	35.9	234
Cr	40	-	0.2
Fe	22	5.8	1.8
K	70	1580	-
La	40	-	-
Mg	-	-	10.3
Na	-	26.2	23.1
Nd	15	-	-
Te	-	-	31.5
Zr	-	129	-

Table 5.1: Manufacturers trace analysis of the starting materials used for solid-state synthesis. Values are in p.p.m.

stainless steel with a stabilised zirconia lining. The milling media was 8mm-20mm stabilised zirconia balls using a ratio of 10:1 media to powder by weight. Milling times ranged from 15 min to 12 hrs

5.3 Density measurement

Density of polycrystalline samples were measured using the 'Archimedes' technique. Samples to be measured were submerged in distilled and deionised water. To remove any trapped air (which may change the apparent density) the samples were placed under a vacuum for 30-40 mins. Before the vacuum was removed, the sample was tapped to remove any remaining air bubbles still adhering to the sample. After removing the vacuum, the water temperature typically dropped by a few degrees. Samples were kept submerged in the water until it had returned to ambient temperature.

Density measurements were performed using a Sartorius CP124S analytical balance with a YDK01 density kit. This allowed for the sample to be suspended in water, on the balance, without any contribution from a suspending wire. The increase in apparent weight, divided by the density of the liquid, gives the volume of the suspended object (eq. 5.1):

$$Volume = \frac{\rho_{water}}{w_w - w_i} \quad (5.1)$$

where w_w is the weight of the sample with the surface water removed and w_i is the weight of the sample immersed in water.

By removing the air from the open porosity, as described above, the volume of the sample can be measured very accurately and the density is calculated using equation 5.2 below.

$$\rho = \frac{mass}{volume} \quad (5.2)$$

These two equations can be combined to give:

$$\rho = \frac{w_d \times \rho_{water}}{w_w - w_i} \quad (5.3)$$

where w_d is the weight of the dry sample.

5.3.1 Calculation of theoretical density from crystallographic parameters

If the unit cell volume, the number of atoms per unit cell and the molecular weight are known then the theoretical density of a material can be calculated using equation 5.4:

$$\rho = \frac{Z \times MW}{V \times N_A} \quad (5.4)$$

where Z is the number of molecules per unit cell, MW is the molecular weight of the substance, V is the volume of the unit cell and N_A is Avogadro's constant.

5.4 X-Ray diffraction

Powder X-ray diffraction was performed using a Philips 1729 diffractometer between 20-100° 2θ using a step size of 0.02°. Cu-K α radiation was used. There was a divergence slit (1°) before and after the sample. There was a 0.2mm receiving slit and a graphite monochromator was positioned after the sample. The instrument was set up in Bragg-Brentano prefocusing geometry. Samples were fine grained powders which typically had a mean particle size in the region of 10 μm .

Two methods were used for mounting the samples. The first involved placing a small amount of the powder onto a piece of single crystal silicon which had been cut with a crystal orientation so that there were no Bragg reflections in the angular range of interest. This powder was then dispersed evenly across the plate as a slurry with acetone and allowed to dry before being placed in the diffractometer. The second method was the back-loading of a traditional aluminium window holder. On occasions this led to additional peaks from the aluminium holder but these were away from areas of interest and were relatively weak and easy to identify.

There was no method of temperature control in the standard diffractometer instrument, although the room in which the instrument was located was temperature controlled.

Peak positions were determined using X'pert Hi-score proprietary software (PANalytical). The diffractometer was externally calibrated using the Si [111] peak of a polycrystalline standard. For some measurements a silicon internal standard was used.

Measurements to determine precise lattice parameters were measured on a Bruker D8 Advance diffractometer between 20-100° 2θ at a step size of 0.02° using Cu-K α radiation.

In-situ high temperature XRD studies were performed on a PANalytical Xpert diffractometer using a Bühler HDK 2.4 temperature stage and a Pt heating strip. Cu-K α radiation using a graphite secondary crystal monochromator was used.

5.5 Neutron Diffraction

Room temperature neutron diffraction data were collected on the GEM instrument at the ISIS Spallation Neutron Source, Rutherford Appleton Laboratory, UK.

Powder samples were sealed in vanadium cans. Time of flight (TOF) data were collected using GEM detector banks 1-7. This equates to an angular range of 1.1° to 169.3°. Data was collected for 20 mins per sample.

TOF data was converted to d-spacing using equation 5.5 which relates the wavelength of the neutron to its speed (via the de Broglie equation) to Bragg's law:

$$\lambda = \frac{ht}{mL} = 2d\sin\Theta \quad (5.5)$$

where t is the time of flight of the neutron from the source, L is the distance from the source, m is the mass of the neutron (1.675×10^{-27} kg), h is Plank's constant and the right hand side of the equation is Bragg's law.

5.6 Refinement of crystallographic parameters

5.6.1 Phase identification

Survey scans used for phase identification were performed; these covered a wide angular range ($2\theta = 10^\circ$ - 100°). These scans were also used to monitor the progress of the synthesis reaction. Phase identification was performed using the proprietary X'pert Hi-score software (PANalytical).

5.6.2 Refinement of lattice constant

Lattice parameters were refined using the least-squares method. A number of programs were tested, including the program UNITCEL and Celref. However, the results from such programs varied and there were often differences between programs for identical data-sets. The best and most consistent results were obtained using the Hi-score package (PANalytical). This software package allowed for the accurate determination of

peak position, the indexing of the cell using the program Treor or Dicvol, and finally the refinement of the lattice constant in one software package. To check the reliability of the result from Hi-score, selected data were checked using a first principles approach.

5.6.3 First principle approach for accurate determination of lattice constant

As an example it is easiest to use un-doped SrTiO₃. We know the space group of this material (Pm $\bar{3}$ m No. 221) and the lattice constant is 3.9051 Å from the Inorganic Crystal Structure Database (ICSD). Even though we can index each line by comparing it with the values from the database it is just as easy to calculate directly from the experimental 2θ values. For cubic crystals, the interplanar spacing, d , can be described by equation 5.6:

$$\frac{1}{d^2} = \frac{(h^2 + l^2 + k^2)}{a^2} \quad (5.6)$$

This can be combined with the Bragg equation to form equation 5.7:

$$\frac{\sin^2\theta}{(h^2 + l^2 + k^2)} = \frac{\sin^2\theta}{s} = \frac{\lambda^2}{4a^2} \quad (5.7)$$

Because the sum $s = (h^2 + l^2 + k^2)$ is always an integer and $\lambda^2/4a^2$ is a constant for a particular pattern, indexing the pattern is simply a matter of finding a set of integers, s , which will divide into the observed $\sin^2\theta$ values to give a constant. Indexing the pattern and calculating the lattice constant can be done in the same series of calculations.

Table 5.2 shows the indexing and calculation of the lattice constant for an un-doped SrTiO₃ sample prepared using the method described in section 5.1 and measured in our laboratory on a Philips PW 1729 diffractometer using CuK α radiation. 2θ positions were determined using the PANalytical Hi-score.

For comparison, the value obtained from the least squares refinement performed by the Hi-score package was 3.9047±0.0001 Å. This agrees with the lattice constant reported

1	2	3	4	5	6	7
Line	2θ	$\sin^2\theta$	$s = h^2 + k^2 + l^2$	$\lambda^2/4a^2$	a (Å)	hkl
1	22.766	0.039	1	0.0390	3.9028	100
2	32.406	0.078	2	0.0389	3.9038	110
3	39.963	0.117	3	0.0389	3.9043	111
4	46.476	0.156	4	0.0389	3.9046	200
5	52.346	0.195	5	0.0389	3.9049	210
6	57.794	0.234	6	0.0389	3.9045	211
7	67.836	0.311	8	0.0389	3.9044	220
8	72.576	0.350	9	0.0389	3.9045	300
9	77.192	0.389	10	0.0389	3.9047	310
10	81.735	0.428	11	0.0389	3.9045	311
11	86.218	0.467	12	0.0389	3.9045	222
12	90.680	0.506	13	0.0389	3.9046	320
13	95.149	0.545	14	0.0389	3.9045	321
$\lambda = \text{Cu}_{K\alpha 1} = 1.540562\text{\AA}$						

Table 5.2: Indexed experimental data and lattice constants for SrTiO_3

in the JCPDS card 35-0734 of 3.9050 Å (at 25°C).

From table 5.2 it is clear that the calculation of the lattice constant for each line gives a spread of results from 3.9025Å to 3.9049Å. Before the widespread use of the least-squares method there were a number of graphical methods used. It is well known that the error in theta decreases to 0 for $\theta=90^\circ$ (see Chapter 11 in reference [116]). A plot of lattice constant versus $\sin^2\theta$ or $\cos^2\theta$ usually give linear plots and the value of the lattice constant can be extrapolated back to $\theta=90^\circ$, thus giving a value of lattice constant without any systematic error.

Figure 5.1 shows a graph of the three extrapolation functions used in the graphical determination of the lattice constant; $\sin^2\theta$, $\cos^2\theta$ and another function known as the Nelson-Riley (N-R) function [117]. The N-R function was the result of a more rigorous analysis of sources of error and showed that equation 5.8 was robust, even at low angles ($2\theta = 60^\circ$).

$$\frac{\Delta d}{d} = K \frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \quad (5.8)$$

It can be seen in Figure 5.1 for data collected using a diffractometer, that these extrapolations do not give linear results. For 2θ values above $50-60^\circ$, the lattice parameter would appear to be independent of θ .

5.6.4 Sources of error in the diffractometer

A modern diffractometer is a much more complicated instrument than a powder camera and is potentially more susceptible to misalignment and therefore introduction of errors. As Cullity [116] pointed out, in a diffractometer it is impossible to measure the same back-reflected cone of radiation on both sides of the incident beam. This would serve as an automatic check of the angular accuracy as it does in a powder photograph. The main sources of instrumental error include:

1. Misalignment of the diffractometer and in particular the zero position of the counter.
2. Absorption by the specimen.
3. A tendency for samples used in the diffractometer to be flat and not strictly conform to the focusing circle.
4. Displacement of the sample from the axis of the diffractometer.

Errors (1), (2) and (3) can be minimised by good instrument alignment and careful sample preparation. Sample displacement is the most common and potentially largest single source of error. Most refinement programs allow for the refinement of this parameter but let us examine it first. The variation in observed angle $\Delta\theta/\theta$ can be related by the following:

$$\frac{\Delta\theta}{\theta} = -\frac{\delta \cos^2\theta}{R \sin\theta} \quad (5.9)$$

where δ is the sample displacement from the diffractometer axis and R is the radius of the goniometer. For a more detailed derivation of equation 5.9, please see ref. [118]

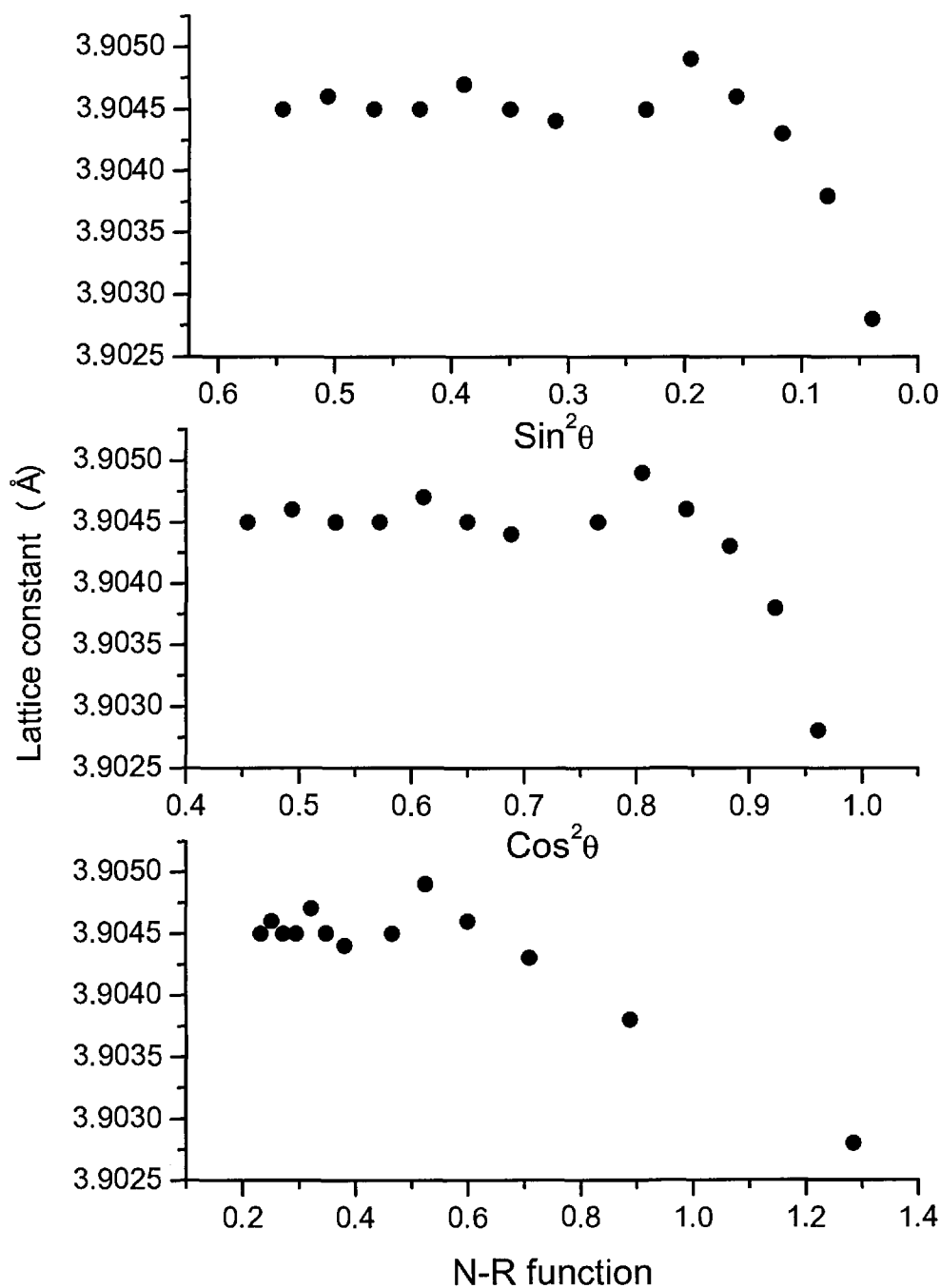


Figure 5.1: Data in table 5.2 for three common extrapolation functions used for the precise determination of cell parameter. Clearly the data, which was collected using a diffractometer, becomes angle independent above $2\theta \cong 50^\circ$. N-R function is defined in eq. 5.8.

pg.160. Figure 5.2 shows the effect of sample displacement in the diffractometer graphically. At low angles, sample displacement by $100\mu\text{m}$ can change the observed 2θ values by up to 0.06° .

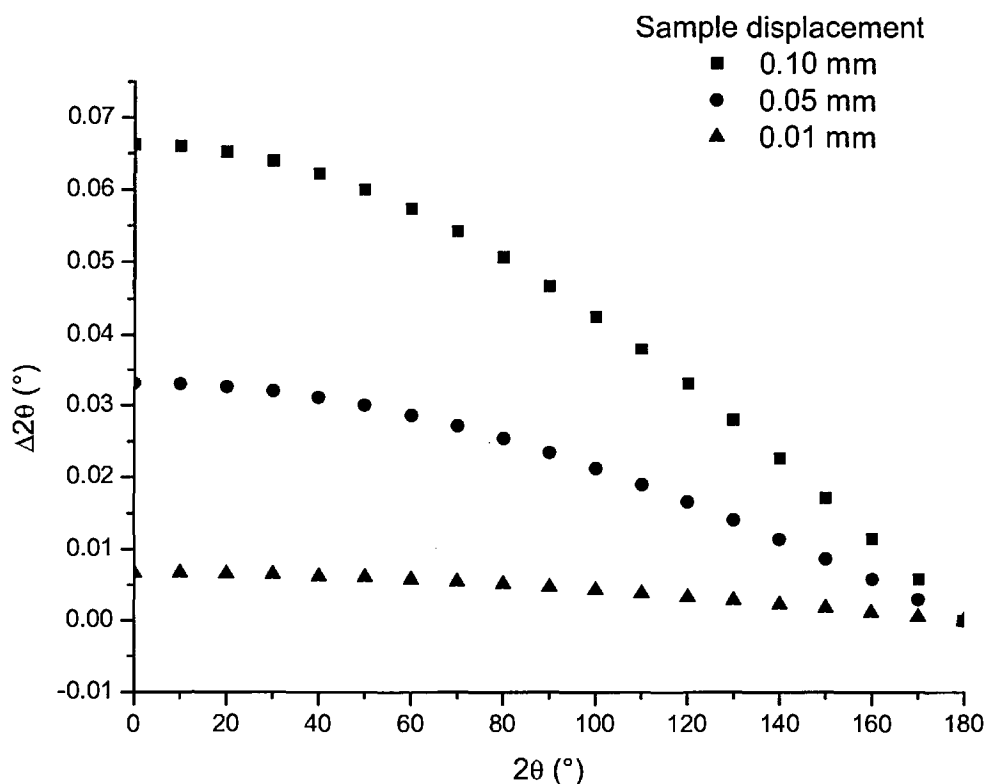


Figure 5.2: Graphical representation of equation 5.9, showing the change in 2θ position for different hypothetical sample displacements. The effect is more pronounced at low values of 2θ .

To obtain the most precise results, we must ensure that the sample is as close as possible to the diffractometer axis in order to minimise errors and any corrections that may need to be made after the measurement. It should also be remembered that the peak positions must also be measured as precisely as possible. This has been made somewhat easier with the aid of computer software now available. Figure 5.3 demonstrates the difference in lattice constants derived from peak positions determined using two different algorithms in the peak searching software. The first determines the peak position by taking the point of maximum intensity and the second takes the peak position as the minimum of the second derivative of the peak profile. The main difference is in the peaks at lower angles (where the requirement for precise peak positions are the highest) although the final outcome from a least-squares fit of this

data is the same within experimental error ($3.9047(1)\text{\AA}$).

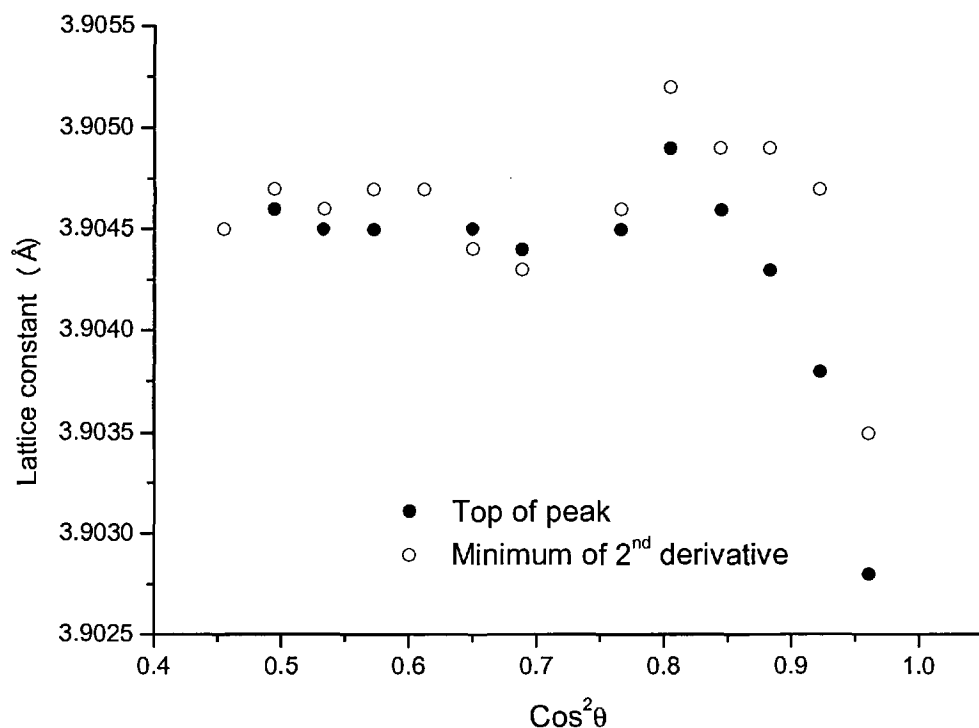


Figure 5.3: Variation in calculated lattice parameter with the use of two different peak searching algorithms. The effect is more pronounced at low angles of 2θ .

The effect of temperature should also be considered, especially as the sample environment in the diffractometer (Phillips) was not temperature controlled. Although the laboratory where the diffractometer was located was temperature controlled, there was still some temperature fluctuation from day-to-day. Given that the bulk thermal expansion coefficient of these materials had been determined to be in the range of $11\text{--}12\text{ ppmK}^{-1}$ using a dilatometer (See Chapter 6), this would equate to the change in the lattice constant of $0.000045\text{\AA}$ per K. Therefore, a fluctuation of $\pm 3\text{--}4^\circ\text{C}$ could change the lattice constant by up to $\pm 0.0002\text{\AA}$.

5.6.5 Rietveld refinement

Details of the data collection procedures for Rietveld refinement have been outlined in sections 5.4 and 5.5.

Full pattern refinement was carried out using the combined GSAS [119] and EXPGUI [120] computer package. The background was always simultaneously refined using a

shifted Chebyshev function. No refinement of any preferred orientation was attempted in either the X-Ray or neutron refinements. Standard deviations were calculated in the GSAS package and were used as stated. Unless stated in Chapter 6, no region of the experimental pattern was omitted during the refinements. Several models were checked and re-checked to ensure all the reflections were indexed and to mitigate the chances of encountering any false minima.

Polycrystalline silicon (the same material used for the external calibration) was used to determine unique instrumental effects which may be present in a pattern which the Rietveld model cannot usually account for. Figure 5.4 shows the diffraction pattern from the polycrystalline silicon measured on the Philip 1729 diffractometer, along with the fitted results. Whilst the model fits well to a majority of the experimental data, the fit for the strongest reflection (111) at $2\theta \sim 28^\circ$ is poor. On closer examination (see fig. 5.5) the model does not describe the peak shape adequately, particularly the peak tail.

Despite this, the lattice parameter calculated for this sample $5.43071(17)\text{\AA}$ is very close to published values in the literature: $5.43054(17)\text{\AA}$ [121] and $5.431073(6)\text{\AA}$ [122] at 25°C .

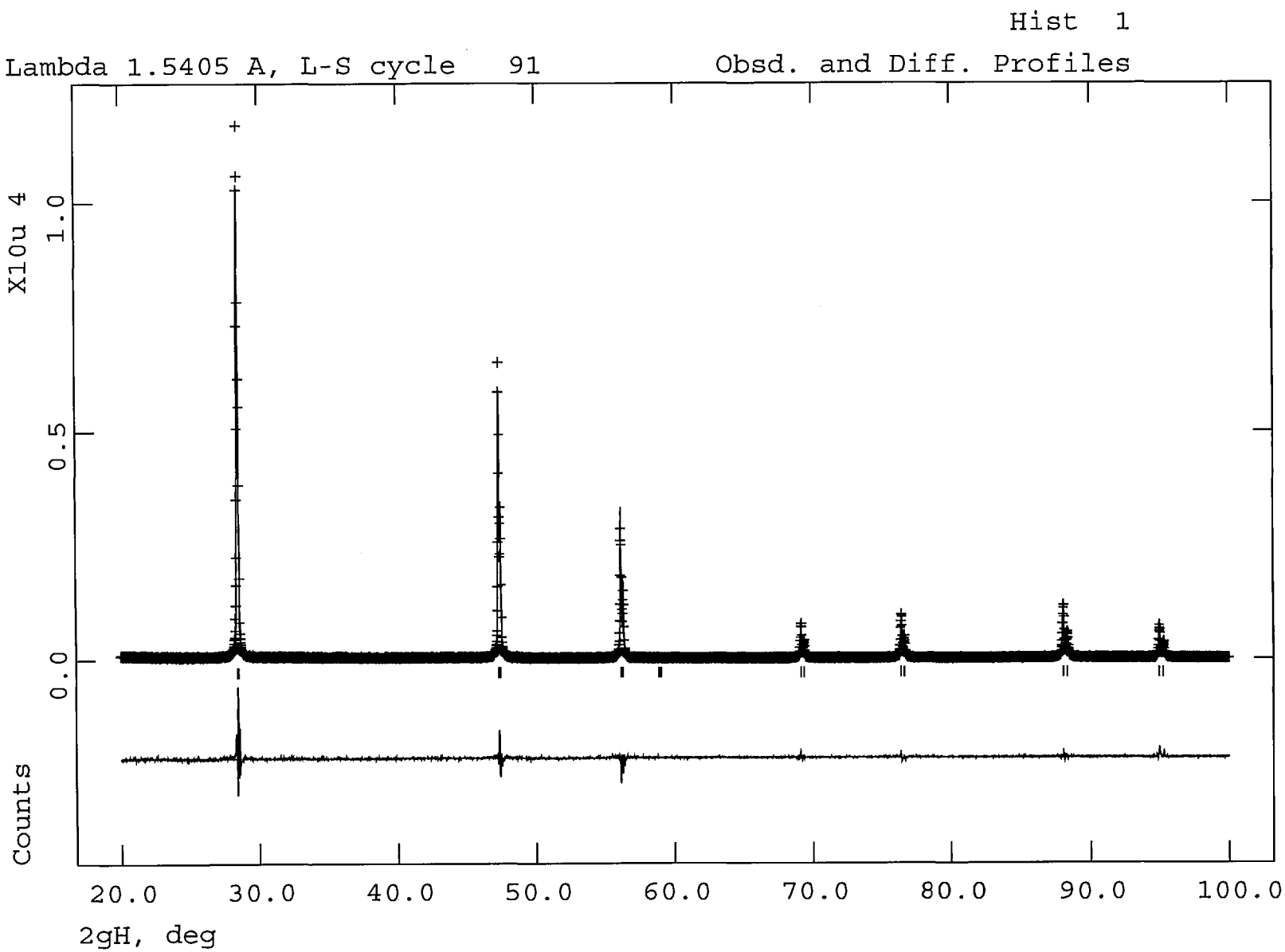
5.7 Chemical analysis

5.7.1 X-Ray Fluorescence (XRF)

Elemental trace analysis was performed with the use of a Bruker D8 XRF instrument with a rhodium X-Ray target. Collection times were in the order of 30 minutes to ensure good counting statistics for quantification. Elemental quantification was performed using the proprietary Bruker software with a standard-less quantification method. No correction was applied for the effect of matrix elements.

5.8 Four-probe DC (4PDC) method

Samples were either prepared as bars with typical dimensions of $3 \times 3 \times 25$ mm, or smaller samples were cut from 13mm diameter sintered pellets with nominal dimensions of $2 \times 2 \times 12$ mm. Sample faces were ground using 1200 grit SiC paper ensuring the



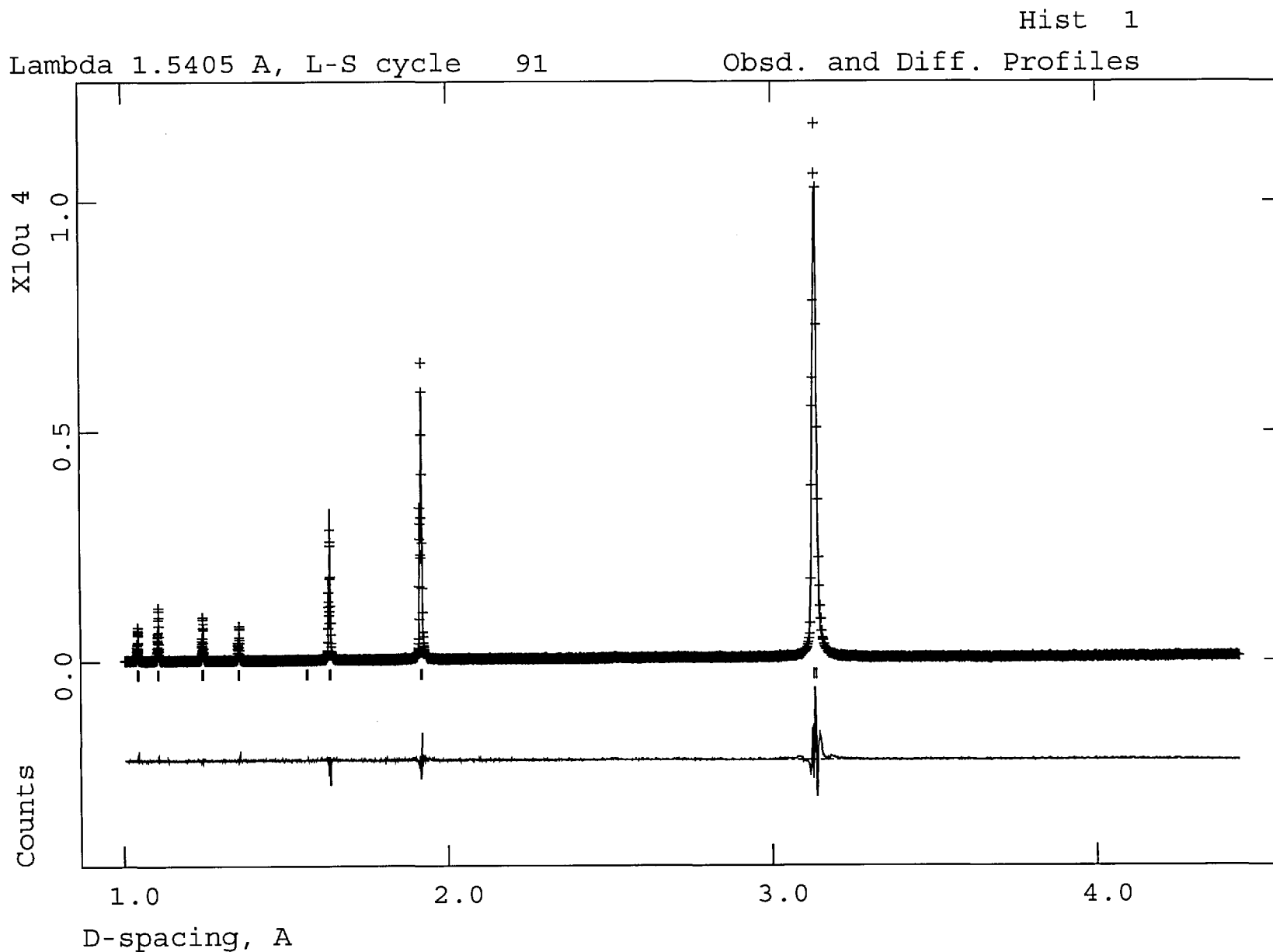


Figure 5.4: X-ray diffraction patterns and refinement of polycrystalline silicon data collected on a Philips 1729 diffractometer under the experimental conditions described in Section 5.4. Experimental data and calculated patterns are shown as crosses and solid lines respectively with the difference curve shown below. Peak positions predicted by the structural model are shown as tick marks below the patterns.

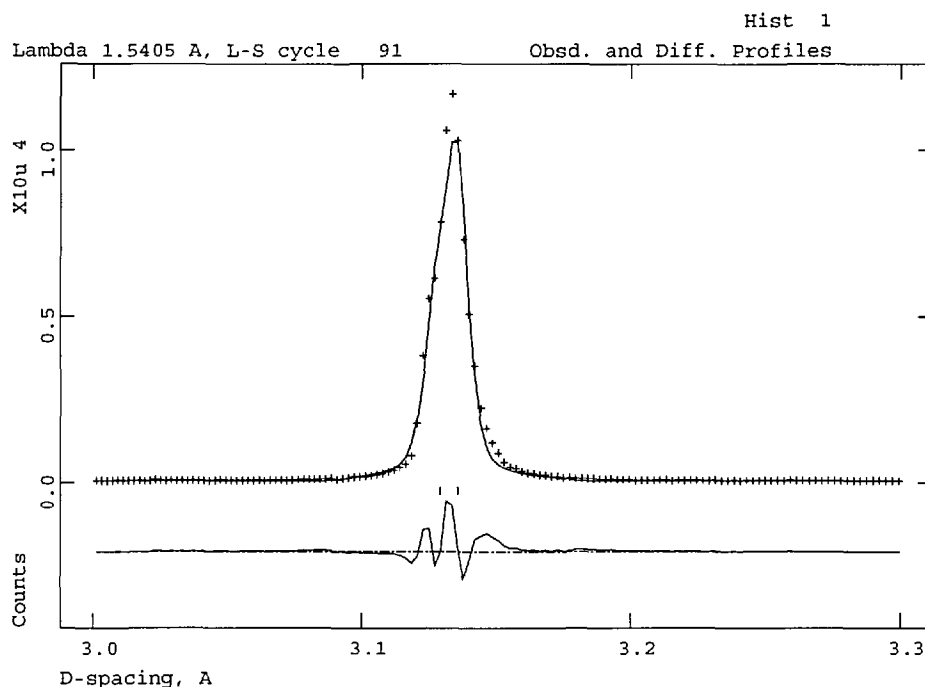


Figure 5.5: An enlarged region from Fig. 5.4 showing the (111) reflection from polycrystalline silicon. A set of peak profile parameters were unable to adequately describe the tail of the reflection.

sample sides were kept parallel to within ± 0.01 mm. Voltage and current probes were attached by twisting 0.25 - 0.4 mm diameter platinum wire around the sample. A small amount of Pt paint was applied to the ends of the bar to ensure good galvanic contact between the current probes and the sample. The separation of the voltage probes was measured just before the sample was placed into the furnace using a pair of Vernier callipers.

Sample conductivity was measured under galvanostatic conditions using a range of currents in forward and reverse polarities. For high resistance samples the currents used were in the range of $5\mu\text{A}$ - $150\mu\text{A}$. For highly conductive samples the current was in the order of 200 mA. The currents were chosen in order to keep the voltage drop across the sample below 2 V.

The current was supplied by a Ministat precision potentiostat (Thompson). The sample voltage and the actual current flowing through the sample were measured using two Keithley 175 multimeters.

5.8.1 Measurements under controlled oxygen partial pressure

The isothermal measurements of the total electrical conductivity (4-probe D.C.) and Seebeck coefficient as function of the oxygen partial pressure, $p(O_2)$, were performed simultaneously using two bar-shaped samples placed in an electrochemical cell of yttria-stabilised zirconia (YSZ). The cell was equipped with two pairs of Pt electrodes, which served as an oxygen pump and a sensor, thus enabling control of the oxygen partial pressure near the samples. The sample for thermopower measurements was placed along natural temperature gradient in the cell (about 15 °C/cm). Two B-type thermocouples were attached to the ends of the sample which were coated in Pt; the 6Rh-Pt leads of the thermocouples also served as thermovoltage probes. The results of the Seebeck coefficient measurements were corrected for the contributions of Pt and 6Rh-Pt alloy [123].

The second sample used for the conductivity measurements was placed in the same cell in a crosswise orientation near the middle of the sample for Seebeck coefficient measurements, i.e. in an isothermal plane of the cell. The criteria for equilibration after a change in either oxygen pressure or temperature was less than 0.05% per minute and $0.001VK^{-1}$ per minute for the conductivity and Seebeck coefficient, respectively.

5.8.2 Evaluation of uncertainties in conductivity analysis

The process of measuring the conductivity is relatively complex and presents many opportunities to introduce errors into the final results. The reasons for using the 4-point DC method are to eliminate the effects of contact resistance and minimise the thermoelectric EMF arising from the Peltier effect if the sample is not at a uniform temperature. The resistivity can be calculated using Eq. 5.10

$$\rho = R \frac{A}{l} \quad (5.10)$$

where R is the resistance, A is the cross sectional area of the sample and l is the separation of the voltage probes.

For a rectangular specimen, the uncertainty in the resistivity will be equal to:

$$\frac{\delta\rho}{\rho} = \sqrt{\left(\frac{\delta R}{R}\right)^2 + \left(\frac{\delta w}{w}\right)^2 + \left(\frac{\delta t}{t}\right)^2 + \left(\frac{\delta L}{L}\right)^2} \quad (5.11)$$

where w and t are the width and thickness of the sample respectively. δw , δt , and δl are the uncertainty in the measurement of the sample dimensions and the voltage probe separation. $\delta R/R$ is the uncertainty in the resistance measurement, i.e. the instrumental contributions to the uncertainty.

Uncertainty in R can be estimated from the instrument manufacturer's specification. The relative uncertainty was 0.2% and 0.03% in the current ($\delta I/I$) and voltage ($\delta V/V$) measurements respectively, therefore:

$$\frac{\delta R}{R} = \sqrt{\left(\frac{\delta V}{V}\right)^2 + \left(\frac{\delta I}{I}\right)^2} = \sqrt{0.03^2 + 0.2^2} = \pm 0.2\% \quad (5.12)$$

Measurement of the sample dimensions was done with a micrometre with an uncertainty of $\pm 0.01\text{mm}$. Typical sample dimensions were $4 \times 3\text{ mm}$ and given that the sample faces were ground parallel to within 0.01mm this equates to a relative uncertainty of $\pm 0.4\%$.

Voltage probe separation ($\delta l/l$) was very difficult to measure precisely. Using vernier calipers, the aim was to measure mid-way between wire diameters on a sample before it was placed into the furnace for measurement. Measuring the voltage probe separation on a sample just before it was placed into the furnace minimised the risk of a wire moving during the mounting process. Figure 5.6 shows schematic of the sample arrangement.

If the assumption is made that we can exactly measure the separation of the voltage probes as shown in figure 5.6, $\frac{\delta l}{l}$ would be $\frac{0.01\text{mm}}{\text{sample length}}$. Depending on the sample, the length varied from a maximum of $\sim 20\text{mm}$, to a minimum of 5mm . Assuming only the uncertainty in the vernier calipers, then $\delta l/l$ would range from 0.06 - 0.2%. In practice, however, it was very difficult to measure exactly on the mid-point of each

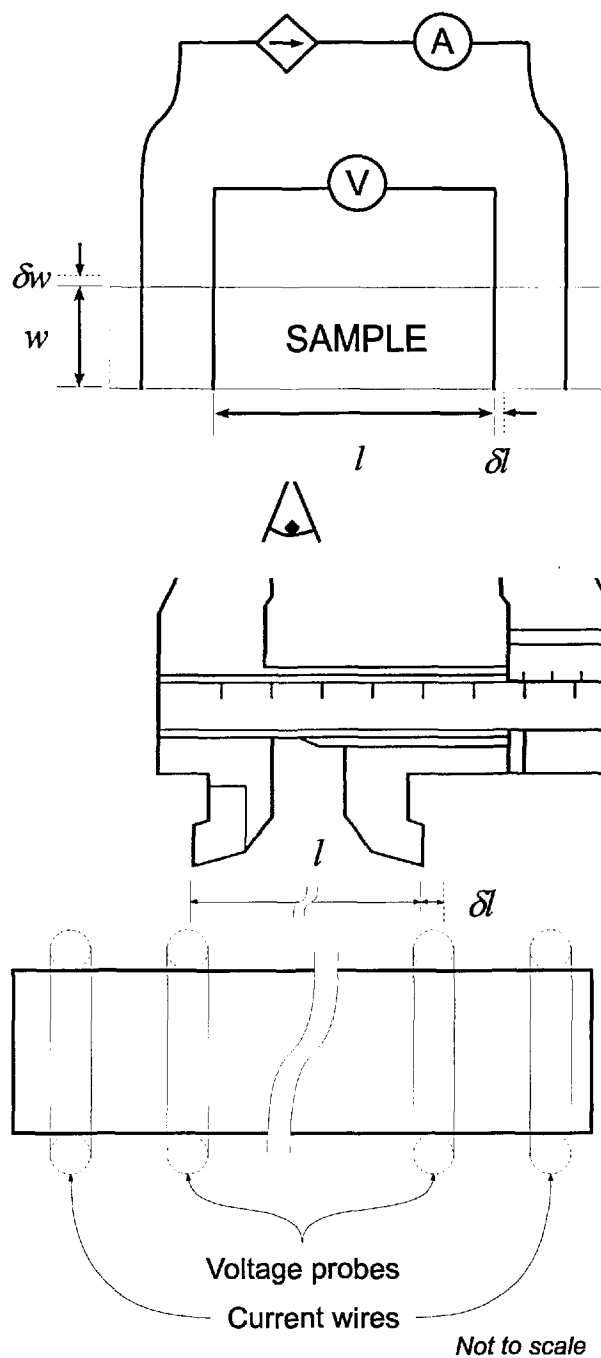


Figure 5.6: Schematic arrangement of 4PDC setup (Top) and an enlarged view showing more detail of the wire diameters for the measurement of l (Bottom).

wire. A reasonable estimate would be that there was a measurement error of a half a wire diameter ($\sim 0.125\text{mm}$). This approximately corresponds to a relative error in l of between 0.7 - 2.5%.

Therefore the total uncertainty in the resistivity would be calculated as follows:

$$\frac{\delta\rho}{\rho} = \sqrt{\left(\frac{\delta R}{R}\right)^2 + \left(\frac{\delta A}{A}\right)^2 + \left(\frac{\delta l}{l}\right)^2} \quad (5.13)$$

$$\left(\frac{\delta\rho}{\rho}\right)_{min} = \sqrt{0.2^2 + 0.5^2 + 0.7^2} = \pm 0.9\% \quad (5.14)$$

$$\left(\frac{\delta\rho}{\rho}\right)_{max} = \sqrt{0.2^2 + 0.5^2 + 2.5^2} = \pm 2.6\% \quad (5.15)$$

The overriding source of error in the conductivity measurements lay in the determination of the geometric parameters but more specifically in the determination of the separation of the voltage probes. Considering that the conductivity of all samples varied by several orders of magnitude in the temperature range studied, even an uncertainty of 2-3% should not have significantly affected the results.

5.9 Impedance studies

Cylindrical pellet samples were used for the majority of the work describe below. They were typically 10-12mm in diameter and 1-2mm thick. Sample faces were polished using $1\mu\text{m}$ diamond paste to finish. Fritless gold paint (Engelhard A1644) was used as the electrode material. The paint was applied to both faces and fired at 800°C for 2 hrs in air. After firing, the electrode resistance was checked to ensure the gold had sintered and the resistance was below $\sim 0.2\ \Omega$ across the diameter of the sample electrode.

5.9.1 Measurement method 1

Impedance measurements were performed using the 2-probe AC method in a spring loaded jig placed in a horizontal tube furnace. Impedance spectra were measured between 10 MHz and 100 mHz ($10^7 - 10^{-1}\ \text{Hz}$) at 50 points per decade using a Solatron

1260 impedance analyser connected to a Solartron 1296 dielectric interface.

Computer controlled measurements were taken over a range of temperatures using the program SMaRT version 2.8 (Solartron). Samples were heated to the maximum measurement temperature and then allowed to equilibrate for at least 3hrs before the first measurement was recorded. Subsequent measurements were taken at 50° intervals during cooling. There was a 2 hr dwell at each temperature to allow for thermal and chemical equilibration.

5.10 Dilatometric measurements

The measurements of thermal and chemically induced expansion were performed using a vertical alumina dilatometer (Linseis L75V/1250) and a gas system with an yttria-stabilised zirconia (YSZ) oxygen pump at the inlet and an YSZ oxygen sensor at the outlet. The total gas flow rate (~ 50 ml/min) and the oxygen partial pressure in the gas mixtures, continuously supplied in the dilatometer, were fixed by the electrochemical pump and two Bronkhorst mass-flow controllers; the sensor was used for permanent control of the oxygen chemical potential in the gas flow. The dilatometric studies were performed using two regimes: (i) continuous heating (3 K/min) up to 1373 K in air, and (ii) stepwise cooling from 950°C down to 650°C (step 50°, dwells 2-7 h) in a CO-CO₂ mixture ($p_{\text{O}_2} = 4 \times 10^{-21}$ - 3×10^{-13} atm.), after preliminary equilibration at 1100°C. Before measurements were taken, the dilatometer was calibrated for the necessary temperature profile at each gas composition using alumina as a blank material.

5.11 Thermal Analysis

Thermogravimetric analysis was performed in flowing air (50 ml/min) using a Netzsch STA 449C Jupiter simultaneous TG-DTA/DSC instrument. Reduced samples were heated in air to determine oxygen lost during the reduction process.

5.12 Electron Microscopy

5.12.1 Scanning electron microscopy (SEM)

Two instruments were used: A LEO Gemini field emission gun (FEG) SEM with an Oxford Instruments Inca EDS microanalysis system and a Hitachi S3400N conventional SEM with a Bruker EDS X-ray analysis system. Images were recorded electronically in secondary electron (SE) and back-scattered electron (BSE) mode.

To prevent the effects of charging in the electron beam, insulating samples were coated with a thin layer of gold using an Emitech K550 Gold sputter-coater.

5.12.2 Transmission electron microscopy (TEM)

Electron Energy-loss Spectroscopy (EELS) was performed using a monochromated FEI Titan 80/300, equipped with a Gatan Tridiem 865. Data was recorded using the proprietary TIA software (FEI) and analysis was conducted using Digital Micrograph (Gatan).

5.13 Isotopic oxygen exchange

Prior to exchange anneals, samples were subjected to anneals in research grade oxygen (99.996%) of normal isotopic abundance for a period of time approximately 20 times greater than the tracer anneal time (0.5 hrs). This was carried out to ensure that the material was in chemical equilibrium at the desired temperature and oxygen partial pressure; in this study all anneals were carried out at a nominal $p(\text{O}_2)$ of 0.2 atm. Samples were then quenched to room temperature, the research grade oxygen removed, and 97% enriched $^{18}\text{O}_2$ introduced. Once again, the samples were rapidly heated to the anneal temperature, annealed for the required time, and quenched. During both anneals the temperature was monitored by a thermocouple situated close to the sample; a PC recorded the thermocouple reading as a function of time. The duration of the isotope anneal was calculated from the temperature-time profile by means of a computer program, which took into account the periods required to heat up and cool down the specimen.

The ^{18}O penetration profiles were determined on an FEI 200 FIB-SIMS instrument. The machine was operated in depth profile mode, with a normal incidence 30 keV Ga^+ primary ion beam. The crater depth was measured after the SIMS analysis by surface profilometry on a Zygo optical profilometer.

Given the relatively low density of the materials under study, a depth profile technique was employed to examine individual grains and small, dense areas containing clusters of several grains. By milling an area large enough to obtain a good signal-to-noise ratio ($\sim 5 \mu\text{m}^2$), the ^{18}O profile could be determined from the shell into the core of a single grain. This method proved very successful. ^{18}O concentration always returned to the background concentration, showing the estimated annealing times were correct and that the diffusion distance was not too deep.

5.14 Sample Synthesis

5.14.1 Initial work

Initial work was performed to confirm some of the results of previous authors, namely the preparation of stoichiometric La-doped SrTiO_3 and La,Ce-doped SrTiO_3 after Marina [66,67]. It was found that the LST compositions appeared to be single phase when examined using XRD. However, layered defect regions were observed in the TEM (see Figure 5.7) as found in earlier studies [56,57].

Attempts to prepare single phase (La,Ce)-doped SrTiO_3 were unsuccessful because CeO_2 would precipitate, even at very low cerium concentrations. It has been suggested that cerium could substitute on the B-site based on the increase in the perovskite lattice parameter as observed by Marina [67] who prepared material using the following stoichiometry: $\text{La}_{0.35}\text{Sr}_{0.65}\text{Ti}_{1-y}\text{Ce}_y\text{O}_{3\pm\delta}$. However, it was later shown that this was a two-phase composite material consisting of $(\text{Ce,L a})\text{O}_2$ and $(\text{La,Sr})\text{TiO}_{3\pm\delta}$.

5.14.2 Cerium-doped strontium titanate

Reports on cerium-doped strontium titanate are relatively scarce in the literature [111, 112]. There are, however, several citations of Ce-doped BaTiO_3 in the literature [124–

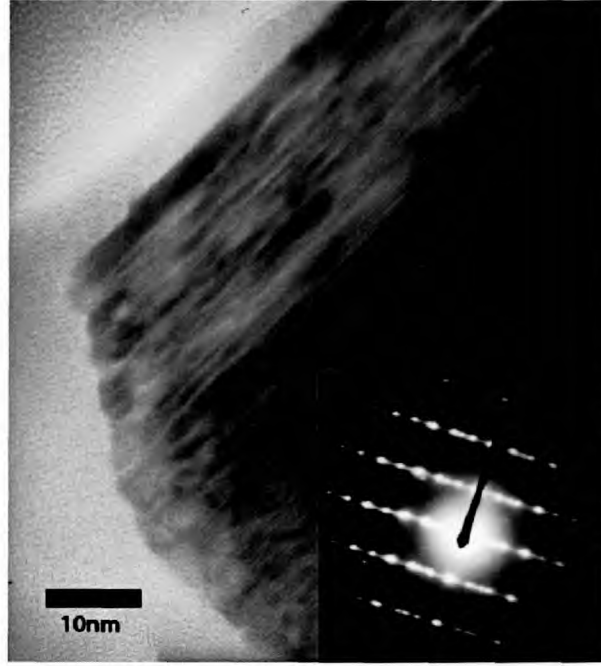


Figure 5.7: A TEM micrograph showing the partially layered phase (striations running SW to NE across grain) found in 10mol% La-doped SrTiO₃. Inset shows the selected area diffraction pattern from the same area. Prominent streaking is indicative of a partially disordered layered structure.

128]. Comparisons of ionic radii for possible rare-earth dopants show that La(III), ($r_{La} = 1.36\text{\AA}$), a well known dopant in strontium titanate, is very similar in size to Ce(III) ($r_{Ce} = 1.34\text{\AA}$). Ce(IV), ($r_{Ce} = 1.14\text{\AA}$) while smaller than Ce(III), could also plausibly substitute onto the A-site. Ce(IV) may well substitute on the B-site but it is probably a little too large to fit comfortably ($r_{Ce} = 0.87\text{\AA} - r_{Ti} = 0.605\text{\AA}$).

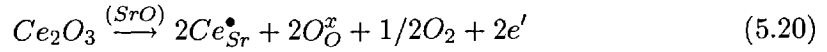
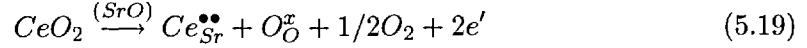
Three compositional lines were examined in detail. Figure 5.8 shows the hypothetical phase field for the SrO-CeO₂-TiO₂ system. Each composition corresponds to a particular donor compensation mechanism.

$$Sr_{1-x}Ce_xTiO_{3\pm\delta} \quad (5.16)$$

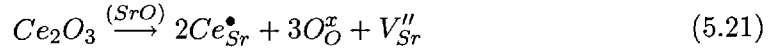
$$Sr_{1-1.5x}Ce_xTiO_{3\pm\delta} \quad (5.17)$$

$$Sr_{1-2x}Ce_xTiO_{3\pm\delta} \quad (5.18)$$

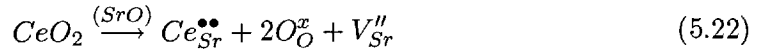
Stoichiometric composition, analogous to the La-doped compounds prepared by Marina [66] ($\text{Sr}_{1-x}\text{Ce}_x\text{TiO}_{3\pm\delta}$), were prepared; these assumed electronic compensation. For Ce(IV) and Ce(III)-doped compounds, the incorporation reaction whereby excess oxygen is expelled (i.e. electronic compensation) would be written as follows:



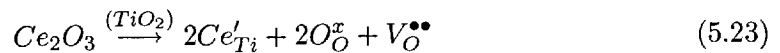
The A-site deficient composition ($\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_{3\pm\delta}$) assumed that V_{Sr}'' is the preferred compensation defect and that Ce^{3+} resides on the A-site. This is analogous to the La-doped compositions prepared by Slater [65]:



An alternative A-site deficient composition, ($\text{Sr}_{1-2x}\text{Ce}_x\text{TiO}_{3\pm\delta}$), was also prepared; additional V_{Sr}'' were 'weighed in', assuming cerium was in the +4 oxidation state on the A-site.



Samples assuming B-site substitution were not prepared. However, should cerium(III) substitute for Ti, then it would act as an acceptor and the incorporation reaction would be written:



And of course Ce(IV) on the B-site would result in isovalent substitution:



These are hypothetical incorporation reactions and it is hoped that experimental evidence presented in Chapters 6 and 7 will allow us to choose between some of these models.

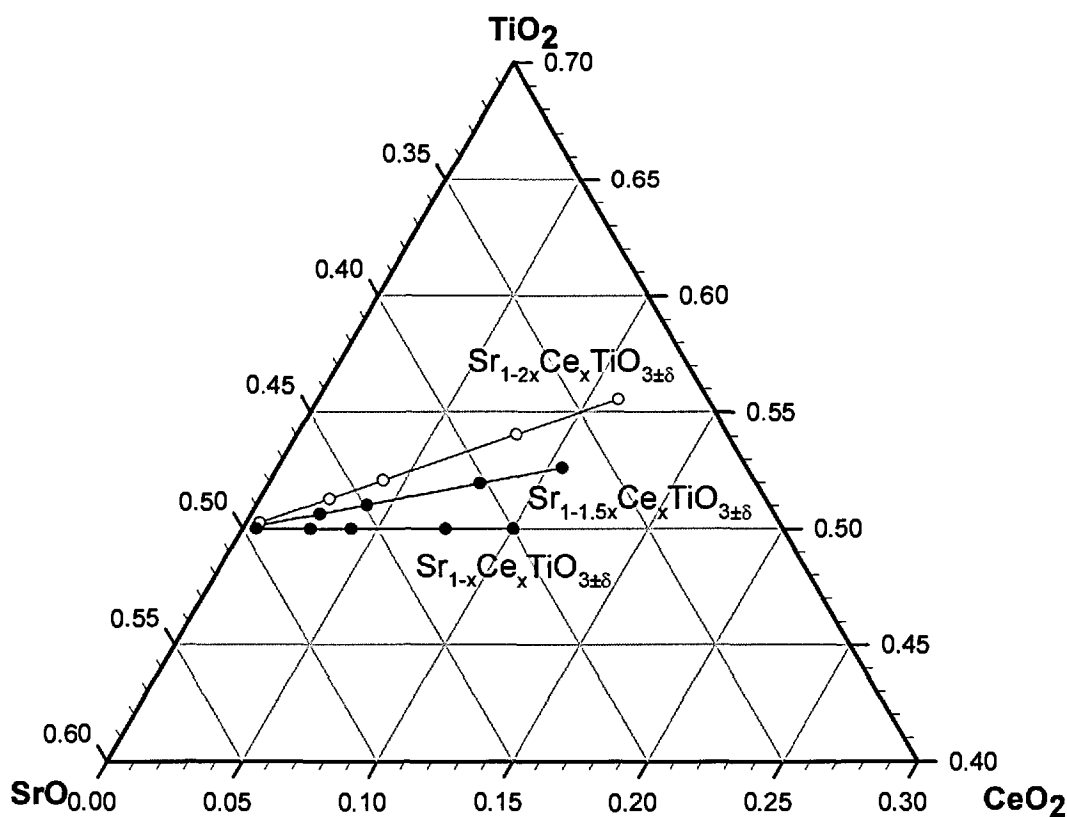


Figure 5.8: Partial ternary phase field for three compositions of interest.

Given that there are three main compositional series, each with different values of x , it can become confusing as to which composition is being referred to. To avoid confusion, from this point onward, graphs and figures will be colour coded to identify each compositional tie. Colour coding will be as seen in Fig. 5.8. Samples with the stoichiometric composition (Eq. 5.16) will be marked red, and the two A-site deficient compositions in Eq. 5.17 and Eq. 5.18 will be marked blue and yellow respectively.

Previous workers had prepared similar compounds at temperatures of 1300-1400°C with

intermediate grinding steps. As mentioned below the concern with this technique was controlling the incorporation of impurities. When initially preparing Ce-doped SrTiO_3 loose reagent powders (after weighing and mixing) were placed directly in alumina crucibles. Potential reaction with alumina was of concern and so, to minimise the contact with the crucible, the reagents were pressed into large cylindrical compacts and placed on sacrificial powder.

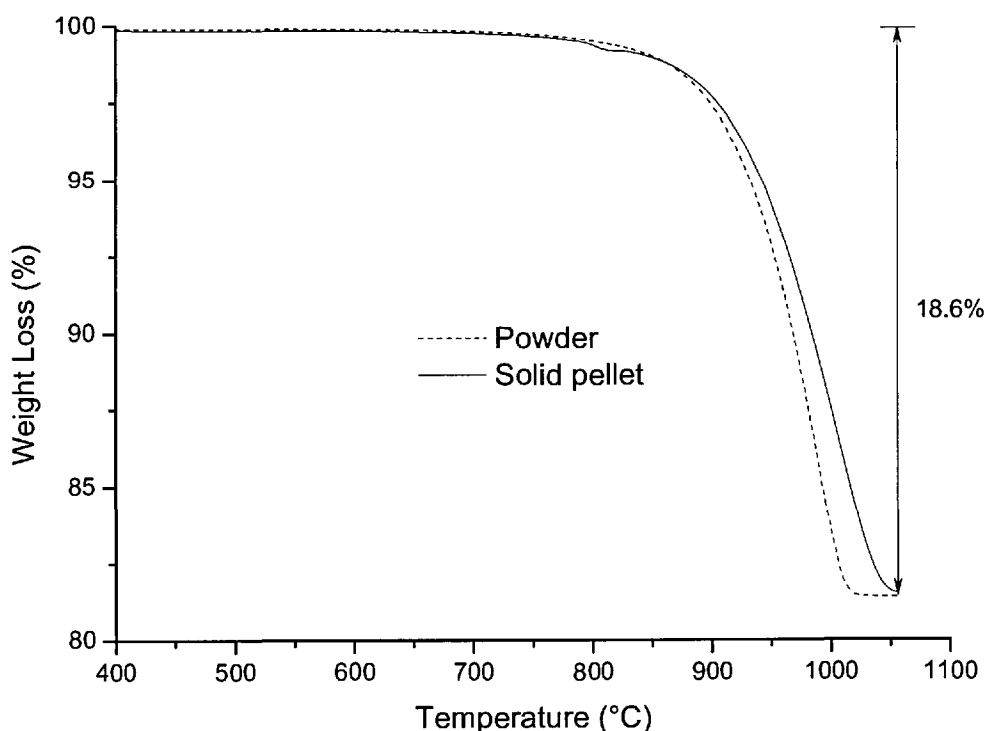


Figure 5.9: Comparison of the reaction of loose, powdered reagents and powder compact. The compacted sample appears to form at higher temperature than the loose powder. There was no apparent difference in the weight-loss between each stoichiometry.

Synthesis from powder compacts was highly successful and appeared to form more homogenous initial powders. However, it is clear from the thermogravimetric data shown in figure 5.9 that the compacted material requires a slightly higher temperature to achieve a similar weight loss. Higher temperatures required for the compact relate to slower outward diffusion of CO_2 , as discussed by Arvanitidis [129].

Unfortunately, thermogravimetric data only shows the weight loss due to the decomposition of SrCO_3 . We were not able to attribute to the formation of any individual phases using differential thermal analysis (DTA) data; these were generally masked

by the signals from the decomposition of SrCO_3 . Measurement of the cubic lattice parameter after extended annealing times, however, would suggest the reaction is complete after 5 hrs. The data in figure 5.10 shows the lattice constant unchanged after annealing for up to 48 hrs at 1380° .

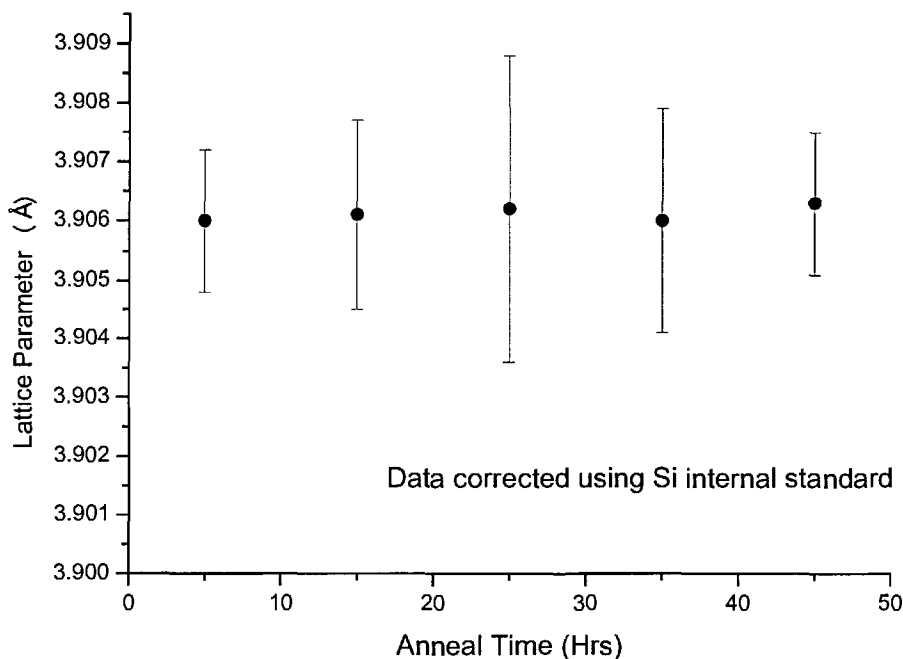


Figure 5.10: Dependence of lattice parameter on the annealing time at 1380°C for a typical A-site deficient composition ($\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$), showing very little change over the first 40hrs.

5.14.3 Phase formation

Samples with a stoichiometric composition ($\text{Sr}_{1-x}\text{Ce}_x\text{TiO}_{3\pm\delta}$) showed very low cerium solubility in air. It is estimated that the solubility of CeO_2 in SrTiO_3 is approximately 3-4 mol%. Under reducing conditions this was found to increase to around 8 mol%. Increasing x resulted in proportionately more CeO_2 precipitating. Figure 5.11 shows the ratio of peak areas for the CeO_2 (111) peak and the SrTiO_3 (110) peak.

It is clear from figure 5.11 that the solubility limit for CeO_2 is around 4 mol%. It shows that the amount of Ce, as indicated by the peak ratio, is not increasing linearly. This may indicate the formation of another Ce-containing phase at higher Ce concentrations. There is no evidence of new phases from examination of the XRD pattern of the $x=0.12$ composition. However, it is most likely due to absorption effects well known in phase

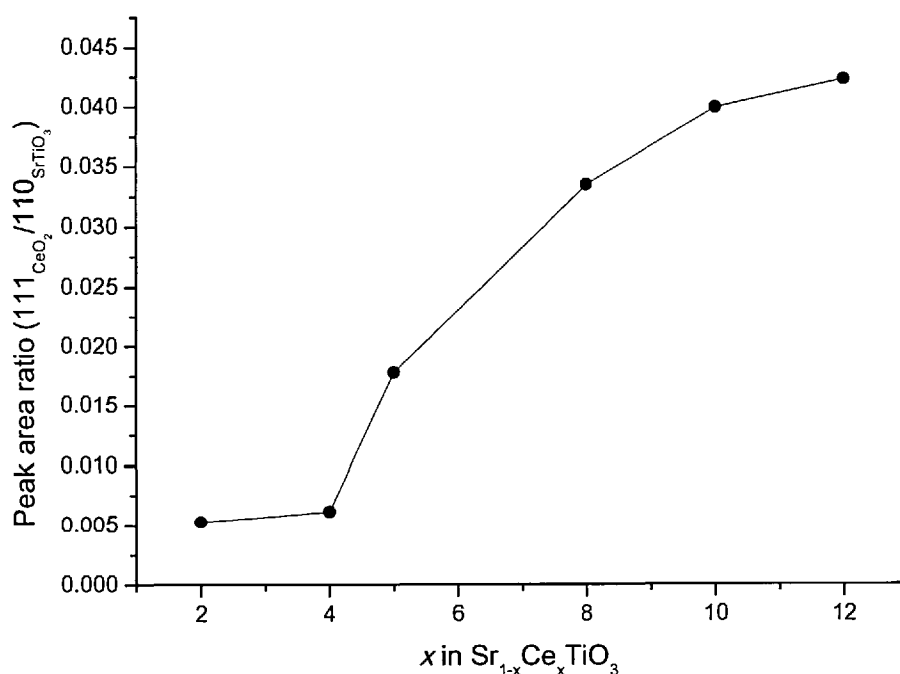


Figure 5.11: Ratio of strongest reflections of CeO_2 and SrTiO_3 , showing increasing CeO_2 content in the 'stoichiometric' compositions.

mixtures that lead to a non-linear relationship between peak intensity and composition [116].

Samples with the A-site deficient composition ($\text{Sr}_{1.5-x}\text{Ce}_x\text{TiO}_{3\pm\delta}$) were found to be single phase up to $x=0.15$. At higher values of x , cerium begins to precipitate. An alternative A-site deficient composition was also prepared ($\text{Sr}_{2-x}\text{Ce}_x\text{TiO}_{3\pm\delta}$). This assumed the incorporation of Ce on the A-site as Ce^{4+} , with the formation of two moles of strontium vacancies (V''_{Sr}). This composition was single phase up to $x = 0.12$, beyond which rutile was observed in XRD pattern.

5.14.4 Sintering and densification

It was very difficult to obtain high density fired ceramic from samples prepared by solid state techniques. This was particularly true for samples with the stoichiometric composition. High energy milling in a PBM significantly improved the densification of these materials. Due to time constraints no systematic evaluation of the milling parameters was possible - but it was found that 24 hrs in the PBM at 250 rpm gave satisfactory results, with an improvement from around 85% to 95+% of the theoretical

density in the most difficult materials.

To obtain dense, polycrystalline samples for further measurements, milled powder was mixed with 1% (by weight of powder) Polyvinyl Butyral (Aldrich) solution in a mortar and pestle to ensure the particles had a good coating of binder. The paste was dried at 70°C. After drying, this material was pressed uniaxially at 600-800 kgcm⁻² into cylindrical pellets or bar shaped specimens and fired in air for five hours at 1470°C. Dense A-site deficient samples were significantly easier to prepare.

High energy milling may have increased the concentration of Zr in the samples (see section 5.14.5 below) but this was not thought to have a significant impact on the properties of these materials.

5.14.5 Elemental analysis

Bulk stoichiometry

Elemental analysis, using energy dispersive spectroscopy (EDS), and grain size measurement was made across the composition range $0.005 < x < 0.15$ for A-site deficient samples prepared in air (details in Table 5.3). The first thing to note is that the intended and actual Ce concentrations are very close, although it appears that some of the samples may have been mixed up, namely, the 5 and 8 mol% samples. It would appear from these results, however, that there was excess strontium in all of the compositions. It is well documented that the solubility of SrO and TiO₂ is very low in SrTiO₃ [130]. The kind of Sr excess measured in these samples would not be soluble. There is no evidence of a Sr-rich second phase in the X-Ray diffraction patterns or in electron micrographs. This suggests there may have been a problem with the Sr quantification from the electron microscope.

Included in this table are the grain size measurements for each sample. While no direct dependence on cerium concentration was observed, it does appear that samples with less Ce had a slightly larger grain size; although this could be due to the increased A/B ratio observed in these samples.

Element	(Expected Ce composition)			Actual composition		
	(0.005)	(0.01)	(0.05)	(0.05)	(0.08)	(0.15)
Ti	1.00	1.00	1.00	1.00	1.00	1.00
Sr	1.09	1.08	1.01	0.96	0.99	0.84
Ce	0.006	0.02	0.071	0.078	0.051	0.15
Sr/Ti						
Expected	0.991	0.971	0.894	0.883	0.924	0.775
Actual	1.091	1.079	1.009	0.955	0.989	0.840
Grain size	7.06	2.16	3.28	3.95	5.12	4.70
(μm)	± 0.74	± 0.46	± 0.33	± 0.45	± 0.74	± 0.62

Table 5.3: Results of EDS analysis over a range of $\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_{3\pm\delta}$ compositions, showing the expected and actual compositions of the samples. All of the data was normalised to $\text{Ti} = 1$ to show data as ABO_3 stoichiometry. Precise calibration is usually required for quantification of light elements. For this the oxygen values have been omitted.

Trace impurities

One of the reasons for investigation of lower synthesis temperatures was the concern over reaction with alumina. Literature concerning the reaction of strontium titanate with alumina is limited. The deleterious reaction between barium titanate and alumina is well documented [131], however.

Quantification of trace elements was of key importance in establishing the role that these elements played on sintering and densification, and the potential effects on the defect chemistry and electrical properties. Titanate-based materials are quite difficult to analyse using traditional wet techniques because they are only slightly soluble, even in very strong acids. X-Ray Florescence (XRF) was identified as the most practical technique for determining the trace element composition in these materials. The trace element composition of some selected samples is shown in table 5.4.

Element	SrTiO ₃	Sample 1	Sample 2
		(p.p.m)	
Al	997	799	712
Ca	886	830	810
Fe	252	211	219
Zr	0.0	1.40 wt%	1.56 wt%

Table 5.4: Trace analysis of commercially available SrTiO_3 (Sigma-Aldrich) and two samples prepared using the solid state technique set out in section 5.1.

Zirconia impurities are due to the relatively large amount of Zr in the TiO_2 starting material (129 p.p.m.); the additional zirconia was probably introduced during the planetary ball milling steps after synthesis. Zirconia impurities would not be expected to have a significant effect on the structure or electrical properties, as Zr should isovalently substitute for titanium. The other main impurities (Al, Ca and Fe) are all roughly the same as the commercially available SrTiO_3 . This suggests that very few additional impurities were introduced during synthesis.

5.15 Discussion and conclusions

5.15.1 Stoichiometric composition

For preparation in air at 1200°C-1400°C stoichiometric compositions ($\text{Sr}_{1-x}\text{Ce}_x\text{TiO}_{3\pm\delta}$) show that cerium only shows limited solubility, up to about 4 mol%, and any additional Ce precipitates as a second phase (CeO_2). It is useful to consider the CaTiO_3 - SrTiO_3 system since Ca(II) shares the same ionic radius as Ce^{3+} and there is complete solubility across the CaTiO_3 - SrTiO_3 phase diagram. Therefore, the reason for the low solubility of Ce in SrTiO_3 can not be due to geometric factors alone. Charge compensation would appear to be the overriding factor affecting the cerium solubility in this material. As other authors have found, cation vacancies are the predominant charge compensation mechanism that operates under oxidising conditions [47, 49, 55]. Therefore, charge compensation by reduction of Ti^{4+} to Ti^{3+} is unlikely under high oxygen partial pressure in these materials.

Under reducing conditions, the mechanism is known to shift toward electronic compensation and reduction of Ti^{4+} to Ti^{3+} is more likely. An increase in the Ce solubility is observed after a very aggressive reduction treatment (1450°C under 10% H_2/Ar). Figure 5.12 shows the effect of a reducing treatment on an $x = 0.10$ stoichiometric sample. Although not completely soluble CeO_2 is significantly enhanced under reducing conditions, which suggests that the solubility limit under reducing conditions is around 8mol%.

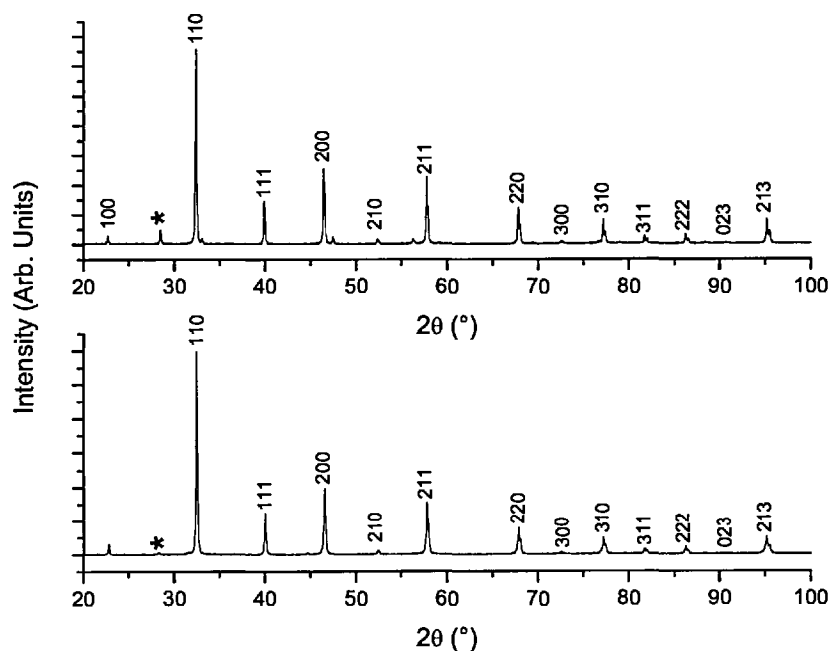


Figure 5.12: Indexed XRD pattern of oxidised (Top) and reduced (Bottom) stoichiometric SCT, showing the increased solubility of Ce under reducing conditions (the strongest reflection from CeO_2 has been marked with an asterisk).

5.15.2 A-site deficient compositions

This composition series was shown to be single phase up to $x=0.15$ which suggests two things. Firstly, that cerium was indeed substituting on the A-site, probably as Ce(III) , therefore acting as a donor; and secondly, that the compensation of the donor charge, in air, was by the formation or 'weighing-in' of strontium vacancies in agreement with the defect model for donor-doped SrTiO_3 .

Ubic *et al.* [132] have investigated the structural properties of the A-site deficient composition, $\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_3$, and obtained very similar results to this research; that is, that the donor charge is compensated for by the formation of A-site cation vacancies. They found that single phase ranges up to $x = 0.40$, which is further than the investigated range in our research. XRD evidence suggested that these compounds were simple, cubic perovskites. However, powder neutron diffraction and electron diffraction showed several reflections that could not be indexed according to the $Pm\bar{3}m$ space group; instead, they found the compound was rhombohedral ($\text{SG} = R\bar{3}c$ #167). As the cerium content increased they found increasing octahedral tilt until a phase-change

occurred at around $x = 0.40$. There was no comment on the variation of the lattice parameter with composition.

5.15.3 Measured elemental compositions and impurities

Elemental analysis using EDS (shown in Table 5.3) shows that when the results are normalised to titanium, i.e. to form ABO_3 stoichiometry, there is additional strontium. The reasons for this are unclear. Great care was taken when preparing samples to ensure the starting materials were dry and free from volatile impurities and that each component was accurately and precisely weighted. Nevertheless there appears to be excess strontium in the analysed samples. Further analysis is required to determine if this is the true stoichiometry.

A more suitable technique, particularly at low Ce-contents, may have been to use a liquid mix technique, such as the Pechini method, or a combustion synthesis route. This technique allows accurately assayed solutions to be mixed which in turn allows for the precise control of cation concentrations.

5.15.4 Conclusions

Successful synthesis of Ce-doped SrTiO_3 has been achieved using standard solid-state techniques. Only a relatively small portion of the Sr-rich end of the phase diagram was investigated. Three stoichiometries were tested, shown on the pseudo-ternary phase diagram in Fig. 5.8 on page 78. From the analysis of the phase formation, it was concluded that cation vacancies were the most likely compensation mechanism under oxidising conditions.

Chapter 6

Structural characteristics of Ce-doped SrTiO_3

6.1 Phase relationships

6.1.1 A/B ratio = 1 (Stoichiometric)

Stoichiometric compositions (i.e. $\text{Sr}_{1-x}\text{Ce}_x\text{TiO}_3$) show very low cerium solubility. This is estimated to be 3-4 mol% by XRD but possibly lower due to the detection limits of XRD. For compositions at 5 mol% ($x=0.05$) a peak due to CeO_2 could unambiguously be observed in the XRD pattern, as shown in Figure 6.1 (red) in which the strongest CeO_2 reflection is seen at $2\theta \sim 28^\circ$. Figure 6.2a shows an electron micrograph of a 5 mol% stoichiometric sample. Ceria is clearly observed as the bright white phase in the Back-scattered electron (BSE) image.

6.1.2 A/B ratio <1 (A-site deficient)

When a strontium deficiency was introduced, forming the stoichiometry $\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_{3\pm\delta}$, the cerium solubility was increased, up to $\sim 15\text{mol}\%$ in this study. This was not a surprising result since the defect model (introduced in Section 3.2) for donor-doped SrTiO_3 suggests that the preferred compensating defect under oxidising conditions is strontium

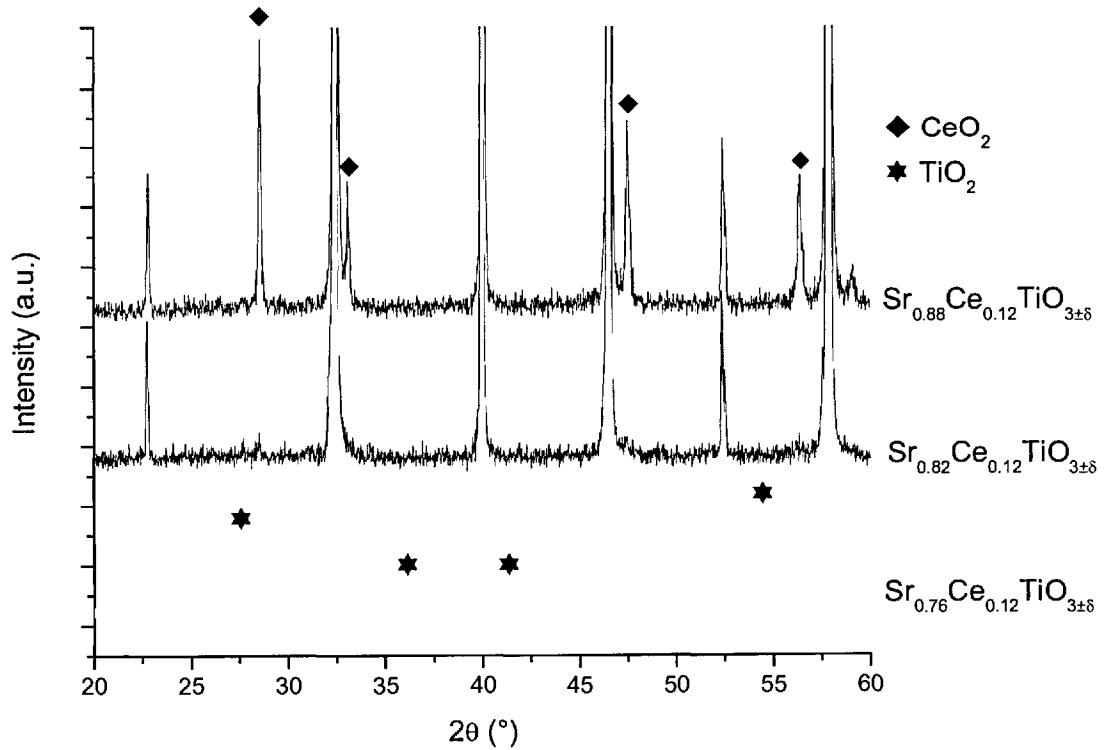


Figure 6.1: Typical XRD patterns, truncated to show impurity peaks, measured at room temperature for each of the three stoichiometries. Each pattern is of a nominally $x=0.12$ sample. In the stoichiometric sample (red) ceria is clearly visible though-out the pattern. The A-site deficient sample, $\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_{3\pm\delta}$ (Blue), is single phase, while the sample with the highest Sr-deficiency, $\text{Sr}_{1-2x}\text{Ce}_x\text{TiO}_{3\pm\delta}$ (Yellow), has a significant amount of rutile (TiO_2) second phase.

vacancies. Figure 6.1 (blue) shows a typical XRD pattern for the $x=0.15$ sample. No other phases other than cubic perovskite phase was observed. Figure 6.2b shows the corresponding electron micrograph (thermally etched to show grain boundaries) where no second phase was observed by SEM.

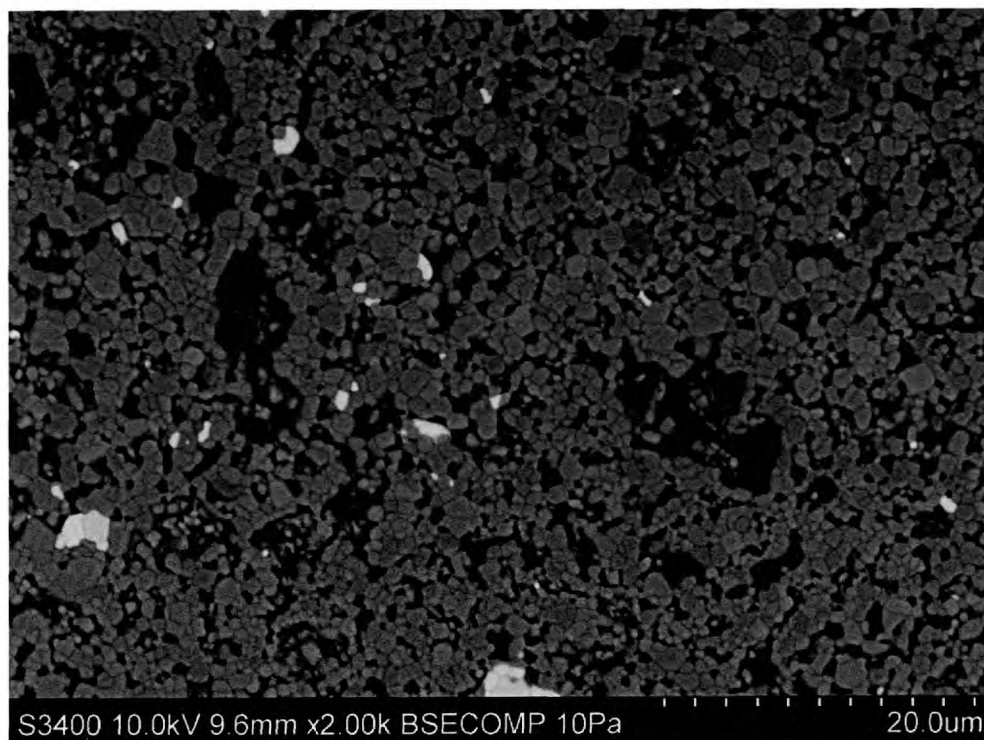
Finally, the third composition investigated, $Sr_{1-2x}Ce_xTiO_3$, which was also an A-site deficient material but with twice the number of strontium vacancies 'weighed in'. This stoichiometry assumed Ce(IV) substituted on the A-site. These samples formed a single phase, by XRD (see Figure 6.1 yellow), up to $\sim 8\text{mol\%}$ Ce; beyond this TiO₂ (rutile) was formed.

6.2 Tolerance factor

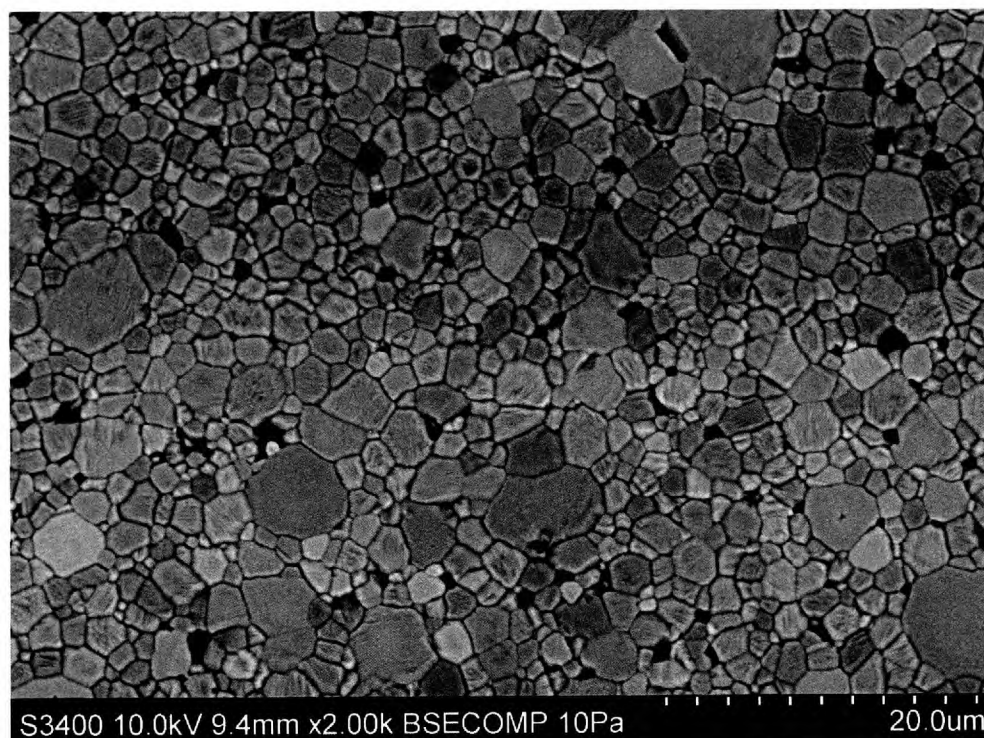
The tolerance factor was used to identify potentially compatible dopants for the study of these materials. We were primarily interested in the doping of the A-site and so elements with an ionic radii close to that of Sr^{2+} were of interest. Table 6.1 shows the ionic radii of elements of interest. The tolerance factor can be calculated using the following equation:

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)} \quad (6.1)$$

SrTiO₃ with $R_A = R_{Sr} = 1.44\text{\AA}$, $R_B = R_{Ti} = 0.605\text{\AA}$ and $R_O = 1.38\text{\AA}$ has a tolerance factor of 1.00; it is an ideal perovskite. For the stoichiometric composition, $Sr_{1-x}Ce_xTiO_3$, at the solubility limit ($x = 0.04$) and assuming that Ce(III) is present on the A-site, the tolerance factor would still be 1.00 (within significant figures). While there have been several examples in the literature of correlation between tolerance factors and structural and electrical properties, the main criticism of the tolerance factor is that it cannot predict subtle changes in structure. CaTiO₃, for example (where $R_{Ca} = 1.34\text{\AA}$ which, incidentally, is also the radii of the Ce(III) ion) has a tolerance factor of 0.97. At room temperature CaTiO₃ has an orthorhombic structure ($Pnma$). So even minor deviations from $t = 1$ can result in significant crystallographic variation.



(a) Stoichiometric sample with nominal composition $\text{Sr}_{0.95}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$.



(b) A-site deficient sample with nominal composition $\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$.

Figure 6.2: Electron micrograph showing typical microstructures of a stoichiometric sample and an A-site deficient sample, (a) and (b) respectively. Ceria is clearly visible as a bright white phase in (a). For the single phase material, (b), cerium was detected by EDS in the bulk of both specimens with no segregation detectable at the grain boundaries.

Table 6.1: Ionic radii of potentially compatible A-site dopants in SrTiO₃. Radii data taken from reference [133].

Element	Ionic Radii ($\text{\AA}$)	
	A-site (CN12)	B-site (CN6)
Sr ²⁺	1.44	1.18
La ³⁺	1.36	1.03
Ca ²⁺	1.34	1.00
Ce ³⁺	1.34	1.01
Ce ⁴⁺	1.14	0.87
Pr ^{3+†}	1.37	0.99
Y ^{3+†}	1.25	0.90
Ti ^{4+†}	1.07	0.61

[†] 12 coordinate values extrapolated from data in reference [133].

Table 6.2: Calculated tolerance factor (t) for selected compositions.

Composition (x)	Stoichiometric	A-site deficient	
		Ce(III) ²	Ce(IV) ³
0.04	1.00	0.99	0.98
0.08	-	0.98	0.96
0.10	-	0.97	0.94
0.15	-	0.96	0.92

¹ Sr_{1-x}Ce_xTiO₃

² Sr_{1- $\frac{3x}{2}$} Ce_xTiO₃

³ Sr_{1-2x}Ce_xTiO₃

Table 6.2 shows the calculated tolerance factor for several compositions of each of the three main compositional variants. There are no values for the stoichiometric composition above $x = 0.04$ because above this the solubility limit is reached.

To calculate the tolerance factor values in table 6.2 the weighted radius for the A-site had to be calculated. It was assumed that Sr-vacancies (V_{Sr}'') had a radius of zero. This gave the same results as those obtained by Ubic [132]. Although this method gives a result, the physical reality of a Sr-vacancy with a radius of zero is hard to imagine for a number of reasons. Firstly, from a geometric stand point, the oxygen surrounding a vacancy could only approach each other a certain amount before touching (assuming a hard sphere model). In addition to this it would mean negatively charged oxygen atoms would have to approach each other, which is electrostatically unlikely. So the likelihood of a zero radius vacancy is low considering geometric and electrostatic factors. Unfortunately, it is not that easy to estimate the size of the vacancy either [134]. Therefore, the approximations of the tolerance factor for the A-site deficient compositions are probably too low, but at present, we can not make any better estimations.

The tolerance factor can be used as a useful guide to the potential crystal structure of a perovskite-based material but should be used cautiously as values used for ionic radii are based on calculation and a degree of extrapolation and therefore should not be taken as absolute. They should be used in combination with other data to establish the true structural parameters.

6.3 Predicted lattice parameter

Several attempts have been made to empirically predict the lattice parameter of perovskite compounds based on the ionic radii of the constituent ions. Similar approaches have worked reasonably well in fluorite materials [135, 136]. The accuracy of predictions by the perovskite models vary considerably. This, presumably, is partly because the authors are using one model to try and cover compounds composed from elements across the entire periodic table. This method relies on the accuracy on the commonly used radii (derived by Shannon [133]) which were calculated or extrapolated from a

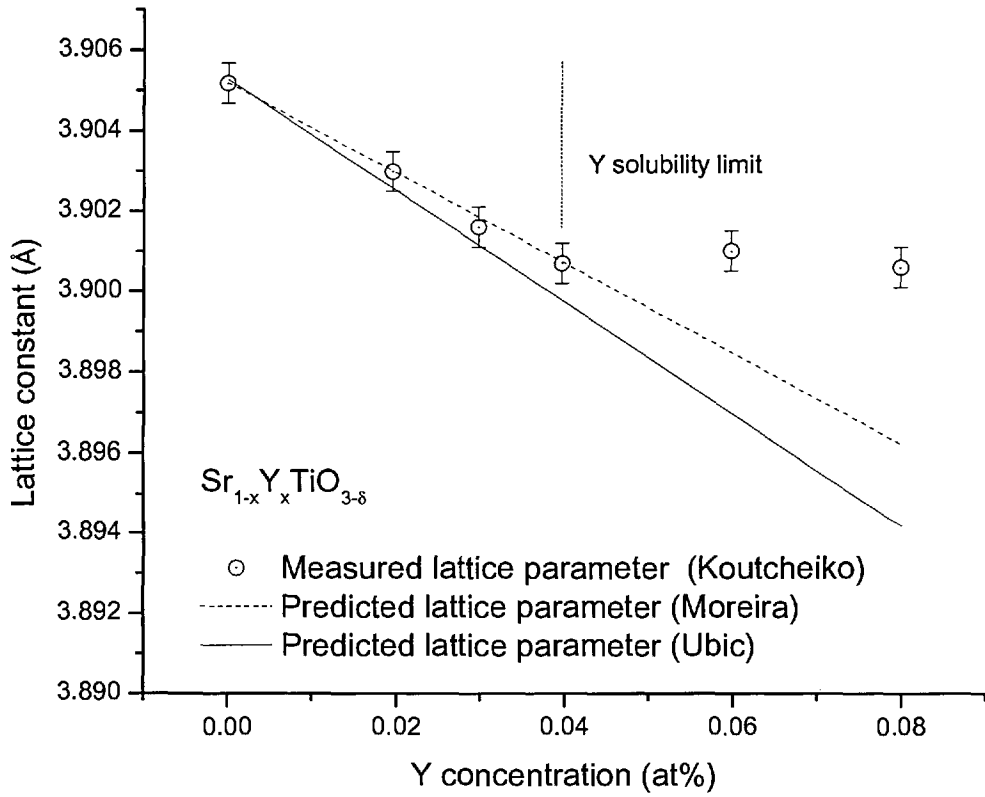
host of different compounds.

There are three published studies on lattice parameter predictions in perovskites. Each study describes around 130 different perovskite compounds. The three predictions for strontium titanate from these studies are: 3.932Å [137], 3.929Å [138] and 3.924Å [139]. These are significantly different from the established value of 3.9051Å. There is a variation of over 0.5%.

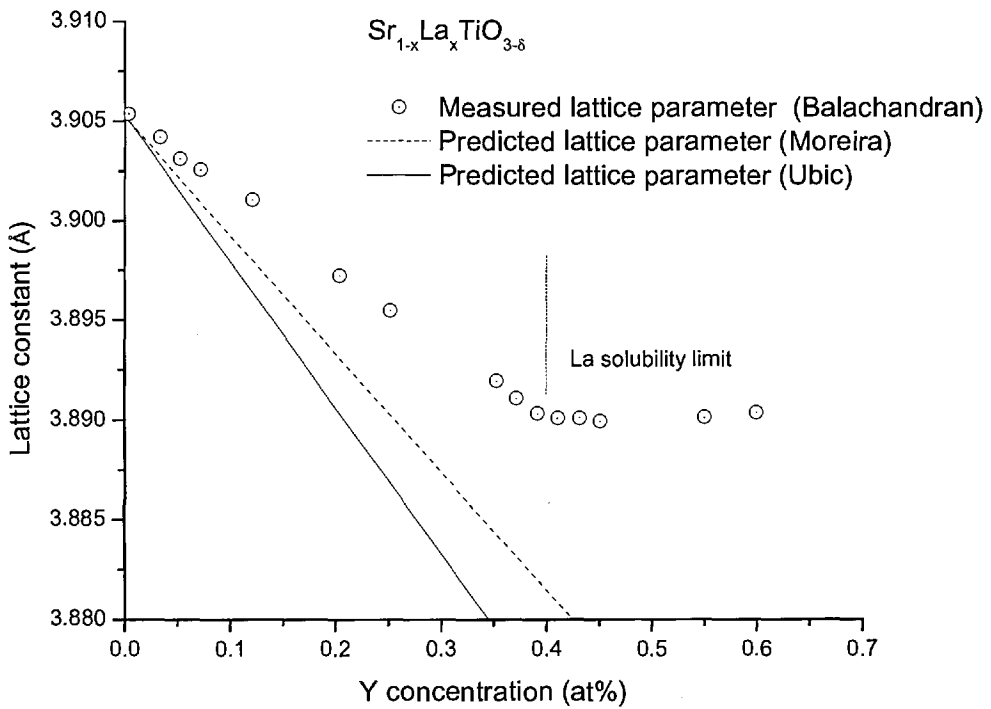
To establish the effect of adding particular dopants to SrTiO₃, adjustments were made to the models of Moreira [138] and Ubic [139] so that the starting value of un-doped SrTiO₃ was as close as possible to 3.9051Å. This was done by slightly altering the oxygen radius used in our calculations from 1.38Å to 1.3985Å, which leaves the A/B cation radius ratio the same. Cation radii were taken as the six coordinate values as this had been shown to give more accurate results in previous studies.

To test the effectiveness of lattice parameter prediction for a compositional series, two experimental data sets from the literature were compared with the predicted lattice parameter calculated from both models. Figure 6.3 shows the experimental data for Y-doped and La-doped SrTiO₃, along with the predictions from the Moreira and Ubic models. In the Y-doped samples, (Fig. 6.3a), both models fit well, given the relatively large error in the predicted values. For La-doped SrTiO₃, neither model predicts the lattice parameter exactly but we know that the phase formation is not simple in the La-doped series (i.e. formation of layered defect etc.) and so this may be partly to blame.

Application of this model to the Ce-doped system shows (see Fig. 6.3c) that the experimentally observed and predicted values differ. The experimental values decrease with increasing Ce concentration but not as quickly as would be expected if all the Ce(III) was substituting on the A-site. Figure 6.3d shows three different scenarios. The first (labelled "1" in Fig.6.3d) assumes that all of the cerium substitutes as Ce(IV) on the B-site. Clearly there would be a significant increase in the lattice parameter if this occurred, which was not observed experimentally. In the second scenario, all of the cerium substitutes as Ce(III) on the A-site, which appears more likely but is

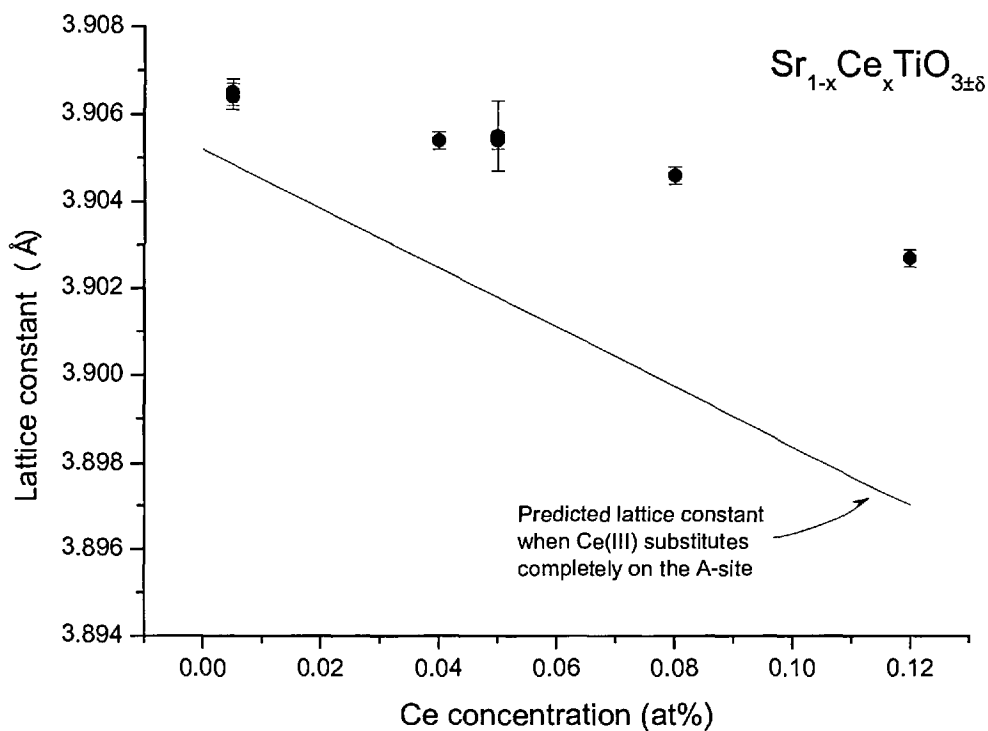


(a)

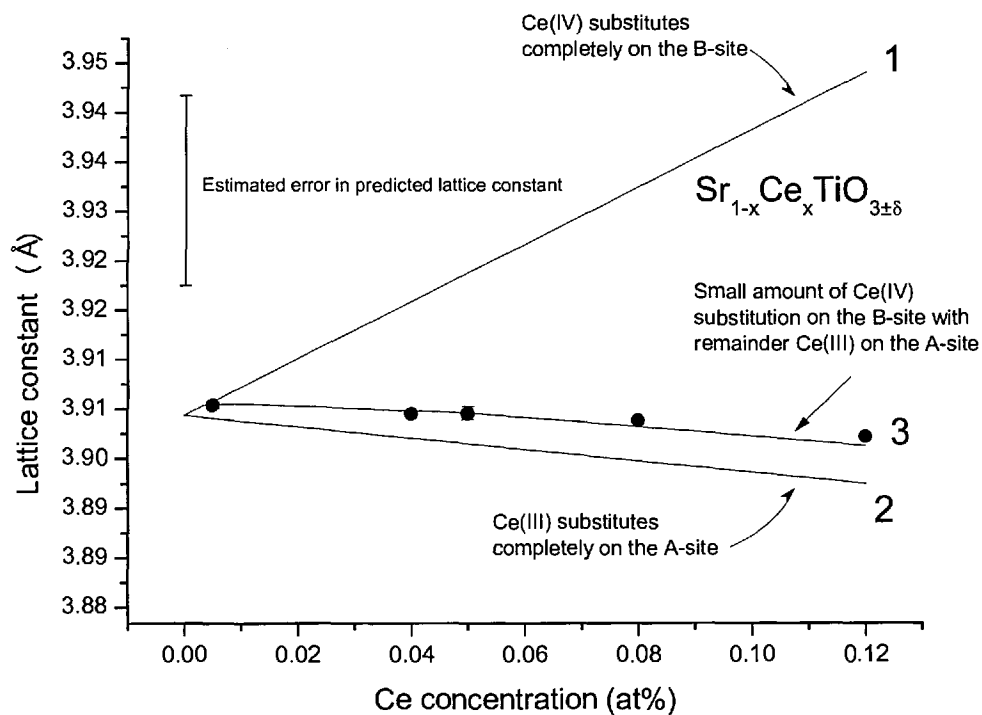


(b)

Figure 6.3: Predicted lattice parameters calculated using the empirical method devised by Jiang [137] and improved by Moreira [138] applied to data from the literature for Y-doped SrTiO₃ [74] and La-doped SrTiO₃ [140]. There is a good fit to the data in (a) using both sets of equations.



(c)



(d)

Figure 6.3: Cont'd. The same method was applied to the stoichiometric Ce-doped SrTiO_3 composition and the results are shown in (c) and (d). The details of the mixed substitution on both the A and B-sites can be found in Table 6.3.

not described very well by the model. In the third scenario there is a small amount of Ce(IV) which substitutes on the B-site, while the majority substitutes on the A-site as Ce(III). By adjusting the amount of mixed occupancy it was possible to fit the predicted lattice parameters and the experimental data. The exact compositions are shown in Table 6.3. However, given the uncertainties in the predicted values this result should be taken cautiously.

Total [Ce]	Mixed stoichiometry	$a_0^{actual.}$	$a_0^{calc.}$
0	$SrTiO_3$	3.9052	3.9051
0.005	$Sr_{0.999}Ce_{0.001}Ti_{0.994}Ce_{0.004}O_{3\pm\delta}$	3.9064	3.9065
0.04	$Sr_{0.968}Ce_{0.032}Ti_{0.992}Ce_{0.008}O_{3\pm\delta}$	3.9054	3.9058
0.05	$Sr_{0.959}Ce_{0.041}Ti_{0.991}Ce_{0.008}O_{3\pm\delta}$	3.9054	3.9055
0.08	$Sr_{0.93}Ce_{0.07}Ti_{0.99}Ce_{0.01}O_{3\pm\delta}$	3.9046	3.9039
0.12	$Sr_{0.891}Ce_{0.109}Ti_{0.989}Ce_{0.011}O_{3\pm\delta}$	3.9027	3.9016

Table 6.3: Hypothetical mixed A and B-site cerium-doped SrTiO₃ showing the predicted lattice parameters with mixed A-B site occupancy and experimental lattice parameters.

Calculations were made for the A-site deficient compositions but, as with the tolerance factor calculations, it was necessary to estimate an effective A-site radius by taking a weighted average of the Sr, Ce and V''_{Sr} sites (the vacancies had zero radius). These calculations, therefore, tend to seriously underestimate the lattice parameter due to zero-radius cation vacancies, as discussed above.

6.4 Experimental lattice parameter

The XRD pattern can be easily indexed as cubic ($Pm\bar{3}m$) which accounts for all of the observed reflections. Increasing the cerium concentration is found to cause a decrease in the size of the unit cell in each stoichiometry; see Figure 6.4.

For the stoichiometric composition, there is a decrease in the lattice parameter shown in Fig.6.4. At 3-4 mol% a second phase was observed in the X-ray diffraction patterns which was identified as CeO₂. This could be considered as the cerium solubility limit in air. If the solubility limit had been reached, however, then we would expect the lattice parameter to plateau as the cerium concentration increased (as is seen in the literature for similar compounds; see Figures 6.3a and 6.3b). However, we observe a continued

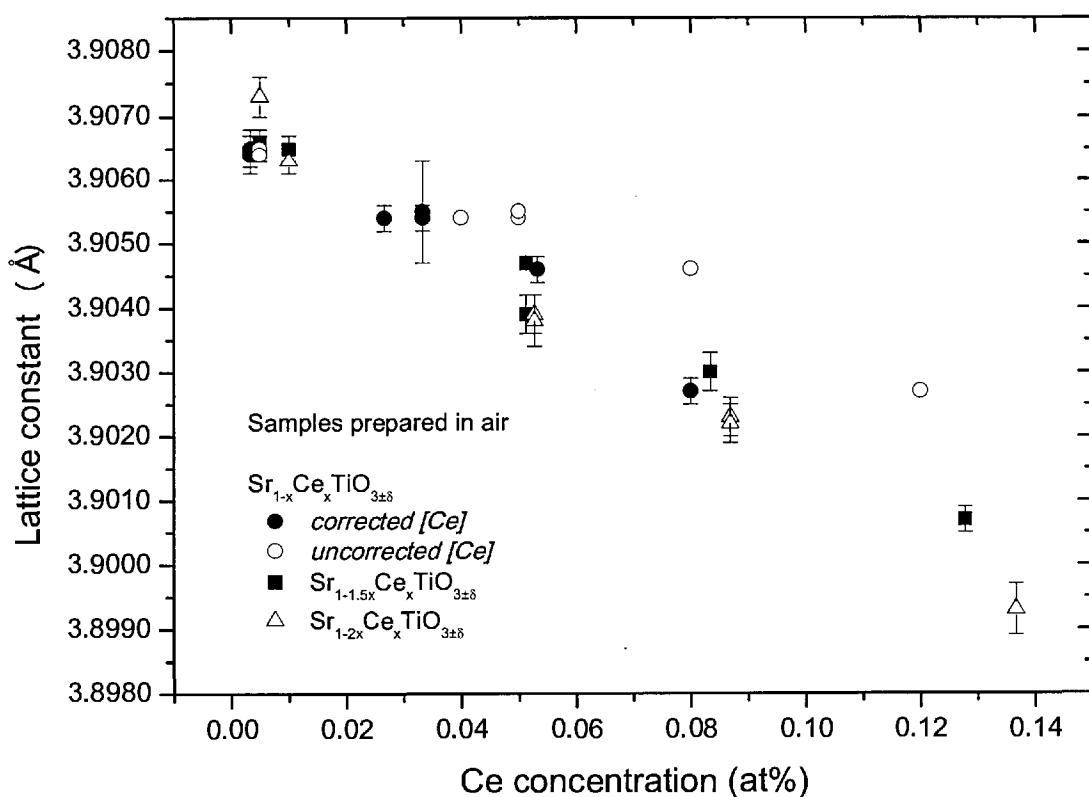


Figure 6.4: Variation of lattice parameter with Ce concentration for different stoichiometries. All samples were refined using the $Pm\bar{3}m$ space group. A correction was applied to the data for the stoichiometric composition, which is explained in the text. This Figure shows that the samples are all probably forming an A-site deficient stoichiometry, $\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_{3\pm\delta}$. As per the established defect model, the only difference is the amount of second phase in each sample.

decrease in the lattice parameter well after ceria reflections appear in the diffraction pattern. The reasons for this are discussed below (see Discussion). It was not possible to precisely calculate the lattice parameter for the ceria second-phase because the peaks were too weak; so we were unsure if there was any significant Sr-doping of the ceria.

For compositions with A-site vacancies, the lattice parameter varied smoothly with the Ce concentration. Figure 6.4 shows the results for the Sr_{1-1.5x}Ce_xTiO₃ and the Sr_{1-2x}Ce_xTiO₃ stoichiometries. On occasions, a second batch of a composition was prepared to check the consistency of the results. The measured lattice parameter between batches agreed very well, within experimental error. Comparison of the observed and calculated lattice parameters did not agree as the calculated values were always underestimated (as was the tolerance factor) due to the problems of having zero-radius cation vacancies in the calculations.

All of the compositions in Figure 6.4 show a slightly higher than expected initial lattice parameter at low Ce-concentrations, of around 0.5 mol%. It would be expected that the intercept at $x = 0$ (i.e. pure SrTiO₃) would be around 3.905 Å. However in all three compositions it is closer to 3.907 Å. This could be due to a systematic offset error in the lattice parameter measurement in part caused by not using an internal standard. Alternatively, there could be a real increase in the LP at low Ce concentrations. This could be due to a different incorporation mechanism operating at very dilute donor concentrations, as observed in other donor-doped titanates [141], or due to the incorporation of a small amount of Ce(IV) on the B-site.

6.5 Structural refinement

6.5.1 Neutron powder diffraction

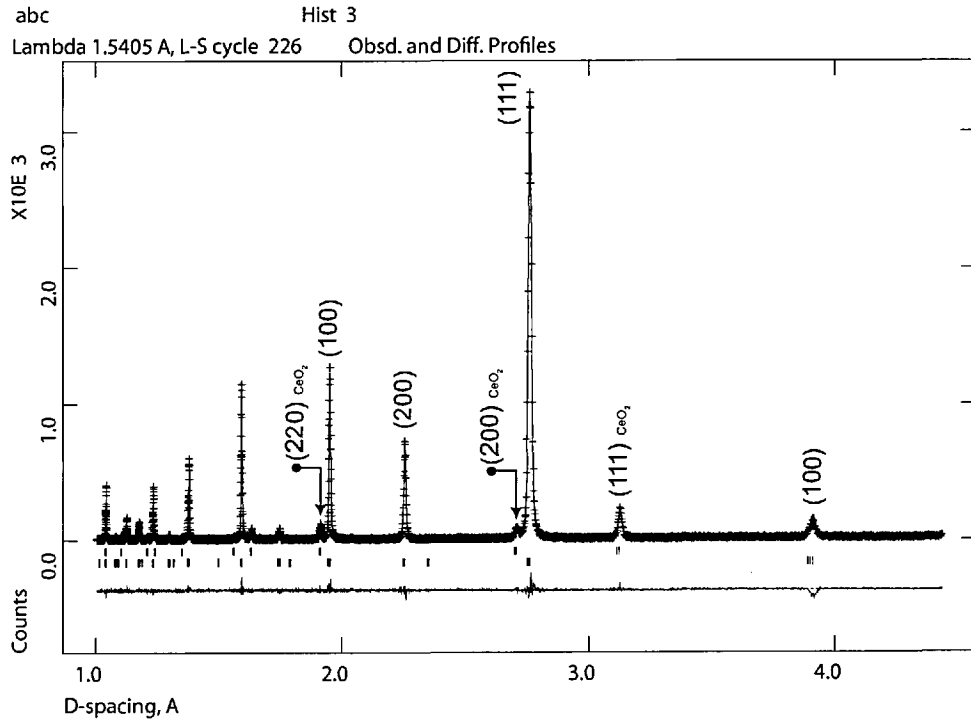
When powder neutron diffraction (PND) data was analysed there were several reflections which could not be indexed using the cubic, $Pm\bar{3}m$ symmetry. The first assumption was that additional reflections were due to a second phase. Figure 6.5 compares both patterns recorded from a sample of oxidised, stoichiometric composition,

$Sr_{0.9}Ce_{0.1}TiO_{3\pm\delta}$, which was known to contain ceria. X-Ray data (Figure 6.5a) shows that reflections due to ceria, the strongest of which can be seen at $\sim 3.1\text{\AA}$, are clearly visible in the X-Ray pattern. Reflections due to ceria are not as clear in the neutron diffraction pattern (Figure 6.5b). However, the additional reflections do not correspond with those of ceria. Figure 6.6 shows an example of neutron diffraction data refined using $Pm\bar{3}m$ space group; reflections that can not be indexed using this space group have been marked.

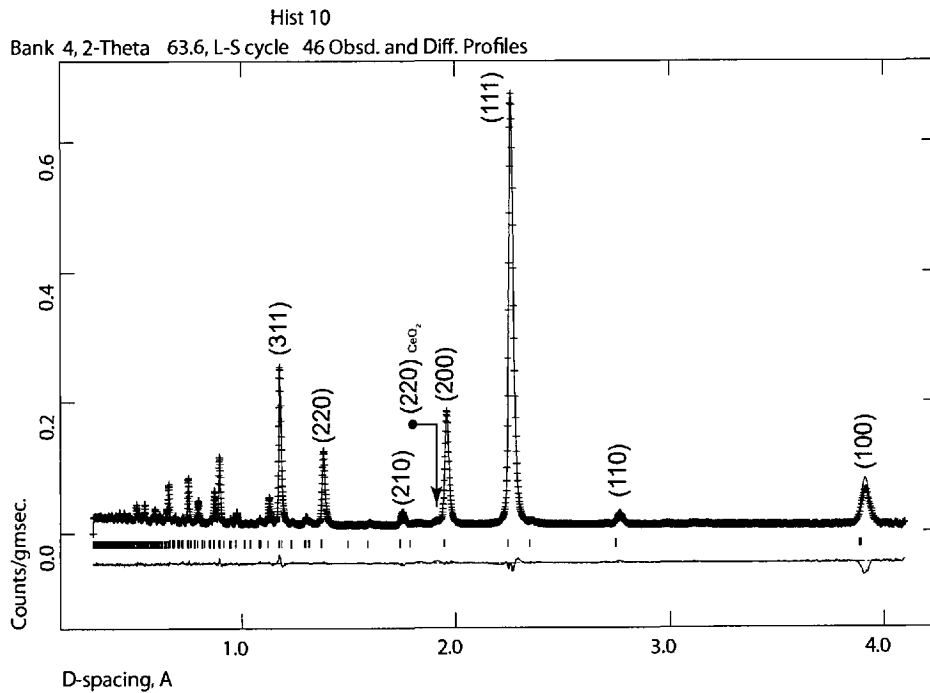
Non-stoichiometric samples (which appear to be single phase by XRD), also display the same additional reflections seen in the stoichiometric samples. These additional reflections in the neutron diffraction pattern can not be indexed using the $Pm\bar{3}m$ space group and were not considered to be caused by a second phase in any stoichiometry.

A certain amount of trial and error was required to index the additional peaks in the neutron diffraction data. Lower symmetry space groups were tested. A reasonable and physically realistic model, based on the $R\bar{3}c$ space group, was tested. This model had been used for similar doped chromate perovskite materials [83] and has recently been suggested as the structure for oxidised, A-site deficient series, $Sr_{1-1.5x}Ce_xTiO_{3\pm\delta}$ [132]. Refinement of a $R\bar{3}c$ space group using the hexagonal unit cell (as opposed to the rhombohedral cell) allows nearly all of the peaks to be indexed, with the exception of a few, very weak reflections. The fit to the experimental data was satisfactory with χ^2 values between 9-12 and R_{wp} -values generally below 5%. Although the model based on the $R\bar{3}c$ symmetry is plausible, and all of the reflections can be indexed, the relatively high χ^2 values suggested that this model may be incorrect.

Attention was turned to the CaTiO₃-SrTiO₃ system. This system was of interest because Ca(II) has an identical ionic radius to Ce(III) ($1.34\text{\AA}$) in a 12 coordinate environment [133]. There is complete solid-solubility across the entire compositional range. However, there are a range of symmetry changes observed across the CaTiO₃-SrTiO₃ phase diagram. These phase changes are generally accepted as $Pm\bar{3}m \leftrightarrow I4/mcm \leftrightarrow Pnma$ from the Sr-rich to the Ca-rich end of the phase diagram respectively [142]. Using this logic, the tetragonal space group $I4/mcm$ was tested and it was this model where the best fit to the experimental data and the most stable refinements were



(a) X-Ray diffraction



(b) Neutron diffraction

Figure 6.5: Comparison of the X-Ray diffraction pattern (6.5a, converted to d-spacing) and Neutron powder diffraction pattern (6.5b) of oxidised material with the nominal composition $\text{Sr}_{0.90}\text{Ce}_{0.10}\text{TiO}_{3\pm\delta}$. Both were refined using the $R3c$ space group. In the X-ray refinement, CeO_2 was also refined as a second phase (shown as the upper tick marks in (a)). Only the (220) ceria reflection is still visible in the neutron diffraction pattern; the others are too weak to be observed at this scale.

Bank 4, 2-Theta 63.6, L-S cycle 392 Obsd. and Diff. Profiles

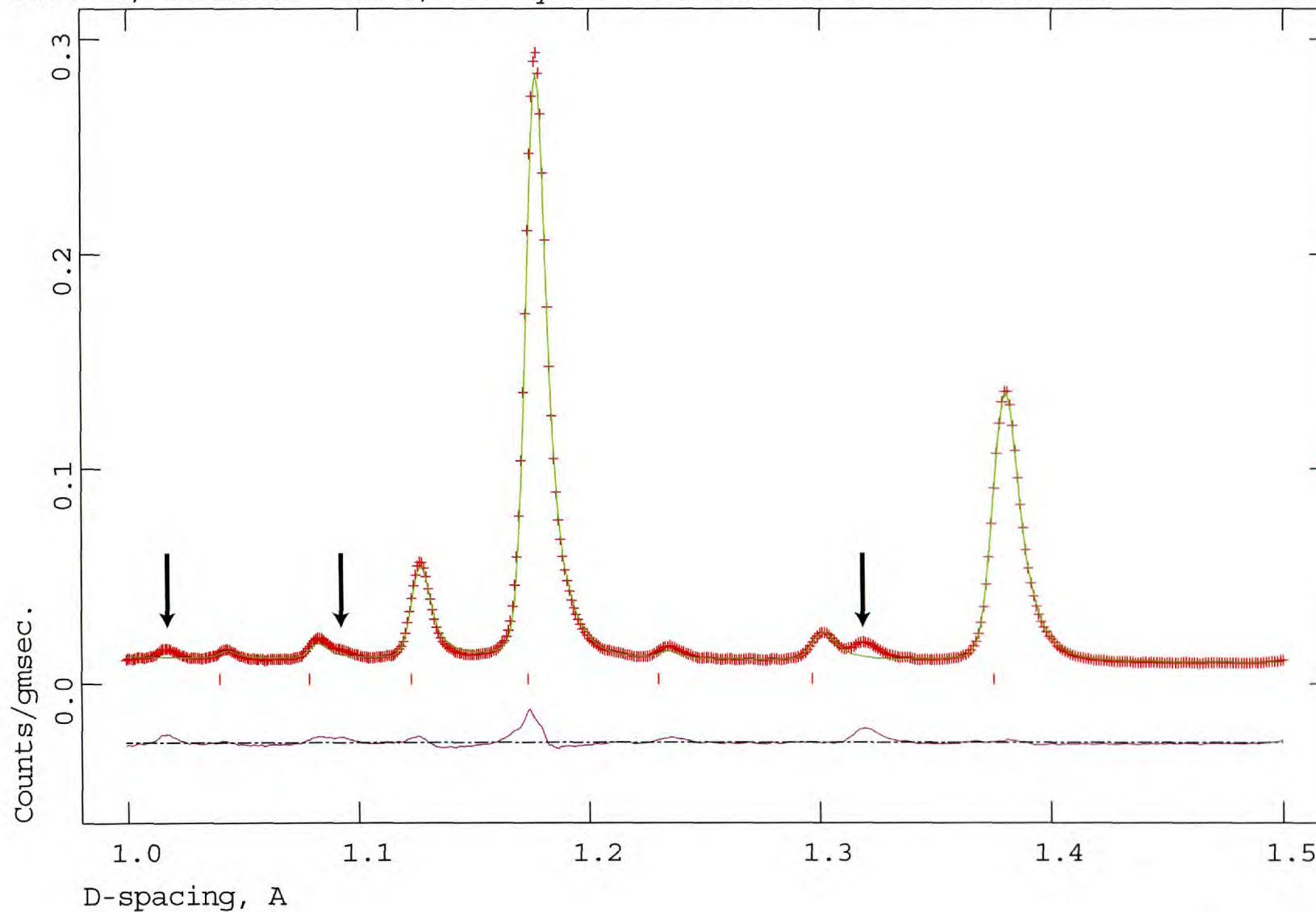


Figure 6.6: Example of additional reflections (arrowed) in neutron diffraction pattern, not accounted for by using $Pm\bar{3}m$ space group. Key: Red crosses are experimental data points; green solid line represents the predicted pattern from the model; tick marks indicate predicted peak positions from the model; and the purple line is the difference between the model pattern and the experimental data.

Chapter 6: Structural characteristics of Ce-doped SrTiO₃

Table 6.4: Selected details of the I4/mcm space group.

Space group - I4/mcm				
a=b≠c				
$\alpha = \beta = \gamma = 90^\circ$				
Atom	site	fractional coordinates, x, y, z		
Ce1	4b	0	0.5	0.25
Sr1	4b	0	0.5	0.25
Ti1	4c	0	0	0
O1	4a	0	0	0.25
O2	8h	x	y	0

obtained. χ^2 values were generally between 4-9 and they were the best fits possible. Results of these refinements are presented in Figures 6.7 and 6.8 and Tables 6.5 and 6.6.

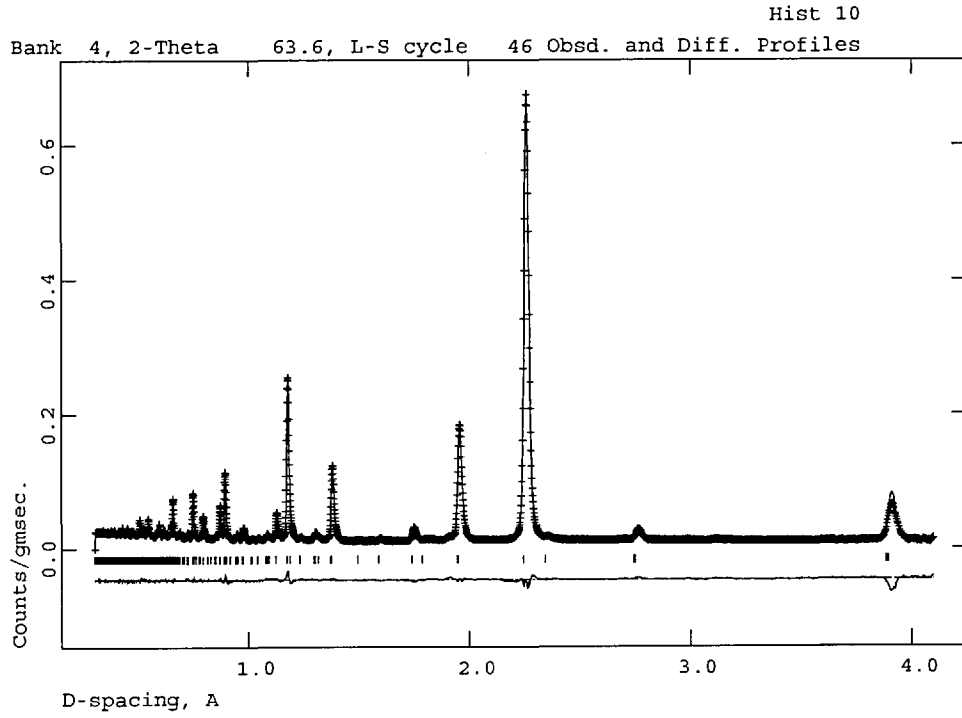
Table 6.5: Lattice parameters and selected crystallographic parameters derived from the refinement of neutron powder diffraction data for both oxidised and reduced stoichiometric samples.

Parameters	Sr _{0.90} Ce _{0.10} TiO _{3±δ}	
	Oxidised	Reduced
Refined Cell	a = b = 5.52049(21)	a = b = 5.52474(18)
parameters (Å)	c = 7.8252(6)	c = 7.8279(5)
x O2 position	0.76087(13)	0.76328(9)
y O2 position	0.26087(13)	0.26328(9)
Sr/Ce $U_{iso} * 100$	0.859(16)	0.671(12)
χ^2/R_{wp}	9.214/0.0447	7.674/0.0456

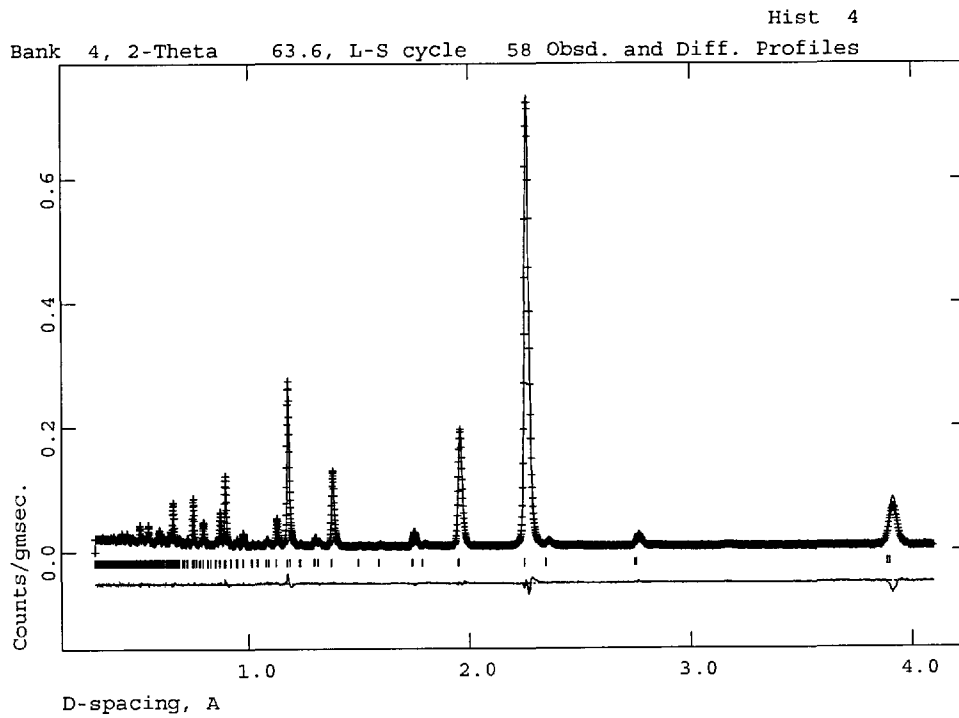
Additional refinements were carried out using the orthorhombic symmetry (*Pbnm*), the reported structure for the Ca-rich end of the CaTiO₃-SrTiO₃ system. Although it was possible to obtain χ^2 values down to around seven, the orthorhombic model shows additional reflections which were not present in the experimental data and so the model was abandoned.

6.5.2 X-Ray powder diffraction

With a satisfactory model derived from the neutron diffraction data, refinement of the XRD data was performed using the tetragonal model. Variation of the structure due to change in the position of the lighter atoms, such as oxygen, was one of the reasons why

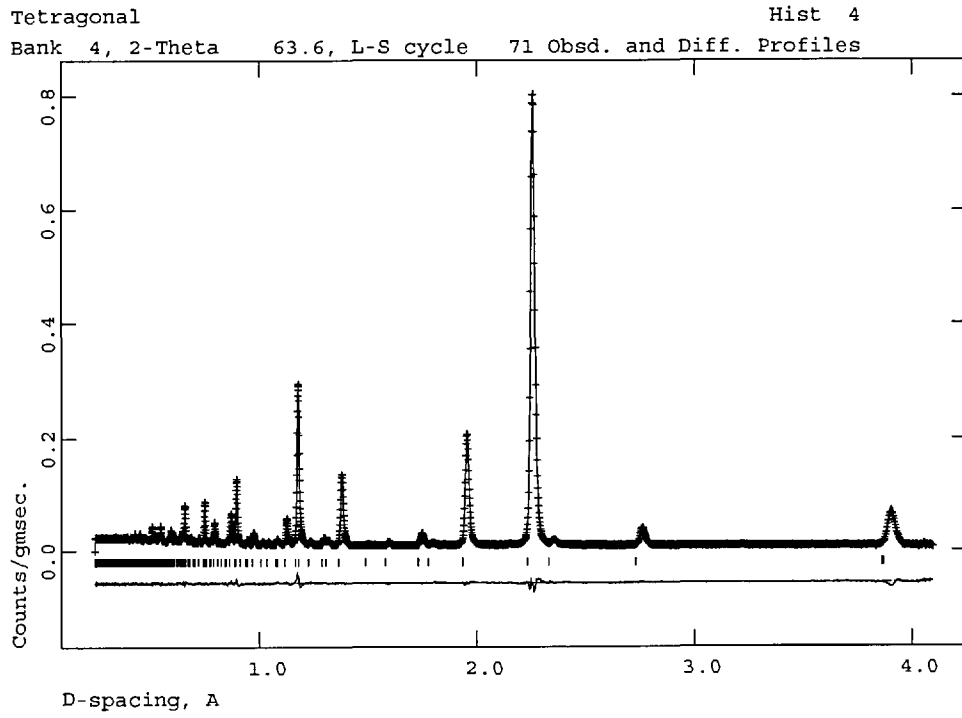


(a) Stoichiometric oxidised

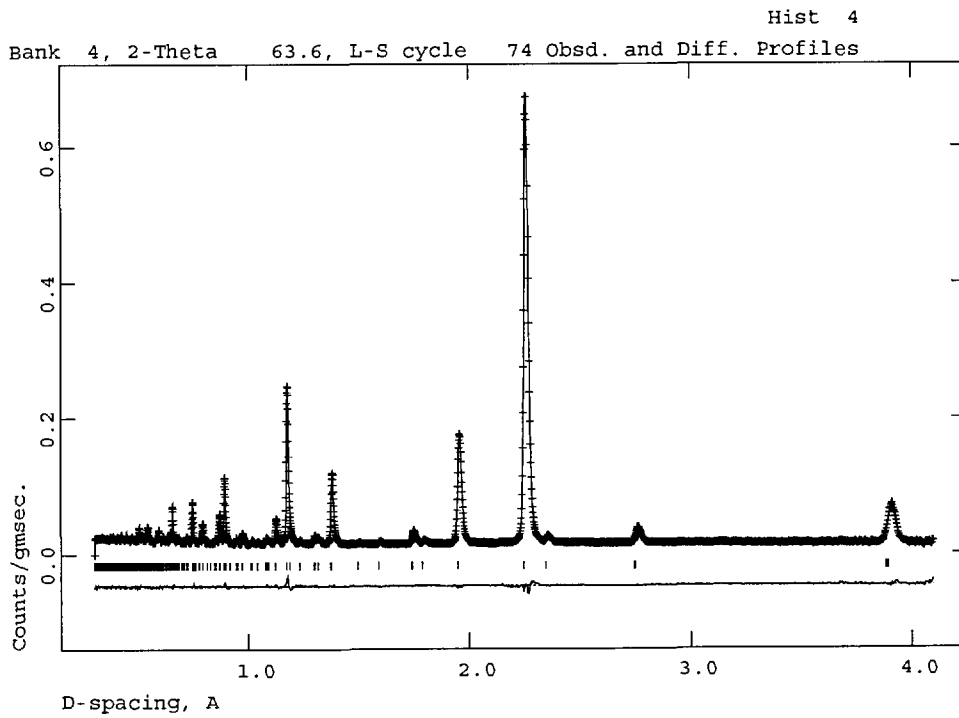


(b) Stoichiometric Reduced

Figure 6.7: Neutron diffraction patterns refined using the $I4/mcm$ space group for oxidised and reduced samples with the nominal composition $\text{Sr}_{0.9}\text{Ce}_{0.1}\text{TiO}_{3\pm\delta}$.



(a) Non-stoichiometric oxidised



(b) Non-stoichiometric reduced

Figure 6.8: Neutron diffraction patterns refined using the $I4/mcm$ space group for oxidised and reduced samples with the nominal composition $\text{Sr}_{0.775}\text{Ce}_{0.15}\text{TiO}_{3\pm\delta}$.

Table 6.6: Lattice parameters and selected crystallographic parameters derived from the refinement of neutron powder diffraction data for both oxidised and reduced non-stoichiometric samples.

Parameters	Sr _{0.775} Ce _{0.15} TiO ₃	
	Oxidised	Reduced
Refined Cell parameters (Å)	a = b = 5.51137(15) c = 7.8110(4)	a = b = 5.51740(13) c = 7.8222(4)
x O2 position	0.76384(9)	0.76601(9)
y O2 position	0.26384(9)	0.26601(9)
Sr/Ce U_{iso} * 100	0.604(15)	0.510(12)
χ^2/R_{wp}	6.776/0.0416	5.428/0.0335

Table 6.7: Selected Ti-O bond lengths showing the variation of reduced and oxidised samples with different cation stoichiometry

Composition	State	Bond length (Å)	
		Ti(1)-O(1)	Ti(1)-O(2)
Sr _{0.9} Ce _{0.1} TiO _{3±δ}	Oxidised	1.95630	1.95363
	Reduced	1.95697	1.95604
Sr _{0.775} Ce _{0.15} TiO _{3±δ}	Oxidised	1.95275	1.95155
	Reduced	1.95561	1.95470

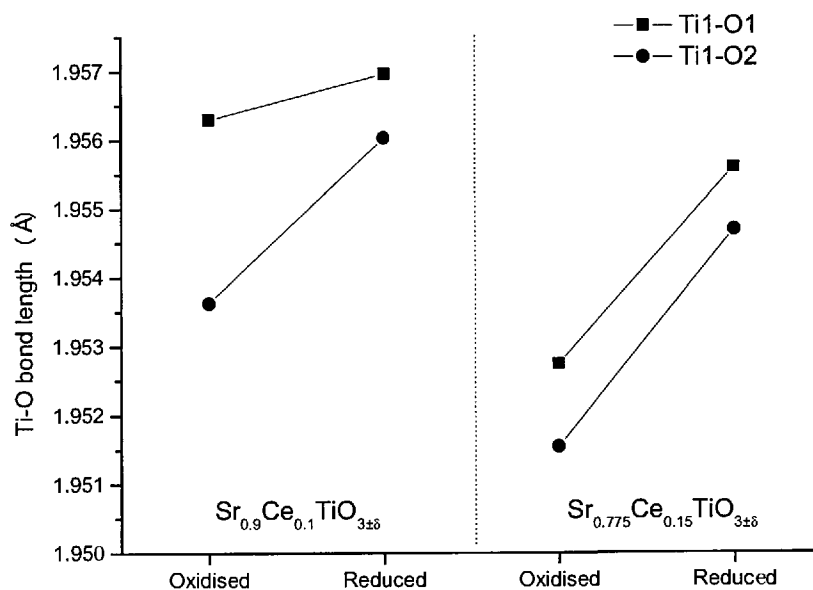


Figure 6.9: Comparison of Ti-O bond-lengths for reduced and oxidised samples.

the XRD pattern was thought to appear cubic. It was only with neutron diffraction that these subtle variations were detected. For X-Ray refinements, positions of the oxygen atoms (from the neutron refinement) were left alone and only parameters such as lattice parameter and cation temperature factors were refined along with instrumental factors such as peak shape. Figures 6.10 and 6.11 show the X-Ray refinements of the same samples used for neutron diffraction (see Figures 6.7 & 6.8). Clearly visible in the XRD pattern in Figure 6.10a is the ceria second-phase (upper tick marks). For refinements containing ceria second phase, the pure compound was used as a model (from ICSD database # 53995).

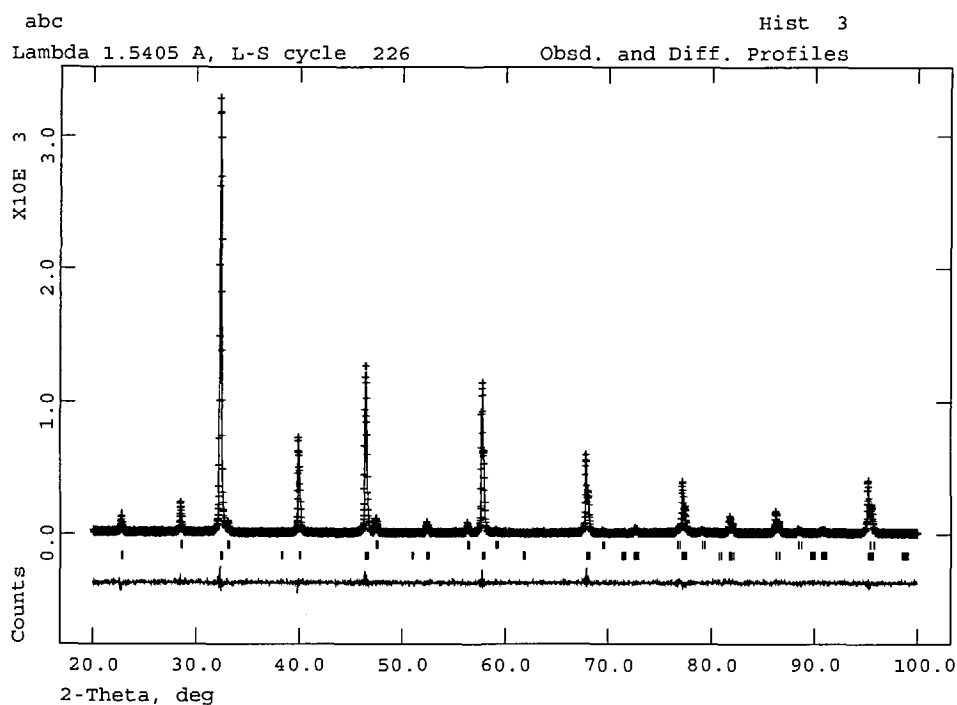
Even though the χ^2 values are satisfactory for the X-Ray refinements, the R_{wp} -values are relatively high (~ 15 -20%). This is typical of X-Ray refinements (compared to Neutron refinements) because of the very high signal-to-noise ratio in X-Ray diffraction measurements.

6.5.3 High-Temperature X-Ray Diffraction (HTXRD)

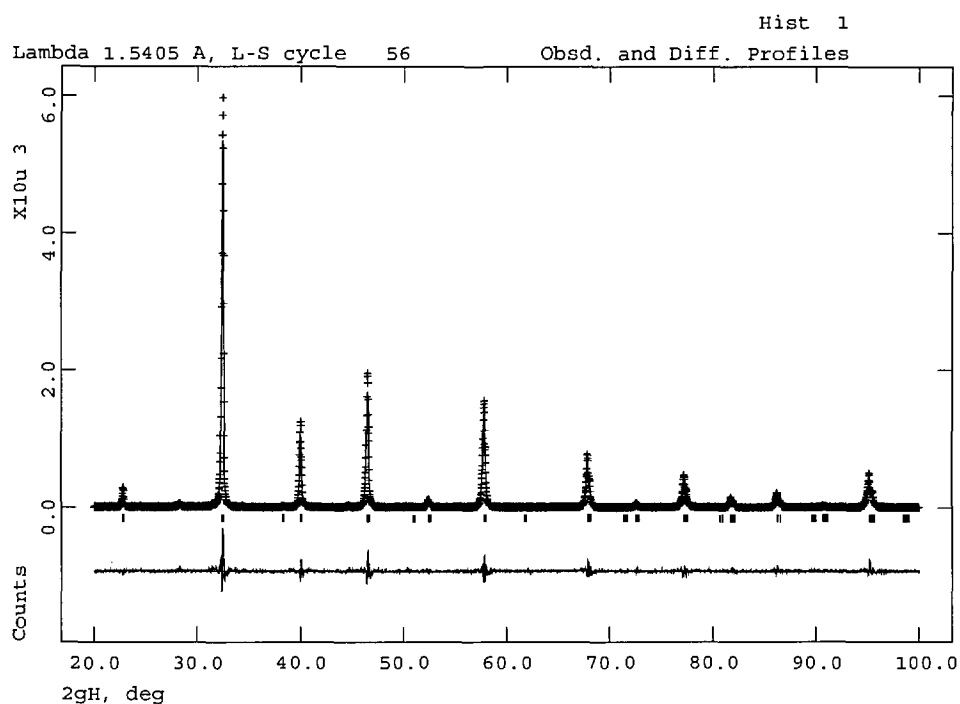
High-temperature XRD was carried out to determine whether these materials were single phase throughout the temperature range of interest, typically 200-1000°C. A typical diffraction pattern is shown in Figure 6.13a. Only a relatively small two theta range was covered but the scan still shows several prominent peaks of the perovskite phase. All reflections have been indexed according the cubic, $Pm\bar{3}m$ symmetry. The $\{200\}$ and $\{210\}$ peaks overlap quite heavily with peaks from the platinum heater substrate. Arrowed peaks in Figure 6.13a are due to ceria second phase (this sample was a stoichiometric composition). The peak marked with an asterisk is an impurity on the heater substrate which did not affect the measurement.

6.6 TEM-Electron Energy Loss Spectroscopy (EELS)

The assumption throughout much of this chapter has been that cerium is incorporated as Ce(III) on the A-site. Although the formation of a single phase in the non-stoichiometric composition supports this, there is no direct chemical evidence for this assumption. EELS was used to probe the location and oxidation state of the Ce ion.

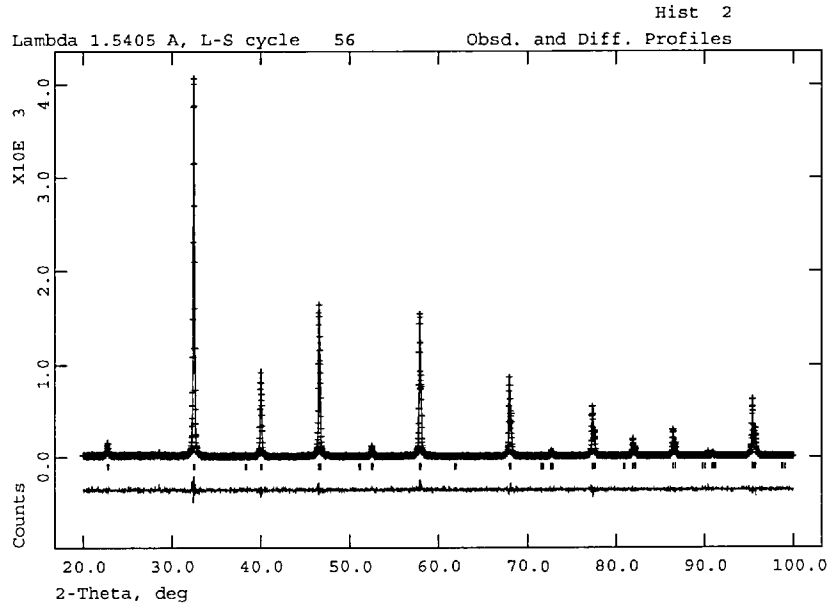


(a) Stoichiometric oxidised

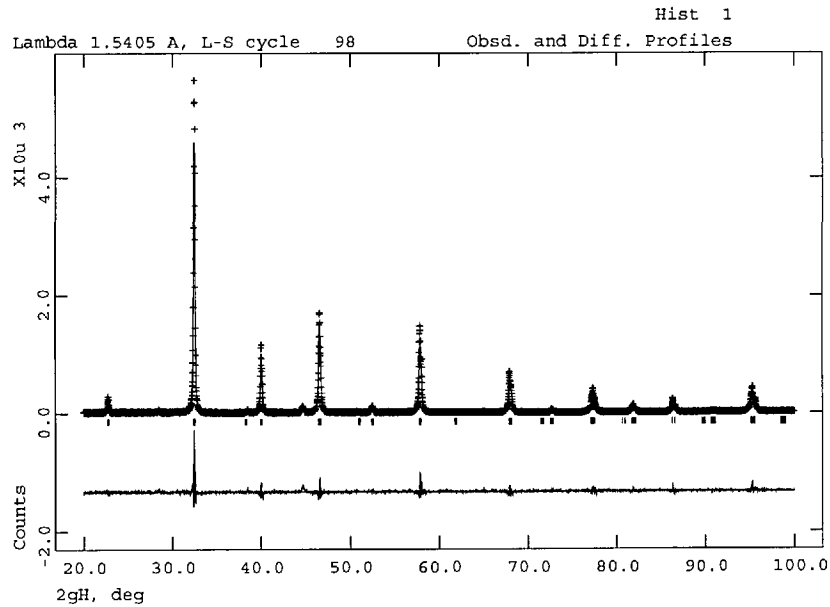


(b) Stoichiometric reduced

Figure 6.10: X-Ray diffraction patterns refined using the model derived from the neutron diffraction data in the $I4/mcm$ space group. This figures shows the results for stoichiometric composition ($\text{Sr}_{0.9}\text{Ce}_{0.1}\text{TiO}_{3\pm\delta}$). No second phase was using in the model for the reduced stoichiometric refinements (b) due to the higher solubility of ceria under reducing conditions.



(a) Non-stoichiometric oxidised



(b) Non-stoichiometric reduced

Figure 6.11: X-Ray diffraction patterns refined using the model derived from the neutron diffraction data in the $I4/mcm$ space group. This figures shows the results for non-stoichiometric composition ($\text{Sr}_{0.775}\text{Ce}_{0.15}\text{TiO}_{3\pm\delta}$).

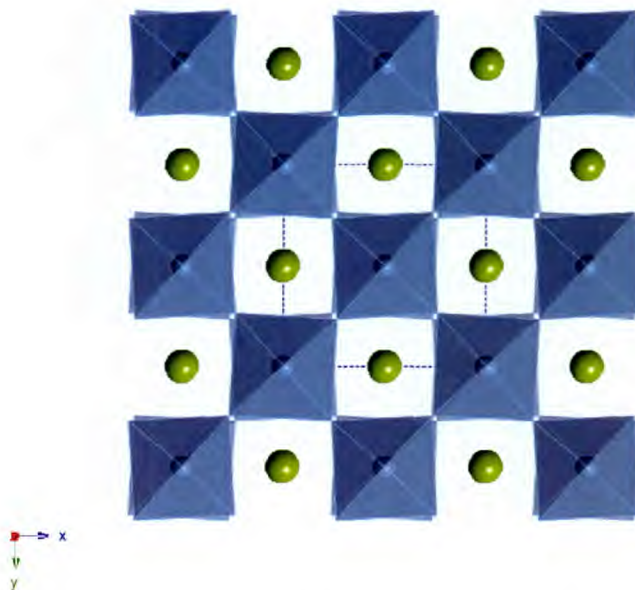


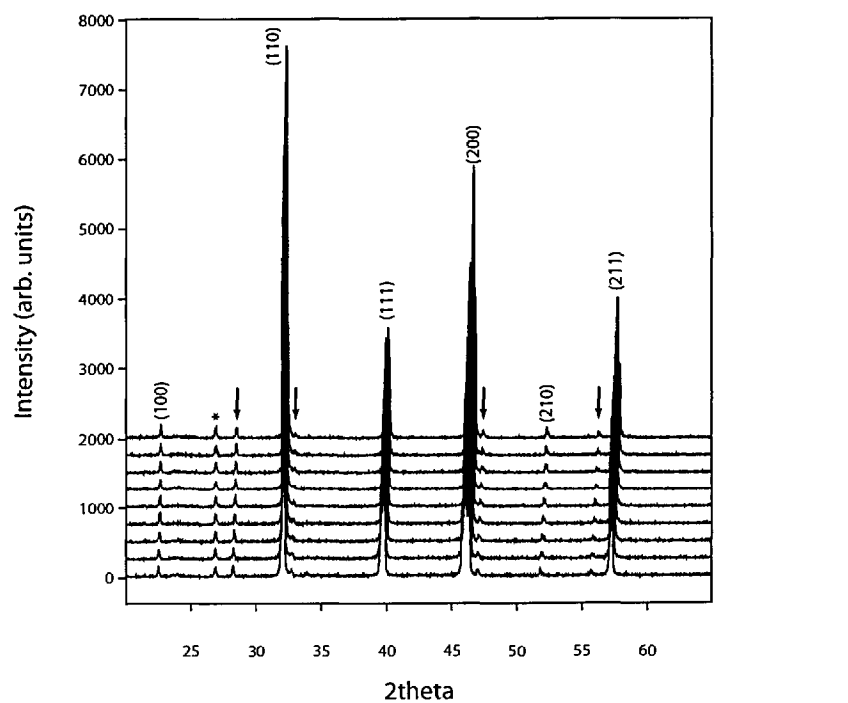
Figure 6.12: The refined crystal structure of oxidised $\text{Sr}_{0.775}\text{Ce}_{0.15}\text{TiO}_{3\pm\delta}$ viewed parallel to the c -axis where small octahedral tilting can be seen. The cubic symmetry observed using X-Ray diffraction was due to the cations, which contribute the most to the diffracted X-Ray intensity, retaining the same positions as in the cubic perovskite. Note the unit cell is drawn as a dashed box.

Only A-site deficient samples were used for the TEM-EELS measurements, to avoid the complications of mistakenly measuring stray Ce signal from a grain of CeO_2 . Two sample compositions were measured one was the same batch as those used for neutron and X-Ray diffraction measurements presented above; namely $\text{Sr}_{0.775}\text{Ce}_{0.15}\text{TiO}_{3\pm\delta}$; the other was $\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$. Both oxidised and reduced samples were examined.

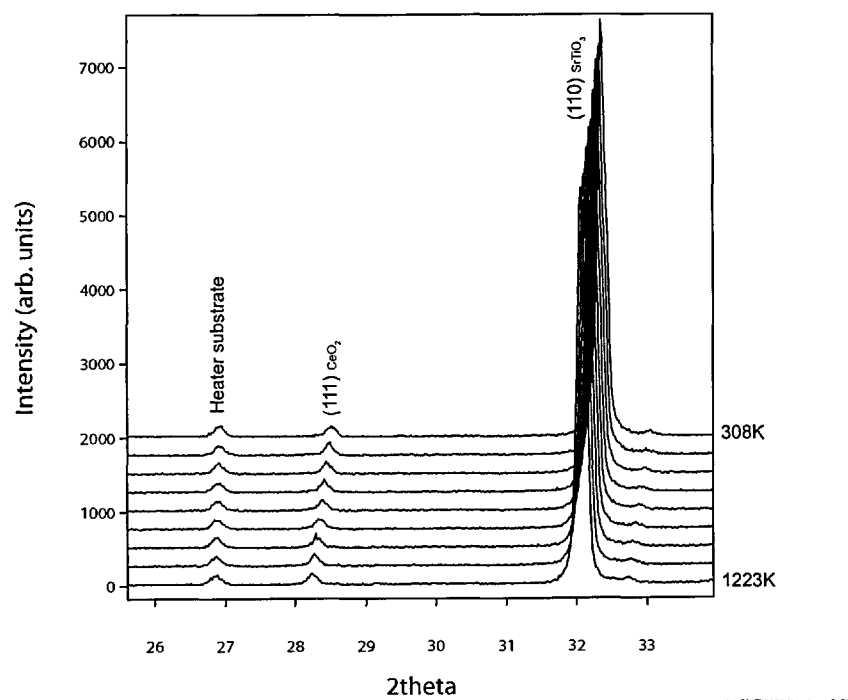
6.6.1 The Ce M edge

Figure 6.14 shows the literature EELS spectra for Ce (III) and Ce(IV). The key differences to note are the relative peak heights and the shoulders observed on the M_4 and M_5 peaks in the Ce(IV) spectrum. There is also a slight chemical shift between the Ce(III) and Ce(IV) peaks but this is very small.

Figure 6.15 shows the cerium M_{4-5} edges for oxidised and reduced $\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$. No shoulders were observed on the high energy side of the peak (which would be typical of the presence of Ce(IV)). However, these features may not have been visible because these samples produced a relatively weak signal, due to a low cerium content (~ 5 mol%).



(a)



(b)

Figure 6.13: High temperature XRD, showing the result of heating in air from 35 - 980°C. No additional peaks, peak splitting or significantly decreased peak intensity was observed during heating, suggesting the material has no phases changes in this temperature range.

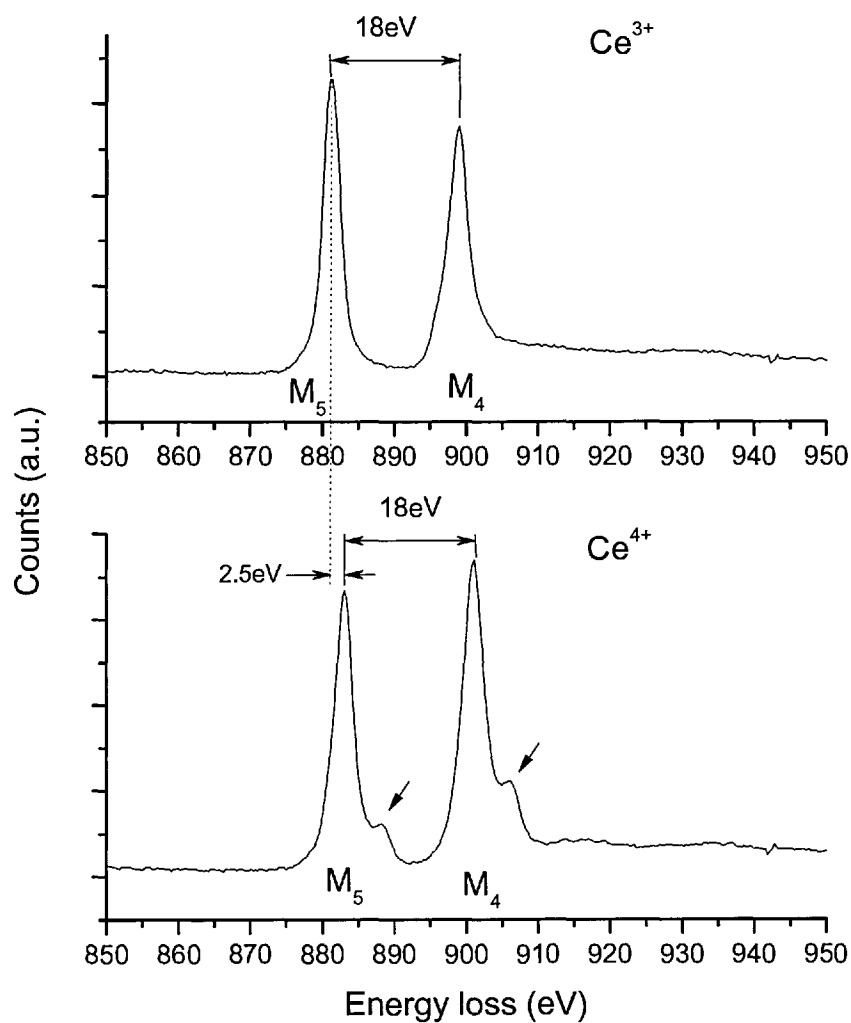


Figure 6.14: EELS reference spectra for Ce(III) and Ce(IV), measured in CeO₂. Key differences between them are the peak intensity variation between the two valence state and the additional higher energy shoulders as seen in Ce(IV).

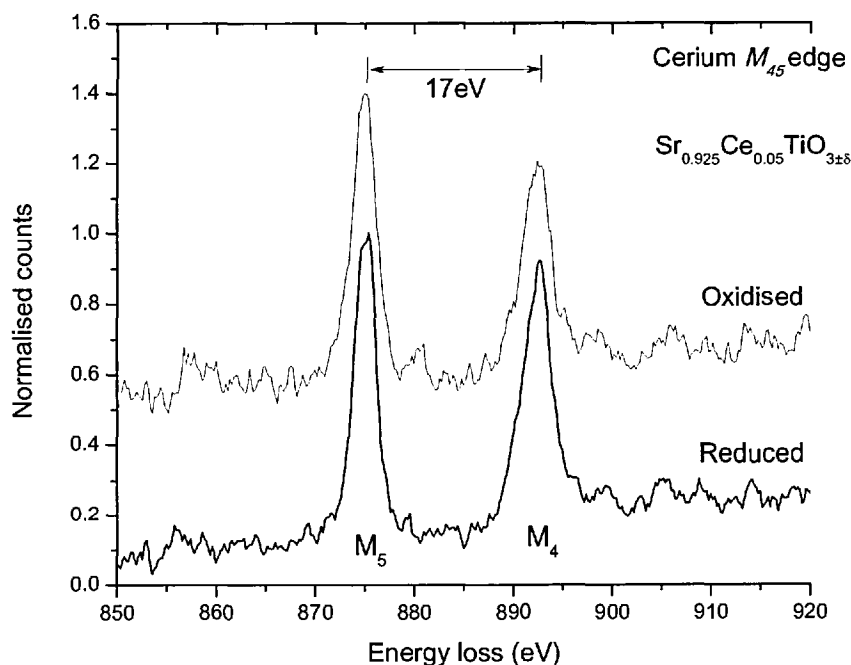


Figure 6.15: Ce-edge energy loss spectrum from oxidised $\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$.

Another important indication of the cerium oxidation state is the relative intensity of the peaks. A strong indication of the presence of Ce(III) is when the lower energy M_5 peak at 870 eV, is more intense than the M_4 peak at 890 eV which is clear in figure 6.15.

At higher Ce concentrations the situation was the same as the $x = 0.05$ samples. This again is clearly demonstrated in Figure 6.16. No evidence of shoulders was observed and the relative peak intensity and similarity to the reference spectrum suggest the presence of Ce(III).

6.6.2 The Ti L edge

Titanium $L_{2,3}$ edges were also in an available energy range for collection. The rationale for examining the Ti-L edges was to try and determine the extent of the $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$ reaction during treatment under reducing conditions. The EELS spectrum taken from an oxidised and reduced sample is presented in Figure 6.17. This figure also includes the Ti $L_{2,3}$ edge recorded from SrTiO_3 by Samet et al. [143]. Data recorded in our laboratory and by reference [143] was at a similar resolution (~ 0.6 eV). The splitting

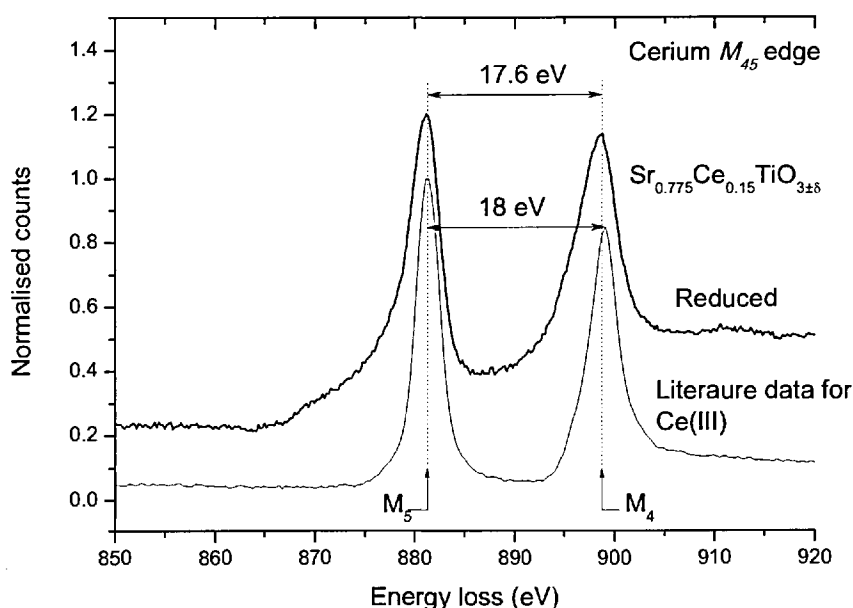


Figure 6.16: $\text{Sr}_{0.775}\text{Ce}_{0.15}\text{TiO}_{3\pm\delta}$, a sample with a higher cerium concentration, showed similar results to the other doped samples. The Ce M_{45} edge data is strikingly similar to the reference data which is also shown. There is a slight difference between the peak separation but this is very small and would not be attributed to Ce(III).

of the L_3 and L_2 edges (due to the oxygen ligand crystal field splitting) varies between the un-doped SrTiO_3 , oxidised Ce-doped SrTiO_3 , and reduced Ce-doped SrTiO_3 . Most obvious is the difference between the L_2 edge. In the un-doped material, the splitting is very clear. However, in the doped material there is a less clearly defined splitting. This has been interpreted as an indication of mixed-valent Ti(III) and Ti(IV) [144–146].

6.6.3 The O K edge

Data recorded for the oxygen K edge was very similar to data from un-doped SrTiO_3 . Figure 6.18 shows the data for oxidised and reduced $\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$ and un-doped SrTiO_3 . All of the data is consistent with other spectra recorded from perovskite titanates [145]. Oxygen edge data is often sensitive to the oxygen coordination environment [147]. The intensity ratio of the peaks labelled 'A' and 'B' in figure 6.18 can be used to highlight differences in the oxygen environment. From Figure 6.18 there is little discernable difference between the doped and un-doped samples. The only possible difference between the two is a shift in the peak labelled D at around 552 eV. There are also some additional features in the doped samples, which have been marked with

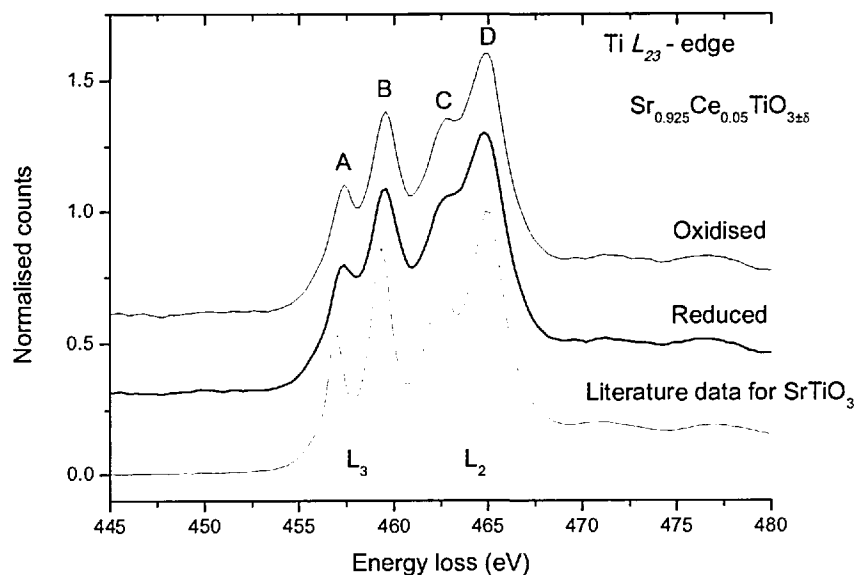


Figure 6.17: Ti L-edge EELS spectra for an oxidised and reduced sample compared with a reference Ti-edge from un-doped SrTiO_3 (from reference [143]).

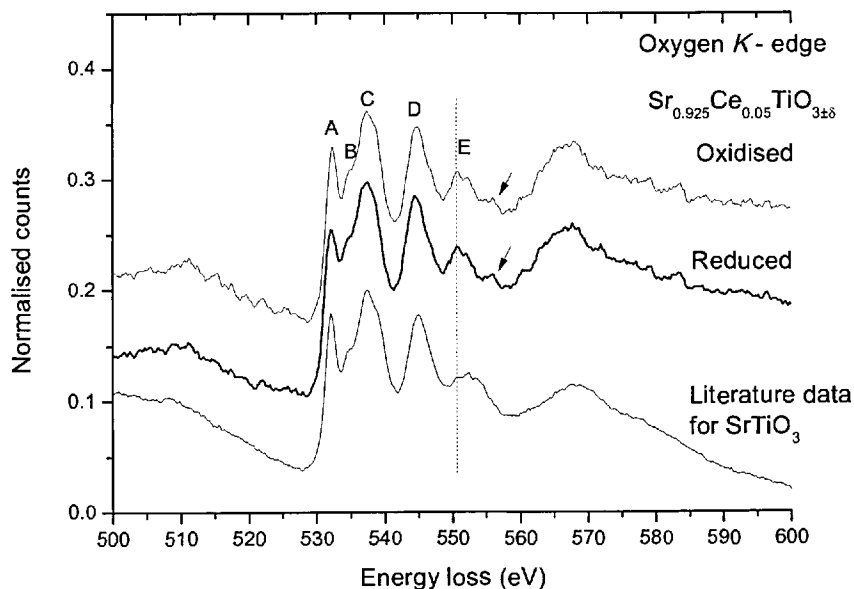


Figure 6.18: O K-edge EELS spectra for an oxidised and reduced sample compared with a reference O-edge from un-doped SrTiO_3 (from reference [143]).

arrows.

6.7 Thermal expansivity

6.7.1 Dilatometric measurements

The Thermal Expansion Coefficient (TEC) is one of the most important properties of any electrode material. As it is generally the electrolyte which is chosen first (and then the electrode material is required to meet the compatibility criteria based on the properties of the electrolyte material), if there is a large difference between the TEC of a cell component then the result is usually delamination of the electrode material. This does not necessarily happen after multiple thermal cycles and may even occur during processing. Tailoring the TEC to match or to be as close as practically possible to other cell components, particularly the electrolyte material, is very important. For an anode material that will see a range of oxygen partial pressures, or even full redox cycles (see Section 2.1.1), it is important that there is also very little volume expansion under varying $p(\text{O}_2)$. The change in volume due to changes in $p(\text{O}_2)$ is often termed 'chemical expansion'.

Figure 6.19 shows the typical thermal expansion behaviour of Ce-doped SrTiO₃ ceramics. In the figure, the solid line represents the continuous heating segment in air. The cooling segment was also recorded but has been omitted for clarity. There was no hysteresis observed during the heating and cooling cycles. Also shown in Figure 6.19 (the individual data points) were recorded under pump-gauge-controlled CO-CO₂ mixture. The experimental procedure used to collect this data was described in section 5.10. Clearly there is very little change in the sample volume even after a significant change in the oxygen partial pressure. Table 6.8 summarises the average thermal expansion data which agrees well with the TEC calculated from the high temperature XRD evidence (see below) and is close to both YSZ and CGO.

Table 6.8: Average linear thermal expansion coefficients of Sr_{0.925}Ce_{0.05}TiO_{3±δ} and Sr_{0.95}Ce_{0.05}TiO_{3±δ} ceramics in various atmospheres.

Composition	p(O ₂) (atm)	T (°C)	$\alpha(\times 10^{-6})$ (K ⁻¹)
Sr _{0.925} Ce _{0.05} TiO _{3±δ}	0.21	127-580	10.95±0.01
	0.21	580-1100	11.95±0.01
	4.2x10 ⁻²¹ 2.9x10 ⁻¹³	650-950	11.50±0.08
Sr _{0.95} Ce _{0.05} TiO _{3±δ}	0.21	127-580	11.03±0.01
	0.21	580-1100	12.06±0.01
	4.2x10 ⁻²¹ 2.9x10 ⁻¹³	650-950	11.74±0.09

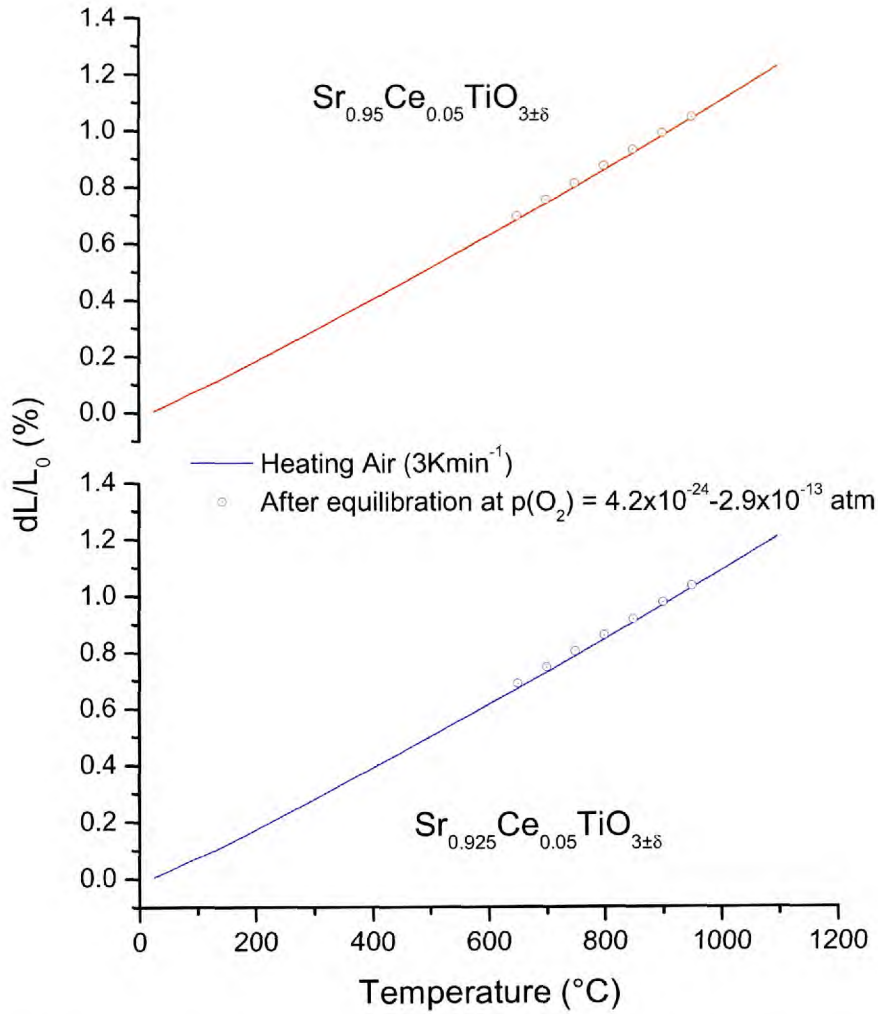


Figure 6.19: Comparison of thermal expansion of Sr_{0.925}Ce_{0.05}TiO_{3±δ} and Sr_{0.95}Ce_{0.05}TiO_{3±δ} ceramics in air (solid lines) and CO-CO₂ mixtures (data points). The data in air were obtained in the continuous heating regime. The data in a reducing atmosphere were collected on temperature cycling with 2-7 h dwells at each temperature.

6.7.2 Calculation from HTXRD

Changes in the lattice parameter were also calculated from high temperature X-Ray diffraction experiments. From these measurements it was also possible to calculate the thermal expansion coefficient (TEC) of the stoichiometric material. The slope of a plot of LP versus temperature will yield:

$$m = \frac{dL}{dT} \quad (6.2)$$

and the relationship between TEC and change in length is:

$$\alpha = \frac{1}{L_0} * \frac{dL}{dT} \quad (6.3)$$

where α is the TEC and L_0 is the original length, before heating. In this case L_0 is the unit cell parameter at room temperature. Figure 6.20 shows the variation of the LP with temperature and the calculated TEC. These values agree very well with other values of thermal expansion in the literature for similar materials (11-12p.p.m K⁻¹) and they also agree well with values obtained in this work, measured using a dilatometer.

6.8 Discussion

6.8.1 Variation of predicted and experimentally observed lattice parameters.

Predicted lattice parameters were calculated using well established ionic radii data. The lattice parameters calculated from these values seem to give physically plausible results. For example, in the case of the incorporation of Ce(III), only on the A-site (shown in Figure 6.3c on page 95) do the predicted values decrease with increasing cerium content. The predicted values are close, but not identical to the observed values. We have explained this behaviour by allowing a small amount of Ce(IV) to reside on the B-site; this may have been possible given that the samples were synthesised in air. Others

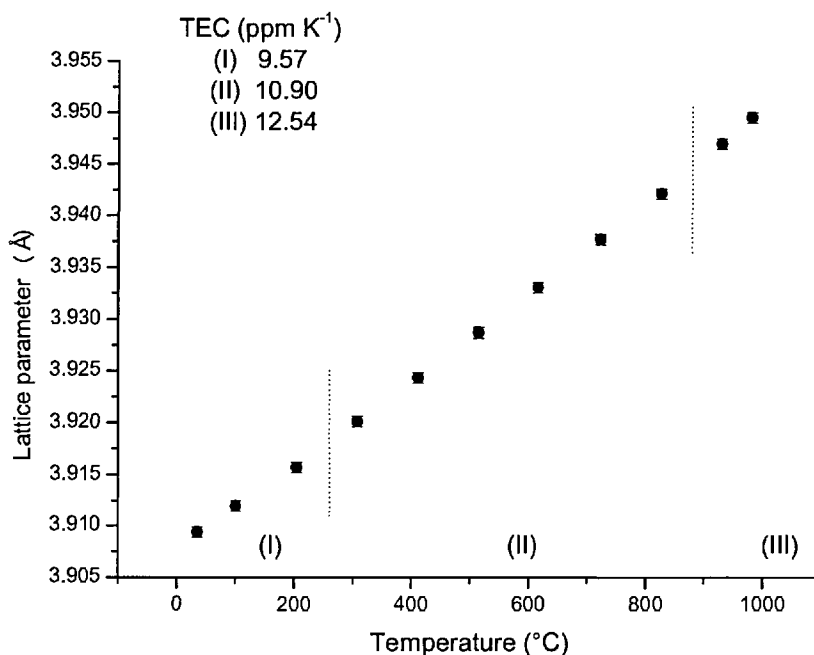


Figure 6.20: Variation of lattice parameter with temperature for the $\text{Sr}_{0.95}\text{Ce}_{0.05}\text{TiO}_3$ composition. TEC agrees well with the literature values and the values measured using a dilatometer in our laboratory.

have suggested mixed A and B-site substitution by Ce(III) and Ce(IV) respectively for compositions prepared in air [148]. The main problem with using the predicted lattice parameters from these models is that the experimental changes we observed were relatively small compared with the errors in the predicted values ($\sim 0.5\%$). Even though we can not categorically prove whether cerium is on the A-site, the models do allow us to say with some certainty that cerium is not substituting entirely on the B-site, which is a useful result.

Examination of the experimentally observed lattice parameters shows some very interesting features. It would seem that (no matter what the starting stoichiometry) all of the observed lattice parameters follow the same trend, within experimental error. As shown in Figure 6.4 when the cerium concentrations for the 'stoichiometric' compositions were corrected, all of the stoichiometries prepared showed the same lattice parameters. The reason the 'stoichiometric' sample was corrected was that the ceria that had precipitated was obviously not incorporated into the lattice and so the actual dissolved cerium content was lower than the nominal starting value. To correct the data we assumed that the A-site deficient phase, $\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_3$, had formed. So, for ex-

ample, if we had prepared a sample with the nominal composition of Sr_{0.95}Ce_{0.05}TiO₃, what had actually formed (in air) was Sr_{0.95}Ce_{0.033}TiO₃ along with the precipitation of some CeO₂. When these corrections were made, all of the data fell on the same line. This result shows two key points. Firstly, the defect compensation in air occurs by the formation of cation vacancies. Secondly, as the Sr_{1-1.5x}Ce_xTiO₃ stoichiometry was the only one to form a single phase, we can assume that cerium(III) is likely to reside on the A-site. These are interesting results which have also been observed in the phase relationships of Nb-doped SrTiO₃, as discussed by Blennow [79].

6.8.2 Vegard's Law.

Vegard's law is an empirical observation that the lattice parameter will vary linearly with the composition in a solid solution. In the case of the SrTiO₃-Ce_{2/3}TiO₃ system, this was not so simple as there are no published ternary or pseudo-binary phase diagrams for this system and there may be several phase changes across the solid solution. Ce_{2/3}TiO₃ can be reasonably assumed to be the end member of the Sr_{1-1.5x}Ce_xTiO₃ stoichiometry. Published lattice parameters for Ce_{2/3}TiO₃, which is orthorhombic (*Pmmm*), where cell constants $a = 3.856 \text{ \AA}$, $b = 3.877 \text{ \AA}$ and $c = 7.754 \text{ \AA}$ [149] were used as a basis for comparison. The a and b values were plotted with all the experimentally observed data and are shown in Figure 6.21. Extrapolation to the Ce-rich side of the phase diagram shows that there is some agreement between the experimentally observed values and the Ce_{2/3}TiO₃ end-member b -axis parameter.

Since only a small area of the phase diagram was investigated, it is difficult to make any firm conclusions from the extrapolation. However, it shows that the experimental data is consistent with the assumption of a solid solution between SrTiO₃ and Ce_{2/3}TiO₃.

6.8.3 Tetragonal distortion.

We have shown that the structure of the compositions prepared in this study all appear to be tetragonal (*I4/mcm*) based on the available neutron diffraction data. After treatment under reducing atmospheres, the tetragonal structure is retained and the lattice parameters increase.

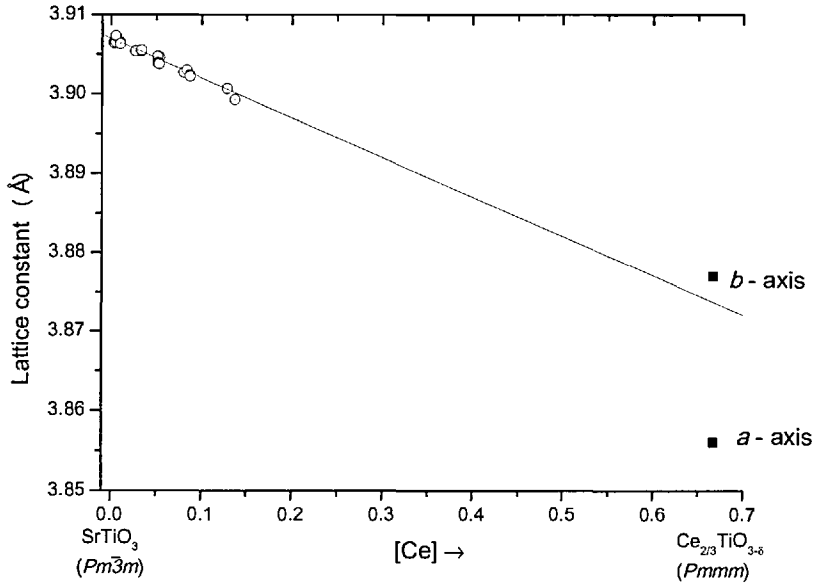


Figure 6.21: Extrapolation of the lattice parameter measurements for all the lattice parameter data in Fig. 6.4. This shows a good agreement with Vegard's Law. However, more data is required to complete the series.

The La-doped system, $\text{Sr}_{1-1.5x}\text{La}_x\text{TiO}_{3\pm\delta}$, has also been shown to have the $I4/mcm$ space group at room temperature for $x \geq 0.2$ [150]. The relationship between the cubic and tetragonal symmetries is summarised in Figure 6.22:

These results disagree with the published data of Ubic *et al.* who found that the $\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_{3\pm\delta}$ series was rhombohedral ($R\bar{3}c$) and showed very good Rietveld refinement fits to their experimental data. They also presented electron diffraction data which supports the case for the rhombohedral space group. However, in our case, even using the same structural models as those used by Ubic, we failed to achieve a good fit to our experimental data.

No temperature dependent neutron diffraction measurements have been performed so far but it would be useful to make these measurements to see if there are any more subtle phase changes throughout the temperature range; for example, a tetragonal to cubic transformation such as those observed in reference [150].

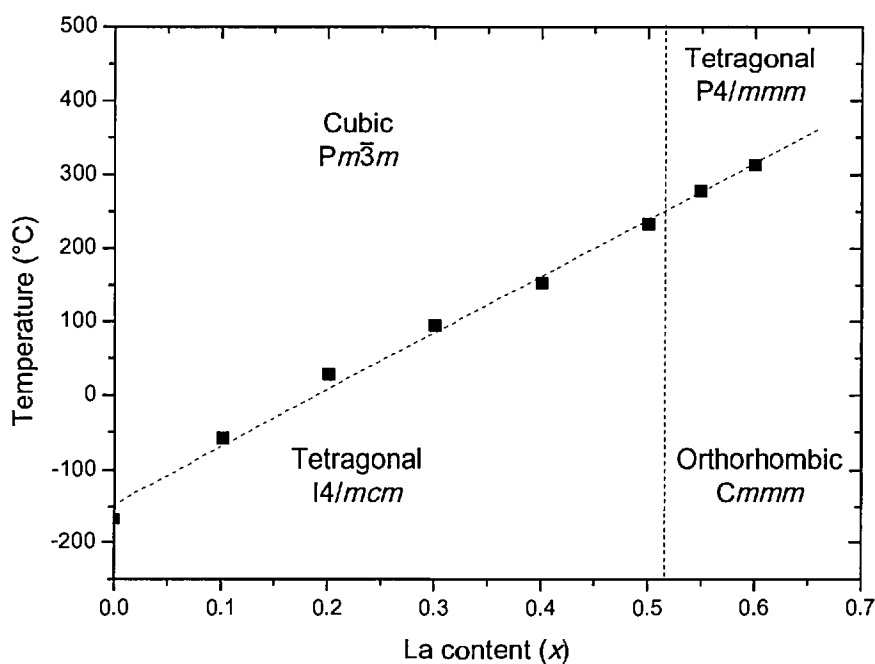


Figure 6.22: Relationship between phases in the $\text{Sr}_{1-1.5x}\text{La}_x\text{TiO}_{3\pm\delta}$ composition determined, using variable temperature neutron diffraction to follow the phase changes in each composition (after Howard [150]).

6.8.4 Coordination and oxidation state of Ce.

Evidence from structural refinement.

Even though there was an indication from the calculated lattice parameters that a small amount of cerium may substitute on the B-site, several Rietveld refinements were carried out in which the Ce occupancy was allowed to vary between the A and B-sites. Even after several cycles, no significant amount (<1%) of Ce was identified on the Ti-site (B-site).

Evidence from TEM-EELS.

From what we can observe, given the relatively low Ce concentration and therefore weak EELS signal, cerium resides on the A-site and is in the Ce(III) oxidation state. This is based on two key observations. Firstly, there are no satellite peaks in the experimental data as there would be if Ce(IV) were present. Secondly, the relative intensity of the M_5 peak is greater than the M_4 peak (see Figure 6.15 and 6.16 on page 112 and 113). This is a strong indication that cerium is in the +3 oxidation state.

6.8.5 Titanium EELS data

When compared to un-doped SrTiO₃ the Ti L_{23} edge data from Ce-doped samples suggests that there may be Ti(III), even in oxidised samples. Another point to note is that the difference between the spectra of oxidised and reduced samples is very small, which is surprising. Given the very small change in the oxygen content suggested from the dilatometry results (in section 6.7.1 on page 115), there is, however, the possibility that there is only a small, as yet un-quantified, amount of Ti(III) in the reduced samples.

Calvert [144] has analysed the Ti(III)/Ti(IV) content in a mixed valence titanate using EELS data combined with a mathematical peak-fitting routine [151]. They have shown there was very little Ti(III) in the perovskite compounds they studied, which had also been prepared in air. However, they also found that their samples more closely resembled a CaTiO₃ standard material. The similarities related to a small difference in one of the L_3 peaks (labelled B above in Fig. 6.17). This variation was attributed to a distortion of the TiO₆ octahedra [144, 152]. This may explain the similarity of our Ti-edge data in the oxidised and reduced states, shown in Figure 6.17. As we know from neutron refinements, these samples have a tetragonal distortion. As for the differences being due to the presence of Ti(III), it would seem unlikely that there would be a significant amount of Ti(III) in a sample prepared in air. To establish some of these details, a more detailed study would be needed (perhaps in combination with some theoretical modelling which can now predict EELS spectra quite accurately). We did not attempt chemical titration methods typically used to quantify Ti(III), as they are difficult to implement in these materials due to the presence of Ce(III).

6.8.6 Oxygen EELS data

Comparing the K -edge data (from the oxidised, reduced and un-doped SrTiO₃ samples) it shows there are five distinct peaks, labelled 'A'-'D'. These are similar to published data for BaTiO₃ [151]. There are some discernable differences between the samples, although they are very small. Key differences are between the relative intensity of the A and C peaks. The oxidised sample and the SrTiO₃ sample appear very similar, whereas the peak labelled 'A' in the reduced sample has a lower intensity. Without detailed

modelling and/or comparison to standard materials, such as CaTiO₃ and BaTiO₃, it is difficult to make any conclusions about the oxygen *K*-edge data at present.

6.8.7 Thermal expansion data

There is good agreement between the thermal expansion coefficient derived from the dilatometric measurements and the values calculated from the HTXRD measurements. The values are also in the range needed for viable use as a fuel cell electrode.

Another key observation was the very small volume expansion seen under reducing atmospheres. In addition to this, there was no prolonged equilibration processes were observed on cooling in CO-CO₂ mixtures. This suggests that the changes during reduction may involve a redistribution of cations rather than significant changes in oxygen content.

6.9 Conclusions

In the stoichiometric samples, the solubility limit in air for Ce is quite low, around 3-4mol% Ce. This was determined by XRD and so the solubility limit could be lower given the detection limits of X-Ray diffraction. In the A-site deficient stoichiometry (which assumes that the Ce substitutes on the A-site for Sr and that the donor charge is compensated by strontium vacancies), the solubility limit is considerably higher (closer to 20 mol %). Ubic [132] has reported a much higher solubility limit in closer to 40mol% in identical compositions. An A-site deficient composition which assumes Ce(IV) on the A-site showed phase separation between 8-12 mol % Ce when rutile precipitated.

Precise measurement of the cubic lattice parameters has shown that no matter what the intended initial composition in air, the A-site deficient composition will always form. It would seem that any other components will precipitate as a second phase. Discrimination between 'stoichiometric' and A-site deficient samples is unnecessary as the composition of a sample that was intended as 'stoichiometric' is actually a mixture of Sr_{1-1.5x}Ce_xTiO₃ and CeO₂. This is the reason why the 'stoichiometric' samples and the A-site deficient samples show such similar lattice parameters and neutron diffraction

patterns. Very similar behaviour has been observed in Nb-doped SrTiO₃ [79].

X-ray diffraction measurements suggested that these materials were cubic. However, it was shown using neutron diffraction that there is actually a tetragonal distortion, due to a slight tilting of the TiO₆ octahedra. The crystallographic positions of the cations remained the same as for the un-doped perovskite and this is the reason why we suspected the X-Ray diffraction patterns appeared to be cubic. The tetragonal structure is different to that suggested by Ubic [132], who found a rhombohedral structure. However, they also found apparent cubic symmetry when examining their samples using XRD. This is in agreement with our results.

EELS data from the Ce *M*-edge strongly suggests that the Ce is in the +3 oxidation state. This is in agreement with the phase relationships for the A-site deficient samples. Occupancy refinements of X-Ray and Neutron data also suggest that Ce resides on the A-site (and therefore probably as Ce(III)).

Ti *L*-edge and O *K*-edge data were a little more difficult to interpret fully, given the limited number of samples analysed. The results for Ti-edge data were very similar for the oxidised and reduced samples. However these differed from the data for un-doped SrTiO₃ quite significantly. This was tentatively ascribed to the slight distortion of the TiO₆ octahedra rather than to the presence of Ti(III) in both the oxidised and reduced samples. Once again, a more detailed investigation is warranted.

Thermal expansion measurements using dilatometry and HTXRD showed that these materials possess suitable expansion properties for use with electrolyte materials such as CGO and YSZ. Interestingly, the dilatometric measurements under CO-CO₂ mixtures showed that there was very little volume change under low *p*(O₂). This hints that there may be no substantial changes to the structure under reducing conditions, which is a positive attribute for an electrode material. However, it may also explain why trying to determine changes in titanium valence state and cerium occupancy were difficult to quantify between oxidised and reduced states.

Chapter 7

Transport Properties of Ce-doped SrTiO_3

7.1 Total conductivity in air

7.1.1 Un-doped SrTiO_3 and lightly Ce-doped samples

Figure 7.1 Shows the conductivity data for un-doped SrTiO_3 and three Ce-doped samples. The conductivity mechanism under oxidising conditions would appear to be similar to that in un-doped SrTiO_3 at temperatures above $\sim 400\text{-}500^\circ\text{C}$ (Region I in Fig. 7.1). The activation energy is similar for all compositions above this temperature: 1.65-1.85 eV. This is typical for strontium titanate. In the samples which have small concentrations of donor dopants, there is a change in slope below $\sim 450^\circ\text{C}$. Un-doped SrTiO_3 does not show this behaviour (Region II in Fig. 7.1). In Region II, the data for the doped samples would appear to indicate decreasing conductivity with increasing donor content; this would be possible if donor ions were counter-doping extrinsic acceptors such as Fe^{3+} or Al^{3+} impurities (as outlined in Section 5.14.5 on page 83).

Measurements for un-doped SrTiO_3 in Fig.7.1 were performed using two electrode AC impedance and gold electrodes. Total conductivity data (measured using four-point DC and platinum electrodes) are shown in Fig.7.2. The four-point DC/Pt data for un-

doped SrTiO₃ agrees well with data from the literature when platinum electrodes were also used. However, the data does not agree with that measured from the same material using AC impedance/Au electrodes. Interestingly, AC and DC data agrees very well between the doped samples, which indicates that the difference in results is probably due to the different electrode materials, particularly at lower temperatures. Gold will probably act as a partially blocking electrode, i.e, it will allow the flow of electrons but block oxygen ion conduction. Platinum can be considered to act as a reversible electrode allowing electronic conduction. While not an oxygen ion conductor in itself, Pt is known to catalyse the reduction of molecular oxygen thus improving the exchange between the sample and surrounding atmosphere. The higher conductivity seen in the SrTiO₃ samples which had platinum electrodes is probably due to the additional partial ionic conductivity, which was blocked when using gold electrodes in the AC impedance samples.

Figure 7.3 shows the difference in total electrical conductivity of 5mol% samples, one stoichiometric and the other non-stoichiometric. Samples for this study were quenched or allowed to furnace cool. Quenched samples were soaked at 1350°C for 12 hrs and then removed from the furnace and placed on a metal block to ensure a very high cooling rate. Furnace cooled samples were cooled at around 2-3°/min. This experiment aimed to identify whether loss of oxygen at high temperatures would be retained during quenching and then to see how this affected the conductivity. It can be seen that under these conditions there was a very little change in the conductivity of either sample suggesting the oxygen loss is very small at high temperatures in air. The difference in magnitude of the conductivity can be attributed to the lower actual Ce content in the 'stoichiometric' sample. As we have seen in the previous chapter, this was more likely to have the stoichiometry $Sr_{0.95}Ce_{0.033}TiO_{3\pm\delta}$, along with some additional CeO₂ second phase.

7.1.2 A-site deficient series

Figure 7.4 shows the total conductivity of the A-site deficient compositions in the series $Sr_{1-1.5x}Ce_xTiO_{3\pm\delta}$, where $x = 0.005 - 0.15$. At low dopant concentrations ($\sim 0.5\text{mol}\%$), the observed behaviour is the same as that in Figure 7.1; that is, there is a 'knee' in

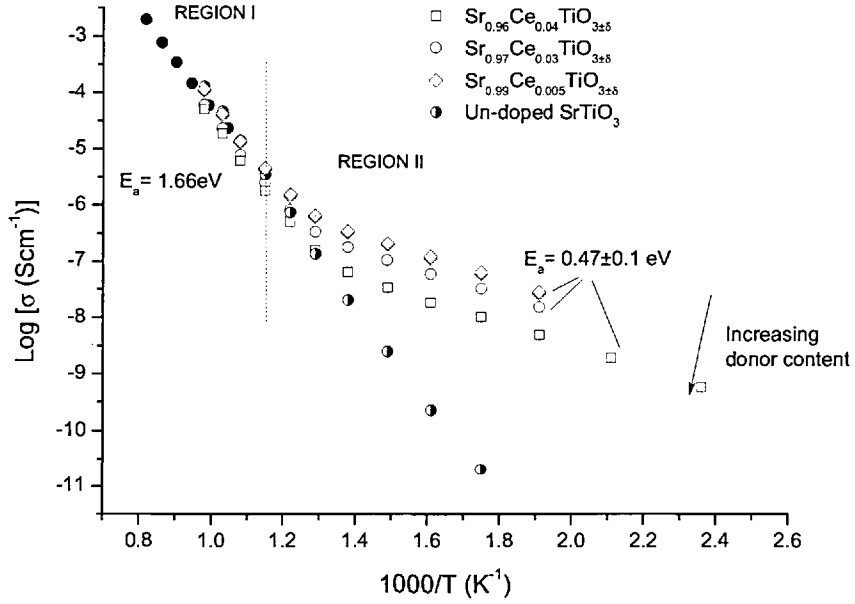


Figure 7.1: Comparison of total conductivity of un-doped SrTiO_3 (Sigma-Aldrich) and a range of lightly donor-doped samples. At low Ce concentrations there appears to be two thermal activation processes occurring between low and high temperatures: Region I, where the activation energy of doped and un-doped SrTiO_3 are very similar; and Region II, where the conductivity is apparently dependent on dopant concentration (for low donor content) but the activation energy remains constant (Open and closed symbols represent AC and DC data respectively).

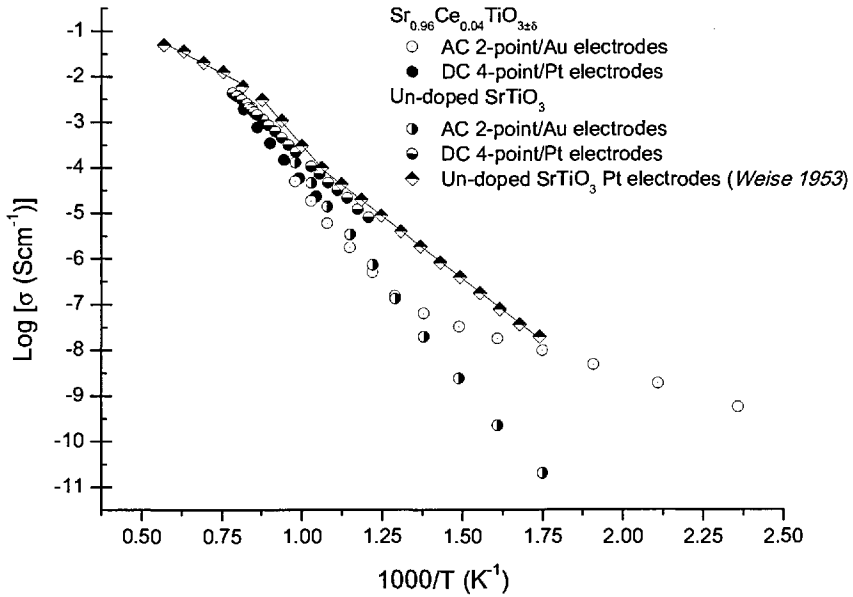


Figure 7.2: Comparison of total conductivity of un-doped SrTiO_3 (Sigma-Aldrich), SrTiO_3 data from the literature (Weise [153] *Data also reproduced in Galasso [62] pp.81.*) and a lightly doped sample (Open and closed symbols represents AC and DC data respectively).

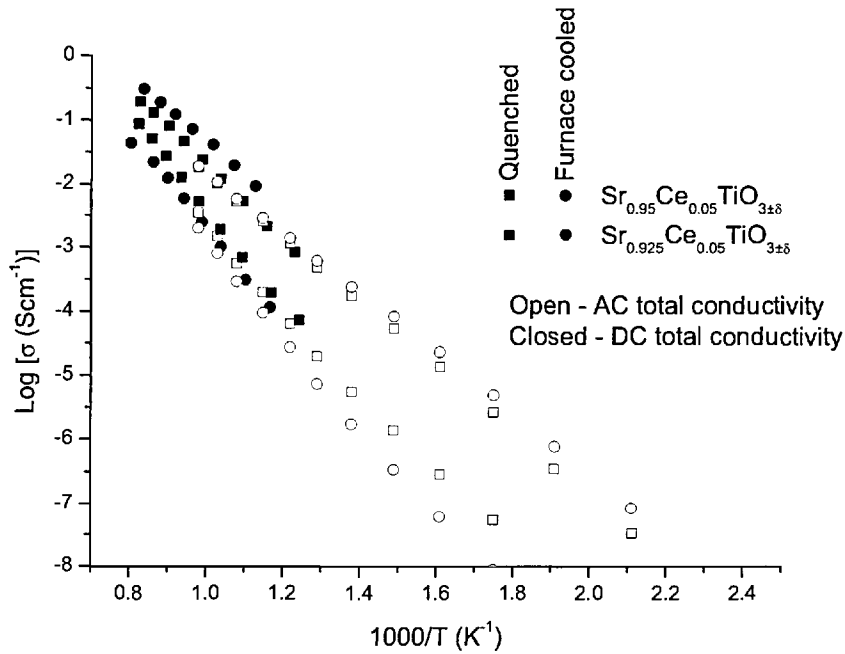


Figure 7.3: Temperature dependent total conductivity variation between samples that were quenched and furnace cooled. Very small differences in conductivity suggest only a small amount of oxygen loss at high temperature (which was confirmed by thermogravimetric analysis; see Fig.7.19) (Open and closed symbols represent AC and DC data respectively).

the $\log [\sigma]$ vs. $1/T$ plot at around 500°C. Above this temperature, the conductivity is the same as un-doped SrTiO₃.

As the cerium concentration increases, there is a steady increase in conductivity at all temperatures, as demonstrated in Figure 7.5. There are some samples which show multiple slopes in the Arrhenius plots, whereas others do not. There is no obvious trend between the cerium concentration and whether the sample will show more than one slope. Each of the samples in this series was measured twice and showed the same result. The variation of the activation energy across the series could be the result of loss of control (temperature or composition) during sample preparation or may indicate the presence of an uncontrolled impurity.

The $x = 0.005$ composition behaves similarly to the compounds in Figure 7.1, with what appears to be an impurity controlled conductivity region at lower temperatures (Region II). At higher dopant concentrations, the conductivity increases by around two orders of magnitude. Figure 7.5 shows the conductivity at various temperatures as a

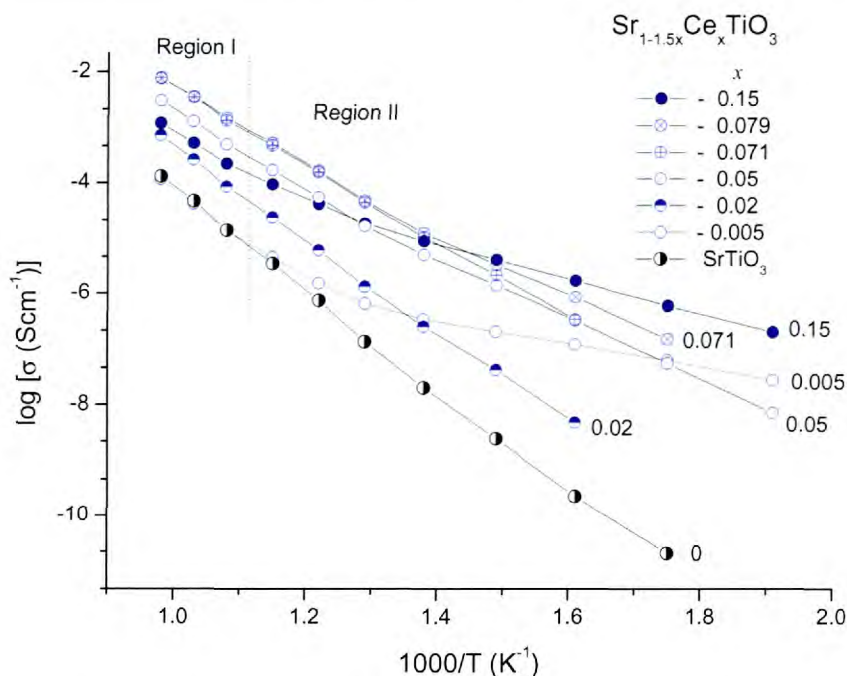


Figure 7.4: Total conductivity, determined using AC impedance and samples with Au electrodes, for a range of A-site deficient compositions.

function of cerium concentration. Without the $x = 0.15$ data point, there would be a steady increase in the conductivity with increasing cerium concentration. We are unsure if the $x = 0.15$ sample is an anomaly.

7.1.3 Electrochemical Impedance Spectroscopy - Measurements in air

Electrochemical Impedance Spectroscopy (EIS) was used extensively to obtain the data presented in the previous section. This was due to ease of sample preparation and because it allowed quick and efficient data collection through the use of computer controlled data acquisition.

As outlined in Section 5.9.1 on page 72, gold electrodes were used exclusively for these measurements. As already mentioned, these essentially act as blocking electrodes for oxygen ion transport. Examples of the data from the EIS studies are shown in Figures 7.6 and 7.7, which compare the response of un-doped SrTiO_3 and Ce-doped SrTiO_3 .

Figure 7.6 shows the data for un-doped SrTiO_3 at 550°C in air. On first inspection (Fig. 7.6a), there appears to be only one arc with a capacitance of $\sim 10^{-9}\text{F}$; this is

Table 7.1: Thermal activation energy for the Sr_{1-1.5x}Ce_xTiO₃ series of compositions shown in Figure 7.4.

Composition x	Activation energy, E_a	
	(kJmol ⁻¹)	(eV)
SrTiO ₃	178.21	1.85
SrTiO ₃ lit.	159.9	1.66
0.005	157.35	1.63
-	45.88	0.48
0.02	164.32	1.70
0.05	146.19	1.52
-	107.9	1.12
0.071	141.53	1.47
-	103.48	1.07
0.78	139.54	1.45
0.15	123.92	1.28
-	65.48	0.68

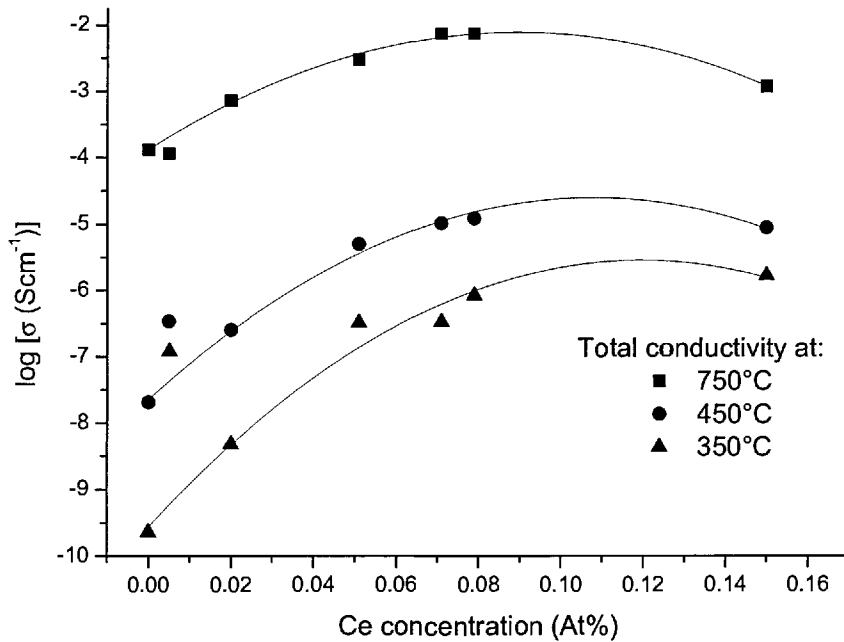


Figure 7.5: Variation of total electrical conductivity with Ce concentration at 750, 450 and 350°C. At high temperature the activation energies are very similar for all compositions. At lower temperatures, there seem to be several thermal activation processes. The result for the 0.005 mol% sample seem unusual. Lines are a guide for the eye.

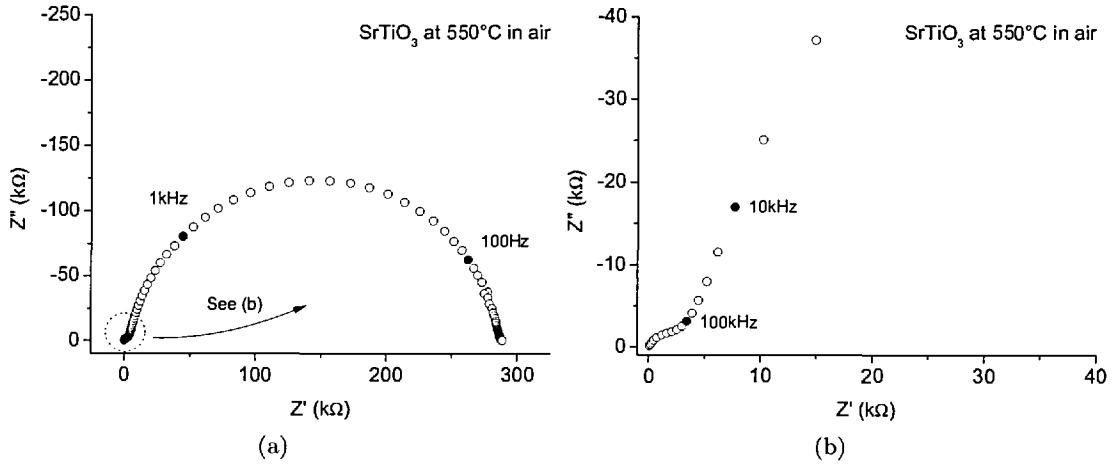


Figure 7.6: Complex impedance plot of un-doped strontium titanate showing grain boundary dominated response and a small, high frequency, arc due to the grain interior.

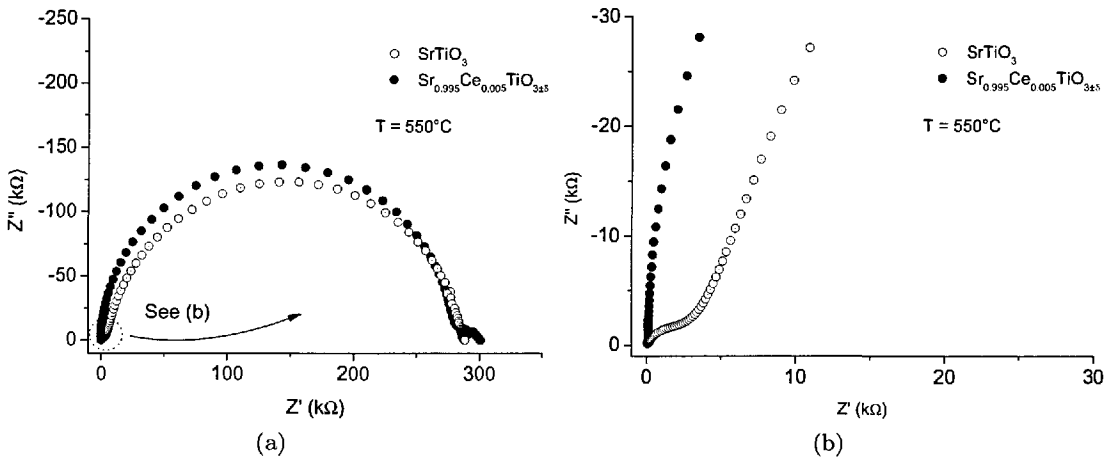


Figure 7.7: Comparison of un-doped and 0.5 mol% Ce-doped strontium titanate. In the doped samples a single arc dominates and the smaller arc associated with the bulk is no longer visible.

typically associated with the grain boundary. An examination of the detail in the high frequency portion of the plot is shown in Figure 7.6b. This reveals a smaller arc with a capacitance of $\sim 10^{-12}\text{F}$; this is typically associated with the bulk response of individual grains.

By comparison, Figure 7.7 shows the data, under identical conditions (550°C, air), for a 0.5mol% Ce-doped sample. Only one arc is observed with a capacitance of $\sim 10^{-9}$ - 10^{-10}F which suggests that it is associated primarily with the grain boundaries. Results for the Ce-doped sample in Fig. 7.7 were typical of all the Ce-doped compounds at all

temperatures; that is, only one arc was observed. There is no indication that the single arc is two overlapping arcs or that there is any discernable small arc at high frequencies to indicate the magnitude of the bulk response.

Another technique which has been successfully employed for SrTiO₃ and BaTiO₃ is the analysis of impedance data using combined impedance-modulus plots [154–157]. Figure 7.8 shows a combined Z'' - M'' or 'spectroscopic' plot. The rationale for this approach becomes clear on inspection of the equations for the imaginary part of the impedance (Z'') and modulus (M''):

$$Z'' = R \left(\frac{\omega RC}{1 + (\omega RC)^2} \right) \quad (7.1)$$

and

$$M'' = \frac{C_0}{C} \left(\frac{\omega RC}{1 + (\omega RC)^2} \right) \quad (7.2)$$

where ω is the angular frequency ($2\pi f$) and C_0 is the vacuum capacitance of the measuring cell. Since the term in the large parentheses is the same in both equations, the size Z'' and M'' will be proportional to R and $1/C$ respectively. In this way it becomes easier to identify arcs with smaller capacitances or overlapping arcs, as they can be clearly resolved in the modulus plot. This can be seen in Figure 7.8 for un-doped SrTiO₃ where the small arc associated with the bulk appears clearly in the M'' vs $\log(f)$ plot. However in the doped sample there is no second peak in the modulus plot.

7.2 $p(\text{O}_2)$ -dependent measurements

7.2.1 Conductivity measurement

Figure 7.9 shows samples prepared in air and then measured under a range of controlled oxygen partial pressures. The samples were heated up to the test temperature (900°C in the case of Fig. 7.9), and then measured from high to low $p(\text{O}_2)$ and then back to

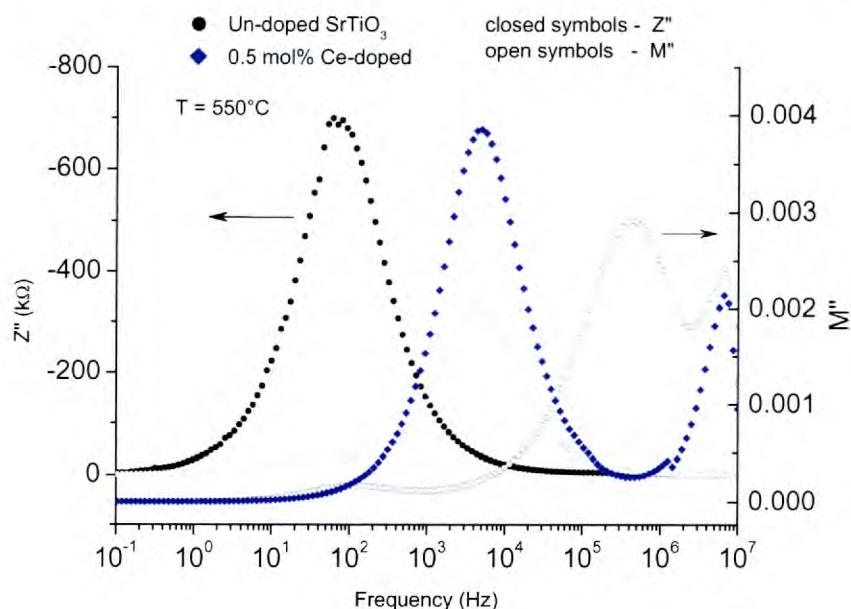


Figure 7.8: Spectroscopic plot of un-doped strontium titanate and 0.5 mol% Ce-doped SrTiO₃. The arc associated with the bulk in un-doped SrTiO₃ is seen very clearly in the modulus plot at higher frequencies. In the doped sample the only discernable peaks coincide in the impedance and modulus plot.

high $p(\text{O}_2)$.

As the $p(\text{O}_2)$ was changed from high to low, all of the samples shown in Fig. 7.9 showed typical $p(\text{O}_2)$ -dependencies: $-1/4$, $-1/5$, and $-1/6$. As described in the caption, the slopes on the graph are not fitted but actual $-1/4$, $-1/5$ and $-1/6$ slopes plotted directly over the data. The theoretical slopes (which were derived on page 24) and the experimental data agree well. In figure 7.9A, however, there seems to be no particular $p(\text{O}_2)$ dependencies. The slope of the data is less than $-1/6$, which is unusual, although this may represent a region of $p(\text{O}_2)$ -independent conductivity. On the return leg (from low to high $p(\text{O}_2)$), it would appear the conductivity becomes practically independent of the $p(\text{O}_2)$ for all samples and does not return to previous values, even after several hours at each $p(\text{O}_2)$ step. Possible reasons for this behaviour are discussed below.

7.2.2 Thermopower measurements

Figure 7.10 shows the Seebeck coefficient measured simultaneously with the conductivity data shown in Fig. 7.9. The conductivity is predominantly n-type (inferred from the negative Seebeck coefficient) for all materials throughout the whole $p(\text{O}_2)$ range,

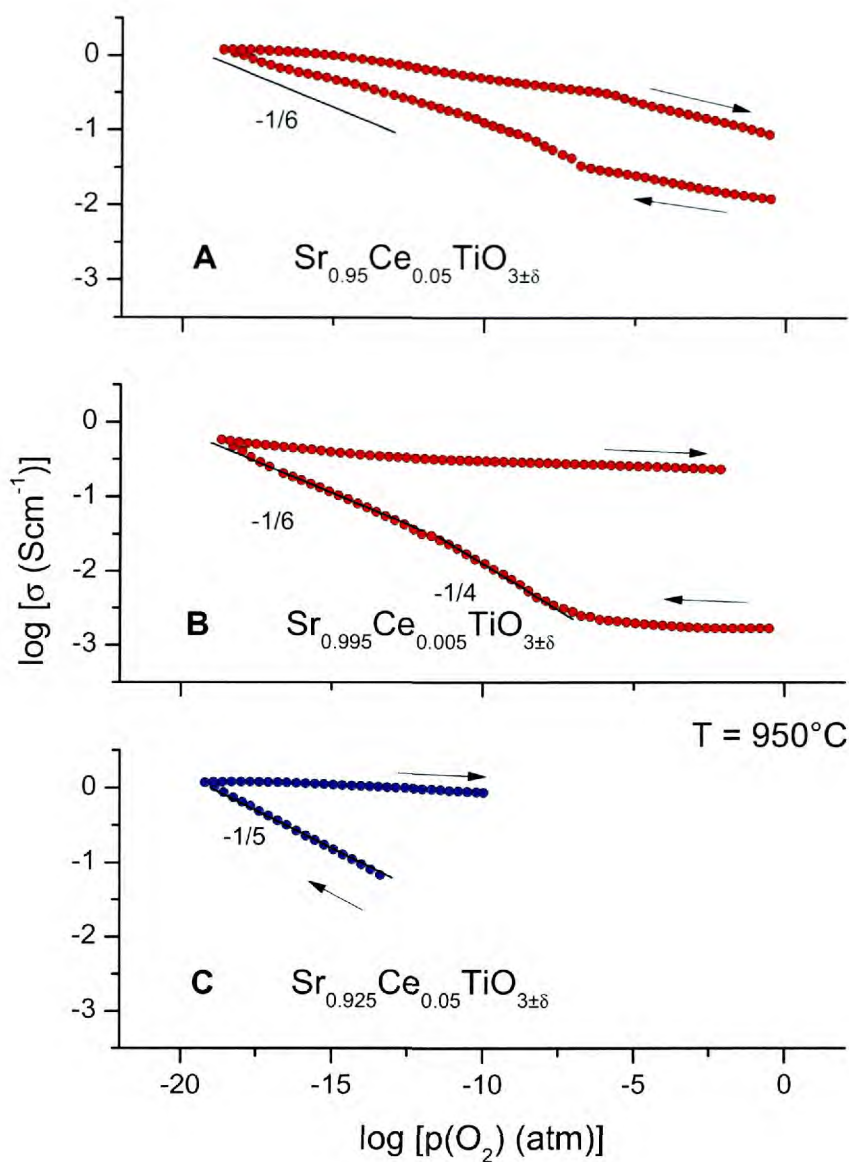


Figure 7.9: Oxygen partial pressure dependence of the total conductivity of as-prepared samples on reduction and subsequent oxidation at 950°C . Each slope has been superimposed (rather than fitted) on the data to show the deviation from the typical $p(\text{O}_2)$ -dependent slopes. The data fits well to the ideal slopes in some case but in others, such as in (A), there seems to be more complex phenomena operating. There is only partial data for $\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$ because of a problem during the experimental run. Unfortunately, due to the lengthy time span of each run, it was not possible to repeat the experiment.

Table 7.2: Average slopes of the conductivity vs. $p(\text{O}_2)$ dependencies for as-prepared samples, calculated using the model: $\sigma_n = \sigma_n^0 \times p(\text{O}_2)^{-\frac{1}{m}}$. Slopes are also marked in Figure 7.9.

Composition	$p(\text{O}_2)$ atm.	$1/m$
$\text{Sr}_{0.995}\text{Ce}_{0.005}\text{TiO}_{3\pm\delta}$	$10^{-19} - 10^{-9}$	-1/6
$\text{Sr}_{0.95}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$	$10^{-19} - 10^{-9}$	-1/9
$\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$	$10^{-20} - 10^{-14}$	-1/5

as is expected for a donor-type material.

It is also interesting to note the magnitude of the Seebeck coefficient (~ -400 to $-800 \mu\text{VK}^{-1}$), which is significantly higher than other rare-earth doped SrTiO₃ which show values around -100 to $-300 \mu\text{VK}^{-1}$ [158–160].

Figure 7.11 shows data that was extracted from the Seebeck measurements over a range of temperatures and plotted in Arrhenius form. For the 0.005at% doped sample a different slope in the Seebeck vs. $1/T$ plot may suggest a different conductivity mechanism at low donor concentrations.

7.3 Reduction Properties

The rate of reduction or oxidation is vital if these materials are to be used as fuel cell electrodes. As indicated by the $p(\text{O}_2)$ -dependent measurements above, even over long periods, it was difficult to re-oxidise these compounds after they had been reduced; this could be an advantage for any potential fuel cell electrode material. These compounds tend to show very slow reduction and oxidation kinetics which is consistent with other titanates [161]. Figure 7.12 shows the reduction profile of three A-site deficient compositions. Clearly, even after 50-70 hrs at high temperature there was still a slow reduction process taking place. However, what can also be seen in Figure 7.12b was that, when plotted against $t^{1/2}$, there are several linear sections. These linear portions of the plot indicate diffusion control (because the diffusion length is proportional to $\sqrt{Dt}$). As mentioned in the figure caption, several linear sections may indicate several different diffusion controlled mechanisms operating during the reduction process.

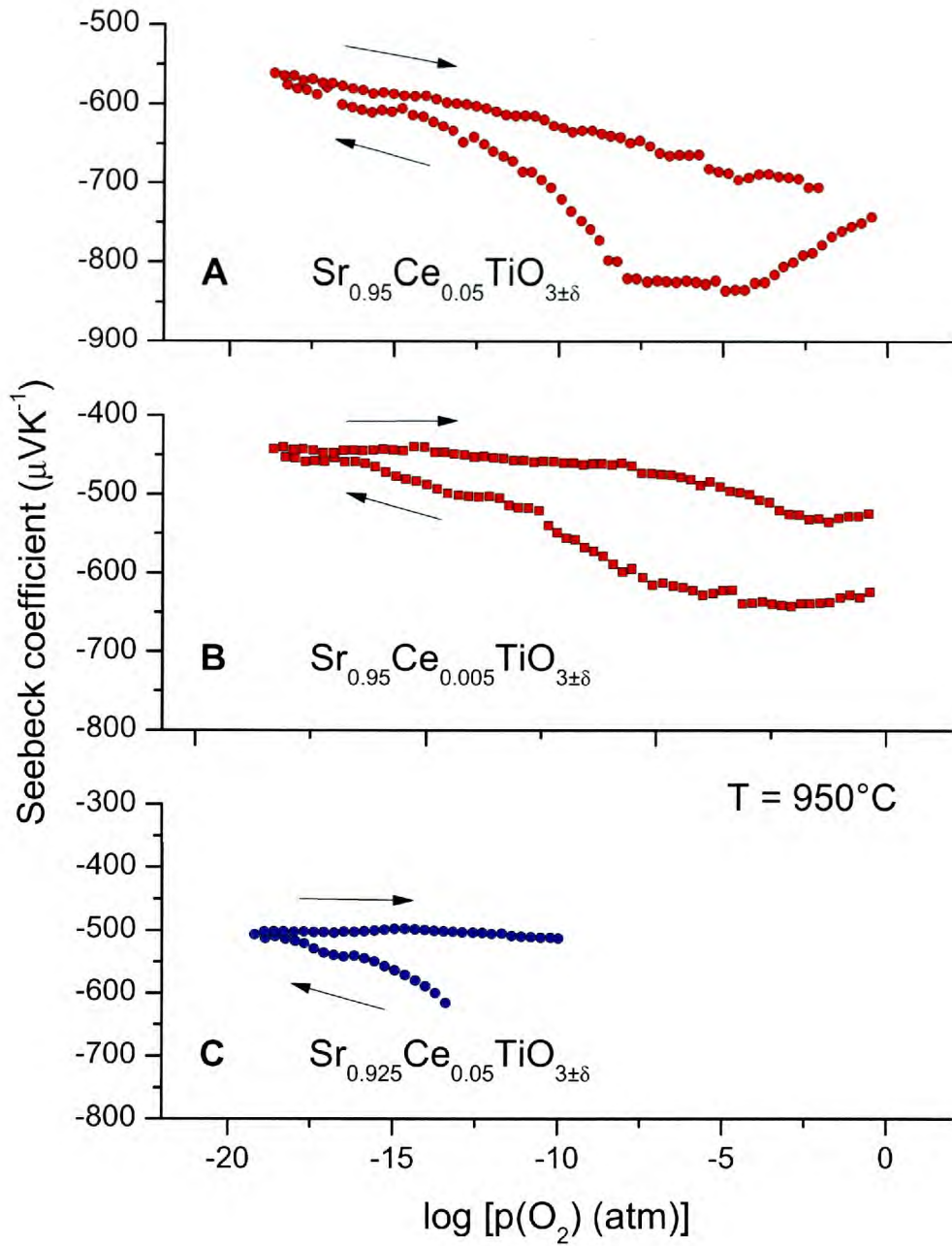


Figure 7.10: Oxygen partial pressure dependence of the Seebeck coefficient of as-prepared samples on reduction, and subsequent oxidation at 950°C .

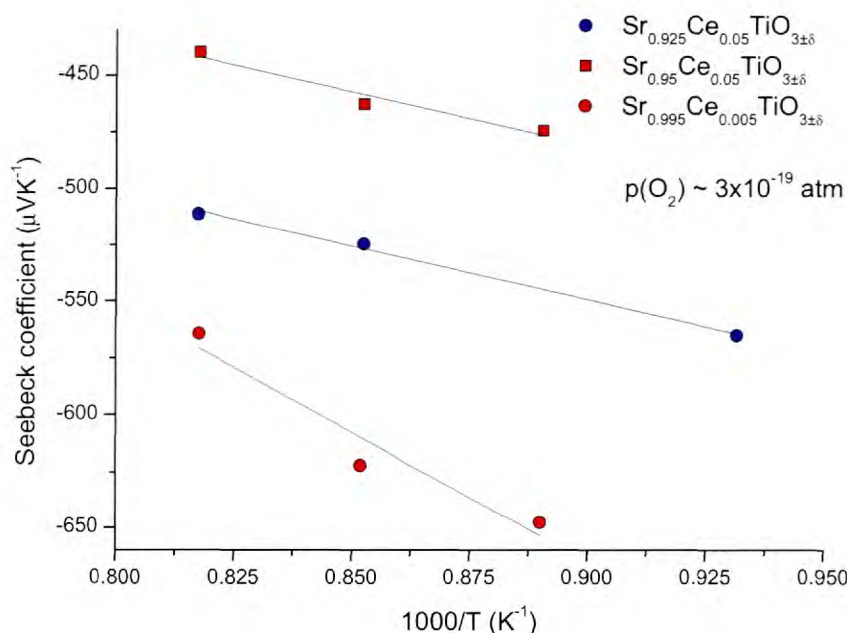


Figure 7.11: Temperature dependence of the Seebeck coefficient of reduced samples at $p(\text{O}_2) = 3 \times 10^{-18}$ atm.

Figure 7.13 compares reduction at 600°C and 900°C. Unsurprisingly, reduction is significantly slower at low temperatures. Reduction at even higher temperatures shows more pronounced effects as demonstrated by the high conductivity in samples reduced for 24 hrs at 1350°C (see Figure 7.14).

7.4 Electrical Conductivity under reducing conditions

After a long period of reduction at temperatures around 800-900°C, the conductivity of Ce-doped strontium titanate is $\sim 1.5 - 3.5 \text{ Scm}^{-1}$. Maximum conductivity, however, depends heavily on the temperature at which the reduction treatment takes place. The ultimate conductivity of these materials would appear to be more dependent on the temperature of the reducing treatment than on the concentration of donors. From *in-situ* measurements, as shown in Figure 7.12, the conductivity is still increasing after some 70 hrs. The upper temperature limit of the conductivity apparatus prevented measurements above 900°C. Samples reduced at higher temperatures (1250-1350°C 10% H_2/Ar) for 24hrs were transferred to the conductivity apparatus for temperature-dependent measurement. Figure 7.14 shows that higher reduction temperatures result in far higher conductivity compared to the samples reduced at 900°C, even though the

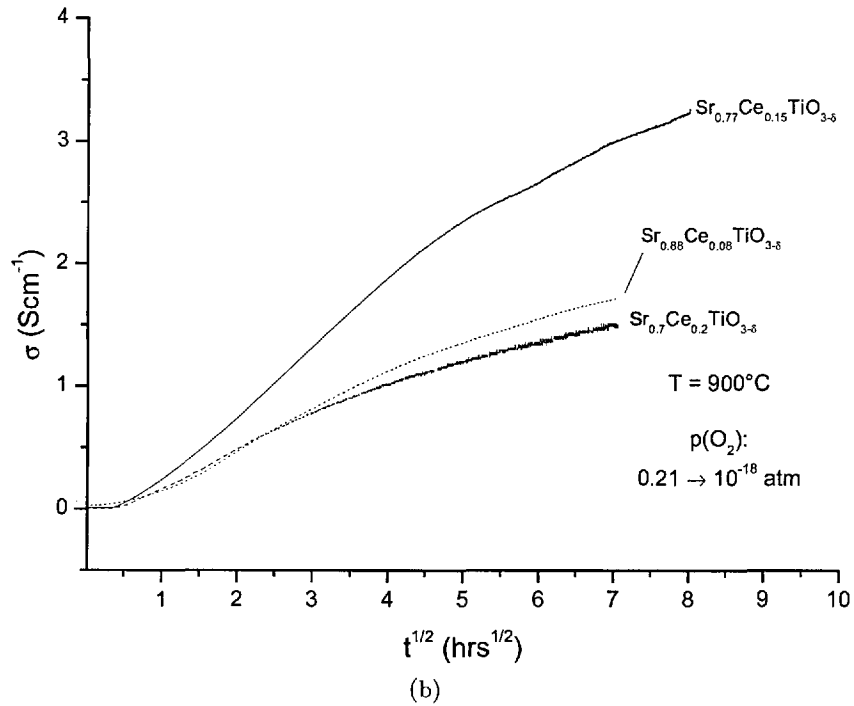
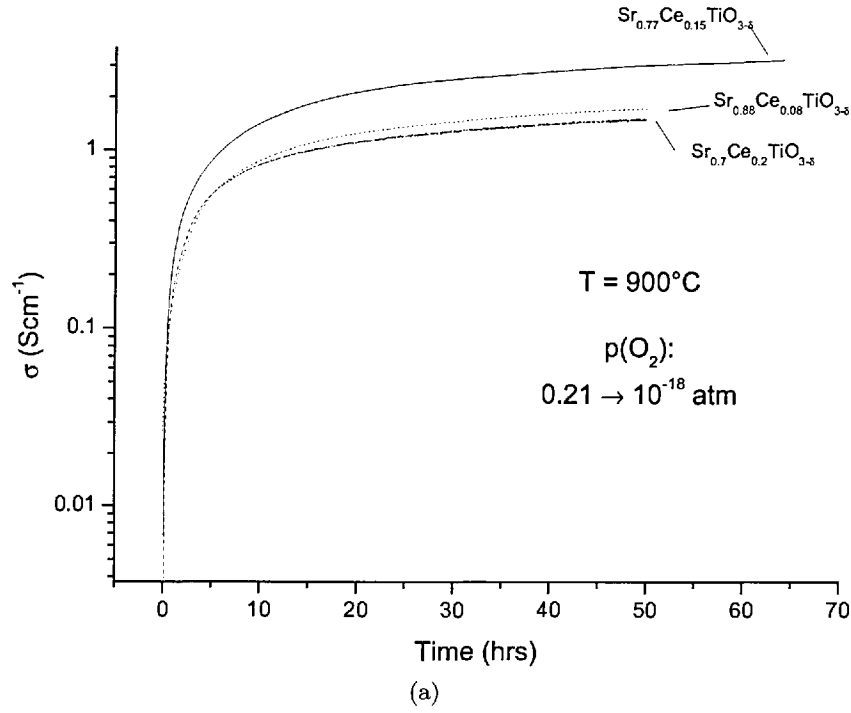


Figure 7.12: (a) Reduction profiles of A-site deficient compositions at 900°C in 10%H₂/Ar. Samples had a cross sectional area of 0.131±0.01cm². (b) Data in (a) plotted against $t^{1/2}$, which shows linear sections which could be related to diffusion controlled processes. There may be several diffusion limited processes during reduction such as diffusion through porosity, surface diffusion processes, across grain boundaries and diffusion through the bulk.

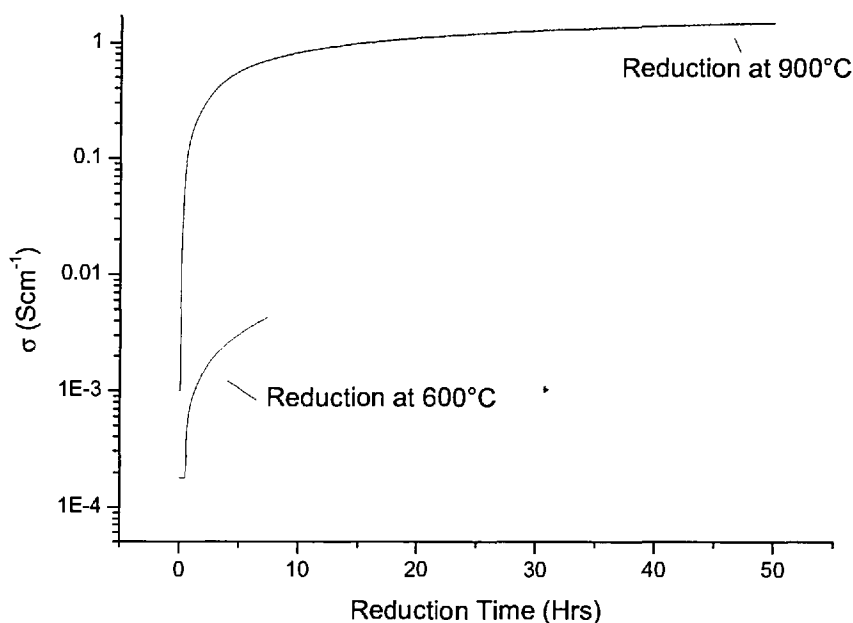


Figure 7.13: Effect of temperature on reduction profile for $\text{Sr}_{0.7}\text{Ce}_{0.2}\text{TiO}_{3\pm\delta}$ in 10% H_2 /Ar. Clearly this has implications for use under fuel cell condition.

reduction time at 1350°C was only 24hrs. It also shows the clear difference between the A-site deficient sample and the stoichiometric sample of the same composition ($x = 0.05$) both of which were reduced under identical conditions.

Consideration was given to that fact that the samples reduced *ex-situ* may have been exposed to a different $p(\text{O}_2)$ during measurement of the conductivity, compared to the reduction process at high temperature. Steps were taken to minimise these variations by reducing and measuring the sample in nominally the same atmosphere. During measurement the sample was allowed long periods ($\sim 3\text{--}4$ hrs) between each measurement in order to equilibrate with the surrounding atmosphere. Measurements were also taken during cooling and heating cycles. Figure 7.14 shows that there was no hysteresis during the measurement, which suggests stability (but not necessarily equilibrium!) during these measurements.

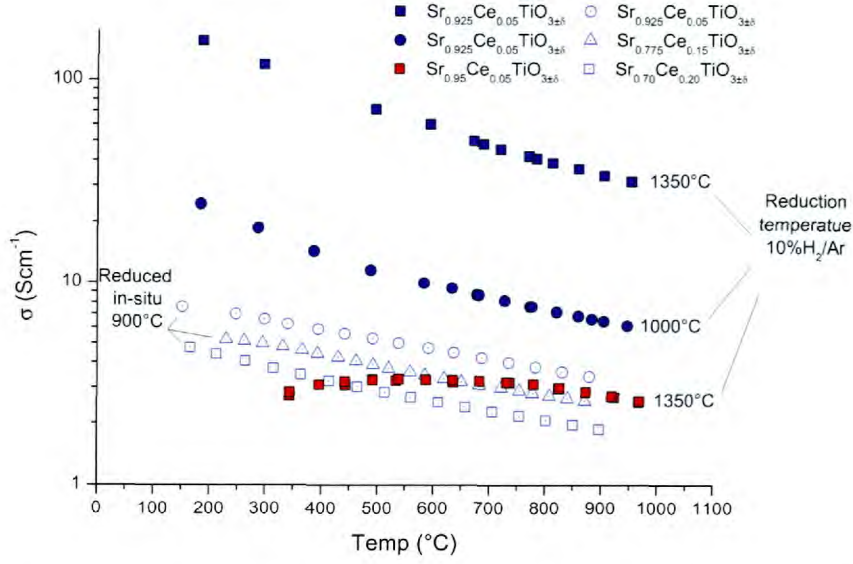


Figure 7.14: Temperature dependent conductivity of reduced A-site deficient compositions. Samples were measured after reduction at the temperatures indicated. The reduction process for those samples reduced at 900°C was shown in Fig. 7.12.

7.5 Diffusion properties

7.5.1 Isotopic oxygen exchange

Figure 7.15 shows the ^{18}O and ^{16}O depth profiles of $\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$ exchanged at $p(\text{O}_2) = 0.21$ atm and 900°C. Three profiles were recorded from three discrete regions of one sample. One profile was taken from an individual grain, while the other two were taken from an area containing several grains. Figure 7.16 shows the sputtered craters from a single grain acquisition (Fig. 7.16a) and a multiple grain acquisition (Fig. 7.16b).

The raw data, shown in Figure 7.15, shows the sharp decrease in concentration near the surface for both ^{16}O and ^{18}O . The sharp initial drop in concentration, which may have resulted from an instrumental effect or an unusual surface layer, resulted in a very sharp initial decrease in the isotopic ratio. It proved very difficult to fit the diffusion equation to this data. Surface layers are considered to play an important role in titanate materials as it has been shown that the quality of the surface can have a large influence on the diffusion profile in SrTiO_3 [162]. Considering the depth of the profile was in the order of 400-1000nm and the final polish on the sample surface was down to $1/4\mu\text{m}$, this

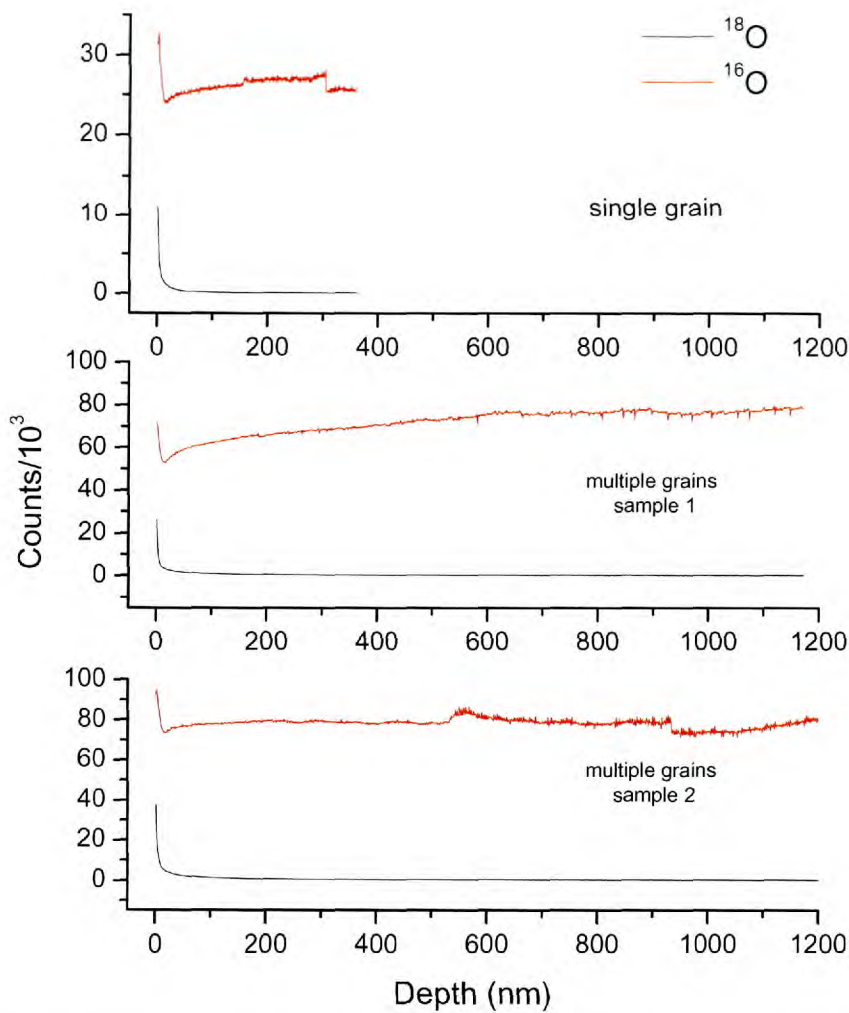


Figure 7.15: FIB-SIMS ^{18}O and ^{16}O depth profile data recorded from a $\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$ sample. The ^{18}O exchange was performed at 900°C $p(\text{O}_2) = 0.21$ atm $t = 30$ mins.

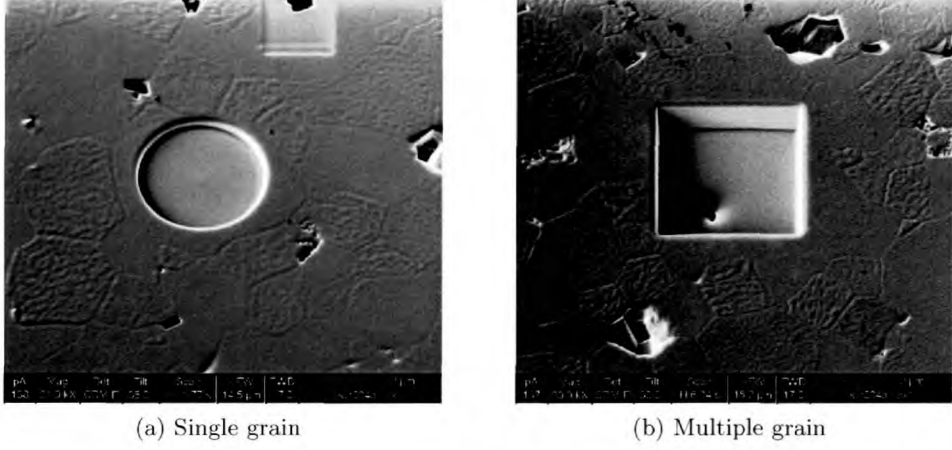


Figure 7.16: Secondary electron images showing the sputter craters after the depth profiles were taken. Grain boundaries can clearly be seen and demonstrates how a single grain profile was achieved. The estimated grain size for this sample is in the order of 3-4 μm . The sputtered collection areas were $\sim 5\mu\text{m}^2$ for all samples.

would mean the surface will be, at best, covered in 250nm scratches. The 1/4 μm media has no doubt caused some subsurface damage but we were not able to assess the depth of subsurface polishing defects. Due to the sharp decrease in initial concentration, the first 25nm of surface data was removed in order to improve the fitting routine.

Figure 7.17 demonstrates what data was removed (Fig.7.17a, shaded) and the data used (Fig. 7.17b) when fitting to the diffusion equation (eq. 7.3). Even with a relatively rough fit to the diffusion equation, the diffusion coefficient (D^*), and the surface exchange coefficient (k), were estimated. Table 7.3 shows that the estimated results agree well with the results published by Kiessling [161] for single-crystal 0.3mol% La-doped SrTiO₃.

$$C(x, t) = \frac{C - C_{bg}}{C_g - C_{bg}} = \text{erfc} \left[\frac{x}{2\sqrt{D^*t}} \right] - \left[\exp \left(\frac{kx}{D^*} + \frac{k^2t}{D^*} \right) \times \text{erfc} \left(\frac{x}{2\sqrt{D^*t}} + k\sqrt{\frac{t}{D^*}} \right) \right] \quad (7.3)$$

where C is the isotopic concentration at depth x ; C_{bg} is the background isotopic concentration; D^* is the self diffusion coefficient; k is the surface exchange coefficient; and

t is the diffusion time

Table 7.3: Calculated D^* and k values extracted from the fits shown in Fig.7.17. Even though the theory does not fit the data from the multi-grain sample, calculated parameters agree well with the literature values for La-doped SrTiO₃ (*see text*).

Region	D^* (cm ² /s)	k (cm/s)	Reference
Single grain	7.2×10^{-15}	2.2×10^{-10}	This work
Multiple grain	4.3×10^{-14}	6.0×10^{-10}	This work
0.3mol% La-SrTiO ₃ single crystal	9.4×10^{-14}	7.2×10^{-9}	[161]

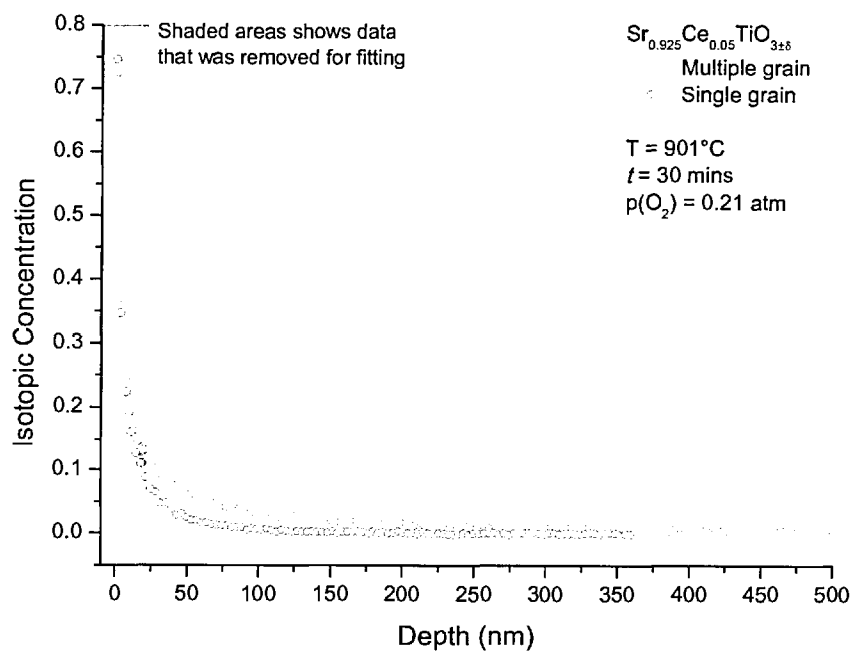
7.6 Thermogravimetry

Evaluation of the oxygen loss in samples prepared in air and the fate of oxygen during the reduction process showed two main features. Figure 7.18 shows that the initial weight loss from SrTiO₃ has significant hysteresis, probably due to the loss of volatile impurities. When the same sample was re-heated, the weight loss was reproducible on heating and cooling. The total weight loss was assumed to be due to oxygen loss alone. From this, the high-temperature oxygen stoichiometry for un-doped SrTiO₃ was found to be SrTiO_{2.98}.

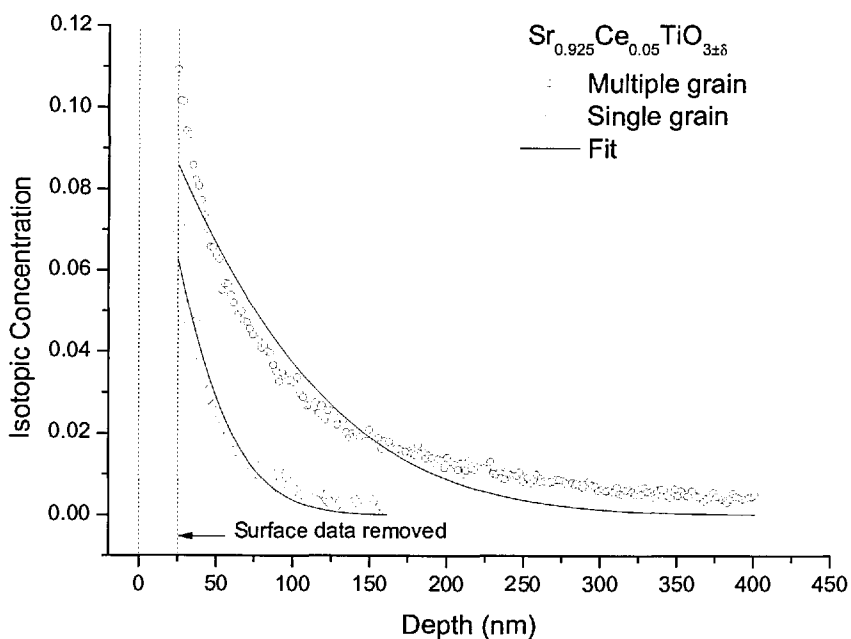
Data for the Sr_{0.775}Ce_{0.15}TiO_{3±δ} sample is shown in Figure 7.19 and again demonstrates the result of the first measurement cycle and the subsequent measurement (i.e. the loss of volatile components). There is actually a slight increase in weight after the second measurement. We are unsure whether this has any significance. Given these materials are oxygen excess, we would not expect significant oxygen loss in air.

Figure 7.20 shows the re-oxidation of samples that were treated under reducing conditions at 1350°C (from the conductivity measurement in Section 7.4). These were then re-oxidised in air. The stoichiometric sample appears to oxidise at a lower temperature than the A-site deficient sample. The overall increase in oxygen content is similar, which suggests similar levels of reduction.

The increase in weight, under oxidising conditions, has been attributed only to an increase in oxygen content. Given this assumption, the oxygen stoichiometry can be back calculated for samples treated under reducing conditions. Figure 7.20 clearly



(a)



(b)

Figure 7.17: (a) The complete data set, showing the isotopic concentration derived from the data in Fig. 7.15. Near surface data were removed because they were thought to contain potentially large errors caused by surface damage and instrumental interference. (b) Expanded view of the truncated data from (a), showing the theoretical fit to the numerical solution of the diffusion equation. Even with suspect data eliminated, the theoretical fit to the data was unsatisfactory.

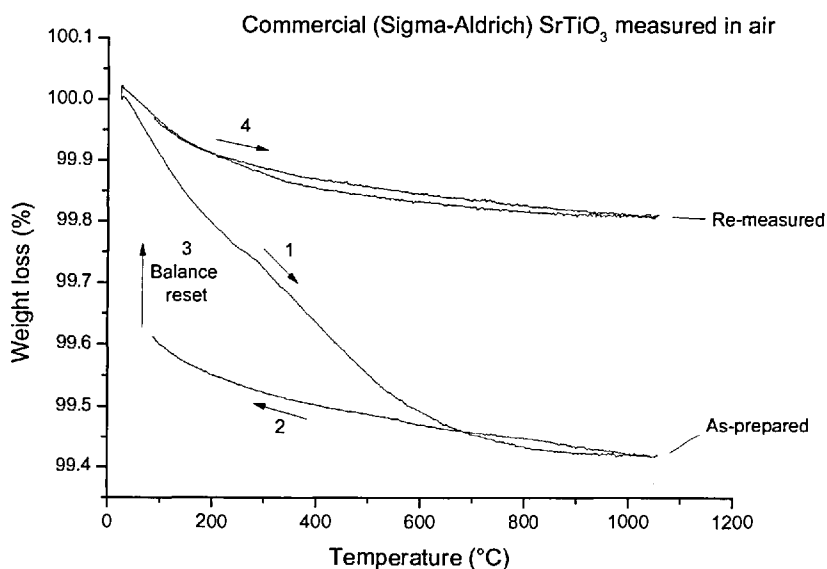


Figure 7.18: Comparison of the weight loss (assumed to be only oxygen over this temperature range) for un-doped SrTiO₃. On the first run there was some hysteresis on cooling, presumably due to adsorbed water or CO₂. When the same sample was re-measured, no hysteresis occurred and the weight loss could be considered due to loss of oxygen only. Heating/cooling rate = 5° min⁻¹.

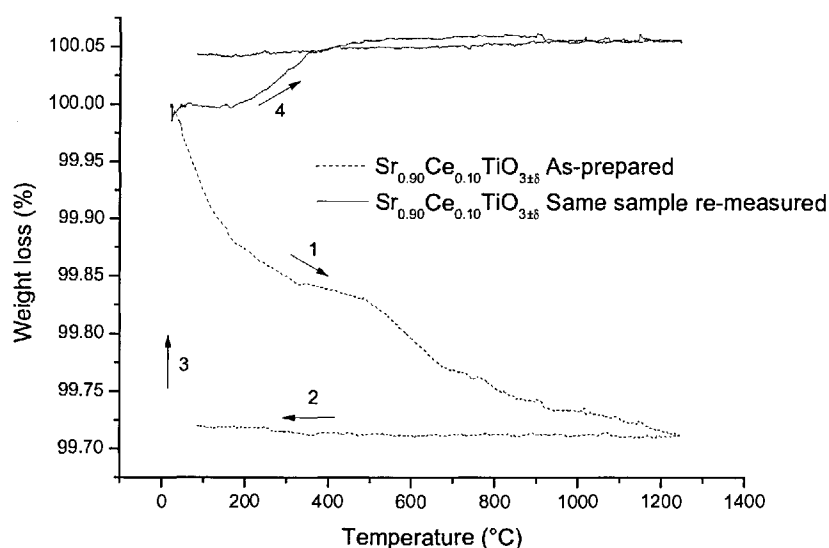


Figure 7.19: As seen in Fig. 7.18, hysteresis was observed during the first measurement. On the second measurement no hysteresis occurred. Once the volatile impurities were removed, we see very little oxygen loss (there was actually a slight weight gain). Heating/cooling rate = 5° min⁻¹.

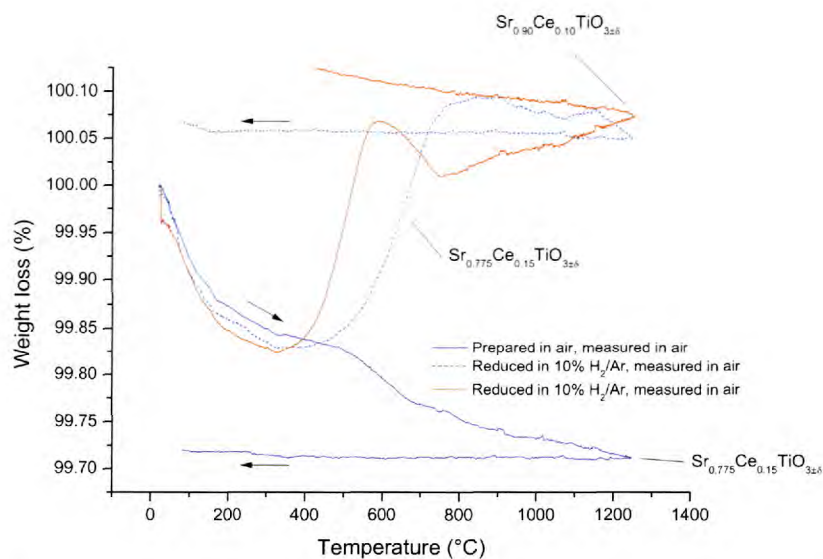


Figure 7.20: Shows samples reduced at 1350°C in 10% H_2 /Ar and then measured in air (from conductivity measurements shown in Fig. 7.14). The weight gain is assumed to be due to oxygen incorporation and differs significantly between stoichiometric and A-site deficient samples. Heating/cooling rate = 5°min^{-1} .

Table 7.4: Oxygen stoichiometry after reduction at 1350°C in 10% H_2 /Ar for 24hrs. The stoichiometry was calculated from reduced samples that were re-oxidised in air. The weight gain was assumed to be entirely due to oxygen.

Sample	Pre-treatment (Measured)	$3 \pm \delta$
$\text{Sr}_{0.90}\text{Ce}_{0.10}\text{TiO}_{3 \pm \delta}$	1350°C - 10% H_2 /Ar (air)	2.973
$\text{Sr}_{0.775}\text{Ce}_{0.15}\text{TiO}_{3 \pm \delta}$	1350°C - 10% H_2 /Ar (air)	2.970
$\text{Sr}_{0.775}\text{Ce}_{0.15}\text{TiO}_{3 \pm \delta}$	air (air)	3.007

shows that the weight changes are measurable but quite small. Calculation of the oxygen stoichiometry from the re-oxidised samples is summarised in Table 7.4. Only very small oxygen loss is observed, even after rather severe reduction. Another point to note is the relatively fast re-oxidation of the powdered samples. This is in contrast to the $p(\text{O}_2)$ -dependent conductivity measurements on dense (or nearly dense) bar samples, which showed significantly slower redox kinetics.

The continued increase in the data for the stoichiometric sample in Figure 7.20 was due to an experimental problem with our thermo-balance and should not be considered as a continuation of the oxidation process.

7.7 Discussion

7.7.1 Electrical conductivity at low dopant concentrations

Conductivity measured in air using AC and DC methods shows some interesting features. In the case of samples measured using AC impedance and gold electrodes, data for un-doped SrTiO₃ and the lightly doped samples shows good agreement at temperatures above $\sim 500^\circ\text{C}$. At low cerium concentrations (~ 0.5 -1 at%), however, a 'knee' was observed either side of 500°C ; un-doped SrTiO₃ does not show this characteristic. We have interpreted this as a shift from an intrinsic conduction mechanism at high temperatures to an extrinsic mechanism, potentially impurity controlled, at lower temperatures. It is also tempting to suggest that the magnitude of the conductivity in the low temperature region decreases with increasing donor content. This would be consistent with a mechanism whereby the small donor content ($[\text{Ce}] = 0.05 \text{ cat\%} \sim 380 \text{ p.p.m.}$) is counter doping existing acceptor impurities ($[\text{Fe,Al}] \sim 1000 \text{ p.p.m.}$), thus reducing the p-type conductivity in air. However, this interpretation should be treated with caution for two reasons. Firstly, the donor concentrations shown in Fig. 7.1 are the nominal values calculated from the amounts weighed in during synthesis and have not been accurately quantified for each sample (and so there is some doubt as to the 'actual' cerium concentration). Secondly, if the 'knee' was a result of a switch to an extrinsic, acceptor controlled, conduction mechanism we would expect that un-doped SrTiO₃ would also show this effect. It clearly does not, even though all of the samples have similar acceptor impurity content (See Table 5.4 on page 83)

7.7.2 Electrical conductivity in an A-site deficient series

The strontium vacancy compensated series ($\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_{3\pm\delta}$) shows an increase in the total conductivity with increasing cerium concentration (see Fig.7.4). However, the $x = 0.15$ sample shows a decrease in the total conductivity compared with the rest of the series (see Fig. 7.5 on page 130). Without the $x = 0.15$ sample, there would be a linear dependence of conductivity with cerium concentration. Further work is necessary to establish whether there is a maximum in the conductivity around 8 mol% Ce or if the data for the $x = 0.15$ sample is erroneously low.

7.7.3 p(O₂)-dependent measurements

An initial inspection of the p(O₂)-dependent conductivity data shows that, at low doping levels, these materials behave in a very similar way to typical un-doped SrTiO₃. Figure 7.9 has been reproduced in Figure 7.21 along with data from the literature for un-doped SrTiO₃ [42] and 2% La-doped SrTiO₃ [43].

This comparison shows a number of important features: No modification was made to either data set, experimental or literature, and the agreement between them is very good. Comparison of the Sr_{0.995}Ce_{0.005}TiO₃ data with un-doped SrTiO₃ shows excellent agreement at low p(O₂), where -1/6 and -1/4 slopes were observed in the doped samples. Between p(O₂) = 1 × 10⁻⁷ - 0.21 atm there is a plateau region in the x=0.005 sample. However, it is unusual for there to be a plateau region following a -1/4 and -1/6 slope. The standard model for the behaviour of a donor doped material (as shown schematically in Fig. 7.22), from low to high p(O₂) (left to right), is -1/6 to plateau to -1/4 slope respectively. Experimental data from Balachandran [43] for 2 mol% La-doped SrTiO₃ is shown overlayed on Figure 7.21, where the typical change from -1/4 to plateau region is clearly visible (the transition to -1/6 is not observable at 900°C). At present we cannot explain the plateau region in the x = 0.005 sample.

The stoichiometric x = 0.05 sample shows a considerable increase in the conductivity compared with the non-stoichiometric sample. The lower conductivity in the A-site deficient sample has been interpreted as counter doping of the Ce(III) donors by strontium vacancies, which should act as acceptors. There are no ideal slopes observed in the x = 0.05 'stoichiometric' sample and we have been unable to make any definitive conclusions about the behaviour of this sample. We suspect these measurements are complicated by the change in the donor compensation mechanism occurring between high and low p(O₂). At 900°C the diffusion of oxygen ions and cations, or their respective vacancies, is still relatively slow and we believe that achieving equilibrium measurements at such temperatures is difficult within reasonable time scales.

Hysteresis in the measured conductivity values was observed from the high-low-high p(O₂) cycle shown in Fig.7.9 on page 134. As suggested above in Section 6.8.7 (page

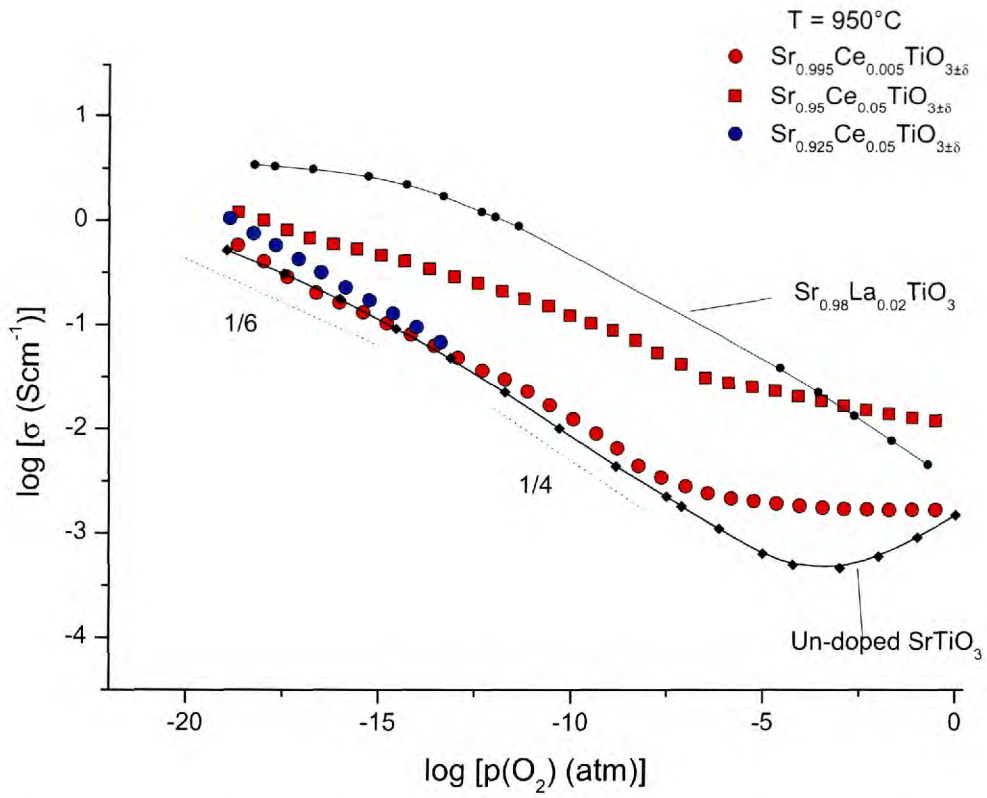


Figure 7.21: Comparison of the total conductivity of as-prepared materials at 950°C with un-doped SrTiO_3 (data from Chan [42]) and La-doped SrTiO_3 (data from Balachandran [43]).

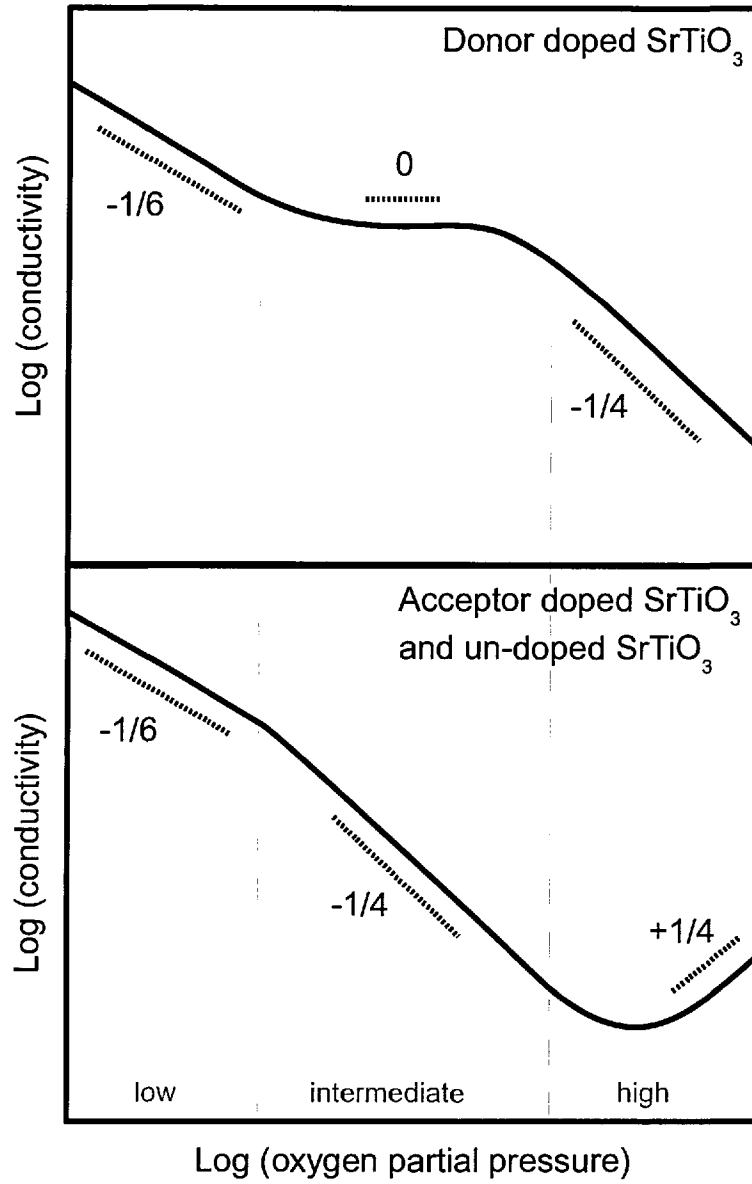


Figure 7.22: Schematic of the oxygen partial pressure dependent behaviour of un-doped, acceptor doped and donor doped SrTiO_3 . (After [44])

6.8.7), there seems to be very little oxygen loss on reduction, and what is lost or gained occurs very slowly in dense bar samples. The simplest answer to the non-reproducibility in the data between low and high $p(\text{O}_2)$ would be that the time between measurements was too short to allow equilibrium to occur. In effect, we have measured a slowly reducing or slowly oxidising sample, rather than a sample at equilibrium. There are similarities in the literature where authors suggest that data, particularly in donor-doped titanates, should not be taken as true equilibrium measurements because of very slow oxygen exchange kinetics [61].

An alternative explanation of this behaviour can be put forward which considers the change in donor compensation mechanism that switches from cation vacancy compensation at high $p(\text{O}_2)$ to electronic compensation at low $p(\text{O}_2)$. For the compensation mechanism to change, it would necessitate the formation of a second phase. This would involve the diffusion of cations and/or cation vacancies and the diffusion of oxygen, depending on the direction of the change. This process is likely to be kinetically limited at temperatures below 1000°C, especially considering the diffusion coefficient for Sr vacancies has been measured to be $\sim 10^{-16} \text{cm}^2 \text{s}^{-1}$ [163] above 1300°C. So for samples prepared in air, where the $\text{Sr}_{1-1.5x}\text{Ce}_x\text{TiO}_3$ composition forms, a shift to reducing conditions should involve the formation of a Ti-rich phase [79]. The kinetics of the formation of this phase (on moving into a low $p(\text{O}_2)$ regime, and its dissolution on returning to high $p(\text{O}_2)$), will no doubt play a role in the equilibration kinetics. We suggest that the formation of a cation vacancy compensated composition from an electronic, stoichiometric composition would be more difficult. This is because to form a vacancy compensated composition would require the simultaneous diffusion of both strontium vacancies and oxygen, both of which will be slow at temperatures below 1000°C.

Estimation of equilibrium time from diffusion coefficients

It is possible to relate the self-diffusion coefficient, D^* , and the chemical diffusion coefficient, D^δ , by a factor known as the 'thermodynamic enhancement factor', γ , sometimes simply called the 'thermodynamic factor':

$$D^* = \gamma \times D^\delta \quad (7.4)$$

Unfortunately, the data necessary to calculate the thermodynamic factor was not collected and so a value of D^δ cannot be estimated. Nevertheless, it is possible to calculate the relaxation times for the electrical conductivity [164] using the following equation by substituting some estimates for the chemical diffusion coefficient.

$$\frac{p(t) - p(\infty)}{p(0) - p(\infty)} = 0.533 \exp \left[-2.47 D^\delta t \left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \right) \right] \quad (7.5)$$

where D^δ is the chemical diffusion coefficient, t is the relaxation time and a , b and c are the dimensions of the sample.

The left-hand side of the equation essentially represents the relaxation level. For example, we can arbitrarily set the left-hand side of the equation to 0.01 (i.e 99% relaxed). We can then solve the equation for t .

Let us assume a temperature of 950°C, and typical sample dimensions of $\sim 3 \times 2 \times 5$ mm. To start with we can say that the self diffusion and chemical diffusion coefficients are the same, that is $D^* = D^\delta = 7.2 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$. Then, using these values, the relaxation time would be in the region of years! The chemical diffusion coefficient would need to be closer to 10^{-7} for the relaxation times to become reasonable, ~ 7 hours. This is possible, as the self-diffusion coefficient is usually 3-4 orders of magnitude lower than D^δ , depending on the thermodynamic enhancement factor. However, we consider this to be unlikely given the extremely low self-diffusion coefficient. Another option to improve the equilibrium in these materials would be simply to use smaller samples, minimising the diffusion path.

7.7.4 Electronic conductivity of reduced samples

The measured conductivity of samples reduced at high temperatures is consistent with other doped and highly reduced titanates: Nb-doped materials [79, 165], La-doped

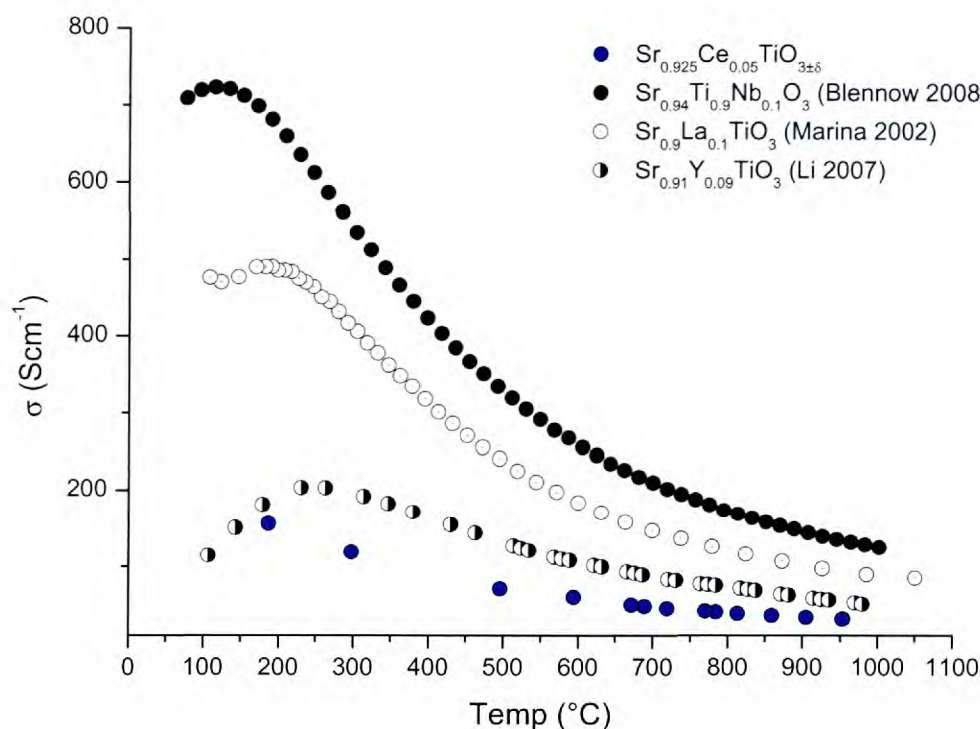


Figure 7.23: Conductivity of highly reduced (1350°C) $\text{Sr}_{0.925}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$ compared with published data from Blennow [79], Marina [66] and Li [167], showing similar temperature dependence of conductivity.

SrTiO_3 [43–45, 66, 166] and Y-doped SrTiO_3 [77, 78]. One of the main factors determining the overall conductivity, however, would appear to be the maximum temperature at which the reduction occurred. Once reduced, many compositions show metallic-like conductivity.

Figure 7.23 shows an A-site deficient sample that was reduced at 1350°C, compared with published data for Nb, La and Y-doped SrTiO_3 . The absolute conductivity of the Nb-doped sample is considerably higher than the Ce-doped sample but this may be due to the 1400°C reducing treatment the Nb-doped sample received [79]. Nevertheless, the shape of the curves are all similar. This behaviour is typical of reduced titanate materials [79, 166]. There is a linear relationship when the resistivity is plotted against the T^2 , as shown in Figure 7.24. This metallic-like behaviour is typical of strong electron-electron scattering. It also shows that the conductivity mechanism is similar in Ce-doped SrTiO_3 and other highly reduced titanate perovskites.

Figure 7.14 on page 140 shows significantly different behaviour for the so-called stoichio-

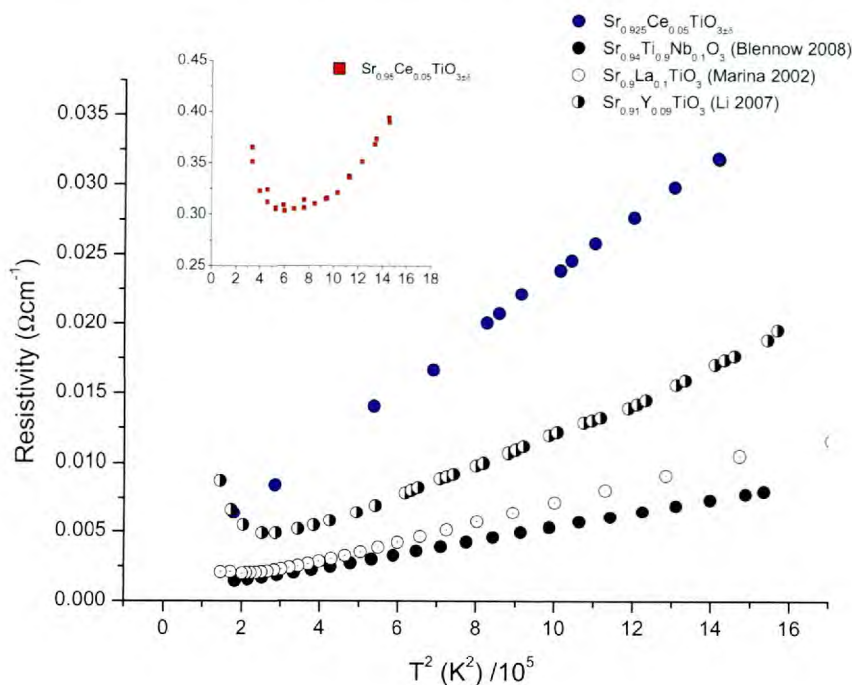
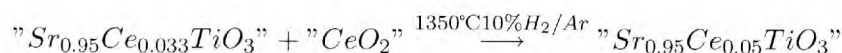
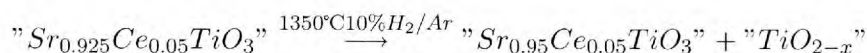


Figure 7.24: Comparison of the resistivity plotted against T^2 , showing a linear dependence for both materials. This is an indication of strong electron-electron scattering which has been shown for other titanates [65,79]. Inset: Data plotted for a nominally stoichiometric sample showing non-linear behaviour which suggests a different conductivity mechanism.

metric sample and the A-site deficient sample. When prepared in air the 'stoichiometric' sample (nominally $\text{Sr}_{0.95}\text{Ce}_{0.05}\text{TiO}_{3\pm\delta}$) precipitated ceria because the actual phase that formed was $\text{Sr}_{0.95}\text{Ce}_{0.033}\text{TiO}_3 + \text{CeO}_2$ (see section 6.4 for more detail). Under reducing conditions the compensation mechanism should shift to electronic and so the ceria should, in principle, dissolve and form the true stoichiometric composition. However, the kinetics of this reaction have not been studied:



Samples that were prepared as A-site deficient were indeed shown to be single phase after synthesis in air. However, under reducing conditions, the true stoichiometric phase should form which would mean a TiO_{2-x} should precipitate [79,168], as shown simplistically below.



There is a clear difference in the measured conductivity of the nominally stoichiometric

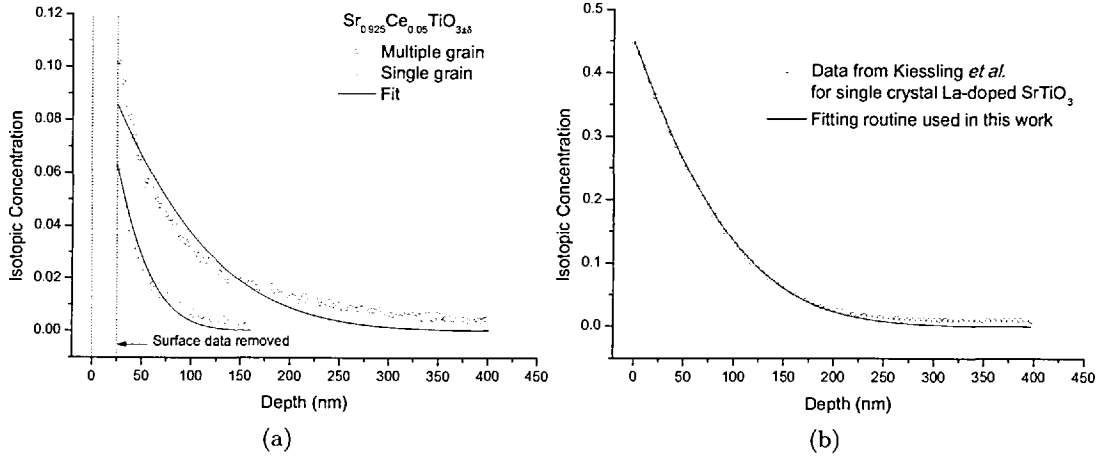


Figure 7.25: Shows a comparison of the truncated experimental data collected in this work and data from the literature (Kiessling *et al.* [161]). Overlaid is the best fit to the diffusion equation, showing an excellent fit to the literature data but a poor fit to the data in this work. Possible reasons for this are discussed in the text.

and A-site deficient samples (see Fig. 7.14 and 7.24). The reason for such a large difference is not entirely clear. It is possible that there are differences in the nature of precipitation and dissolution of second phases as the compensation mechanism shifts under different oxygen partial pressures. More work is needed in the area to fully understand the details of the systems under reducing atmospheres and the fate of second phases upon changes in $p(\text{O}_2)$.

7.7.5 Isotopic oxygen exchange

There is a clear difference between data collected from within a single grain and data collected from multiple grains. This is shown in Fig. 7.17 on page 144 and reproduced in Fig. 7.25. This behaviour may suggest enhanced diffusion along grain boundaries. However, typical grain boundary effects are generally confined to the deeper regions of a depth profile where bulk diffusion does not extend. This means the effect of grain boundaries on the depth profile should only become apparent at the end of the profile. Data for both the single grain and polycrystalline region, shows that attempts to fit Eq.7.3 to this data give poor results throughout the entire profile, not just in the tail region. There is a comparatively good fit, using the same fitting routine, to the experimental data of Kessling *et al.* [161] shown in Figure 7.25b. Literature data shows what would appear to be a typical grain boundary 'tail', which is identified as a

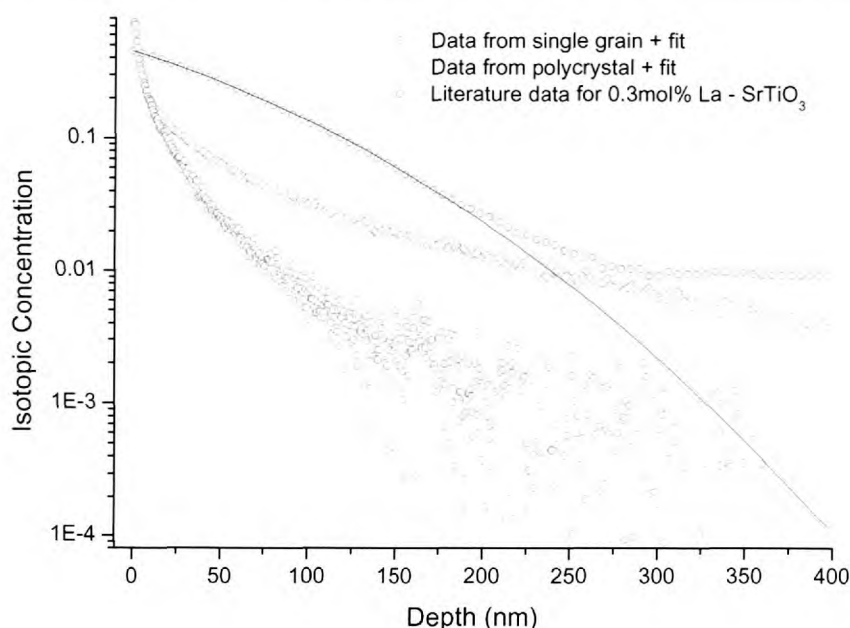


Figure 7.26: Depth profile data displayed on a semi-logarithmic plot which demonstrates the clear difference between data gathered in this work compared with that in the literature. Data from the literature were fitted using the Matlab fitting routine commonly used in our laboratory.

slightly elevated isotopic concentration in the deepest region of the profile. Considering the data in Ref [161] were from a single crystal, we would not expect to see such an effect. However, this may be an artifact of the data digitisation process as it was taken from a diffusion profile with linear axes and so accurate reproduction of the very low isotopic values was not possible. Alternatively, there may have also been imperfections (from crystal growth or processing) in the single crystal, which resulted in fast diffusion paths which would give similar results [162].

Returning to our data, a semi-logarithmic plot (as shown in Fig. 7.26) highlights the differences between the two experimentally observed profiles, i.e. the single grain and polycrystalline sample, and the literature data. It shows the completely different shape of the experimental profiles compared to the more typical oxygen diffusion profile taken from the literature. We are currently unable to explain the reason for the shape of our profile. Given that Equation 7.3 does not describe the experimental data over the entire depth range, it appears as though some other (as yet undetermined) process or combination of processes may be occurring. The influence of surface defects and polishing damage may play an important role in such shallow depth profiles.

Effect of chemical diffusion

Samples used in the isotopic exchange experiments were reduced samples (1350°C in 10%H₂/Ar for 24 hrs). However, they were exchanged at an oxygen partial pressure of 0.21 atm. This led to the obvious conclusion that the unsatisfactory fit of the isotopic exchange data was due to a chemical diffusion process occurring in parallel with the self-diffusion process. This has not been entirely discounted but, the exchange procedure involved an annealing step of some 10hrs at a $p(O_2) = 0.21$ atm. Even though the samples were still blue-black and conductive, annealing for this period should have allowed sufficient equilibrium time before the isotopic anneal, which lasted for 30 mins.

7.7.6 Oxygen loss at high temperatures and under reducing conditions

Thermogravimetric data shows that oxidised, doped samples do not lose a measurable amount of oxygen at high temperatures in air. This is not surprising as the nature of donor doping means there will be a driving force towards oxygen excess in these materials. That is to say once the donor content is greater than the typical acceptor impurity content, there will no longer be any extrinsic oxygen vacancies as there are in acceptor-doped materials such as Fe-doped SrTiO₃.

Under reducing conditions there will inevitably be some oxygen loss according to the reaction:

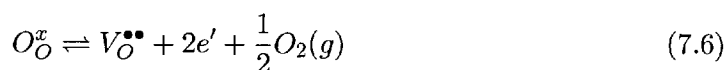


Figure 7.27 shows the oxidation profiles for samples treated under strong reduction conditions. Figure 7.27 also shows published oxidation data for reduced Nb-doped SrTiO₃. Clearly the amount of oxygen lost, even at high temperatures and under strongly reducing conditions, is relatively small compared to the changes seen in other perovskites such as the cobaltates. The oxygen stoichiometry for the reduced samples is shown in Table 7.4. Another interesting point to note is the lower temperature onset

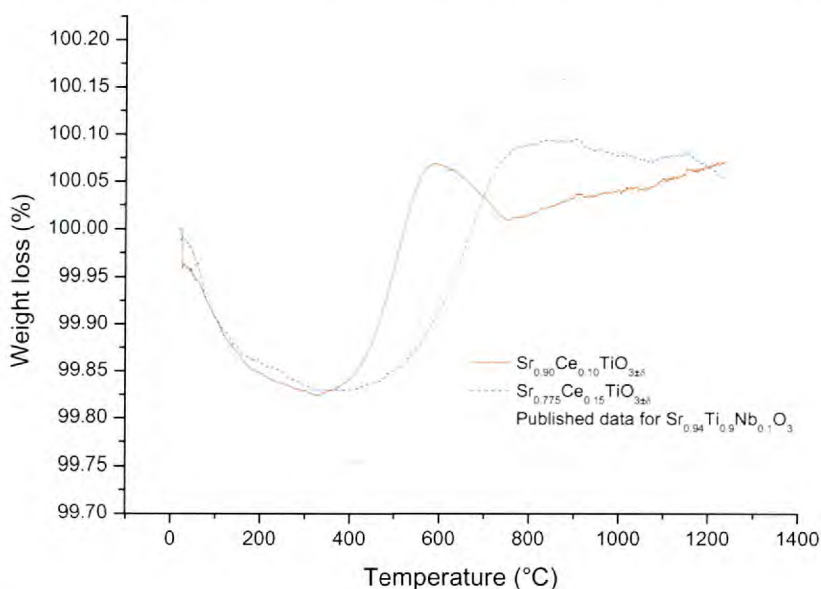


Figure 7.27: Shows a comparison of the oxidation data for a range of donor-doped compositions. Each of these samples was reduced at high temperature under low oxygen partial pressure. The change in weight and the temperature at which re-oxidation occurs is similar for all samples.

of oxidation seen in the nominally stoichiometric sample. This is likely to be due to the interaction with second phase material in one or both of the samples. Whether it is the precipitation of CeO_2 in the 'stoichiometric' sample or the dissolution of TiO_2 in the A-site deficient sample, is unclear, and further work is needed to establish the details of these phase kinetics.

7.8 Conclusions

In air Ce-doped SrTiO_3 shows increased electronic conductivity over un-doped SrTiO_3 . However, these values on their own are not high enough for efficient fuel cell operation. Under reducing conditions the conductivity was increased markedly. The conductivity was sufficiently high that successful use as an electrode material could be expected. The conductivity mechanism in air showed typical semiconductor properties and under reducing conditions showed a metallic-like conductivity when heavily reduced, as observed in other titanates.

Very slow equilibrium kinetics were observed during $p(\text{O}_2)$ -dependent measurement which led to unusual hysteresis in the data shown in Figure 7.9. This is thought to

be for two reasons. One is the dual defect mechanisms which operate at high and low $p(\text{O}_2)$. In these materials (no matter what the choice of initial stoichiometry) a second phase must precipitate, or dissolve, when moving between high and low $p(\text{O}_2)$ regimes. This process necessitates cation and oxygen ion diffusion that will be very slow at temperatures below 1000°C. It is the combination of these factors that probably led to the very slow equilibrium times which resulted in the measurement of non-equilibrium data.

Isotopic exchange and SIMS depth profiling has shown that the oxygen diffusion kinetics are very slow in these materials. An adequate solution to the diffusion equation could not be found for the data, even when potentially deleterious data was removed. We have also shown that there may be some enhancement of the oxygen ion diffusion along grain boundaries. We have estimated values for D^* and k . However, problems encountered in fitting the diffusion equation to the experimental data were due to the unusual diffusion profiles. It was shown that the fitting procedure worked very well for literature data. It provided diffusion and surface exchange figures almost identical to those quoted in the literature. This experiment needs to be repeated to see if similar diffusion profiles are obtained.

Thermogravimetric data has also shown no measurable oxygen loss in these materials when measured in air. However, a small amount of oxygen is lost under reducing conditions. The re-oxidation of reduced powder samples occurs relatively quickly compared with dense bar samples used for conductivity and isotopic exchange measurements.

Chapter 8

Conclusions and Future work

8.1 Conclusions

The aim of this work was to identify a new material capable of use as a redox stable anode material. This required a material with suitable stability and conductivity under reducing conditions but which also showed stability at higher $p(\text{O}_2)$. Broadly this goal has been achieved with Ce-doped SrTiO_3 .

Key points from this research are as follows:

1. Synthesis, defect chemistry and phase structures:
 - (a) Successful synthesis of Ce-doped SrTiO_3 has been demonstrated. This material has not received a great deal of attention in the published literature, particularly in relation to defect chemistry or use as a fuel cell material. Results of the synthesis are in agreement with the published literature [111, 114, 115, 132]. One key difference between Ce-doped samples and La-doped samples is that under oxidising conditions, no layered structures appear to form. Instead, CeO_2 precipitates as a second phase.
 - (b) From a synthesis perspective, Ce-doped SrTiO_3 appears to obey the defect model for donor-doped SrTiO_3 .

- (c) The oxygen partial pressure used for synthesis should determine the choice of stoichiometry or vice versa. If this is not followed, the phase preferred under a particular $p(\text{O}_2)$ regime will form according to the defect model set out in Chapter 3.
- (d) The above point was demonstrated by the similarity in the lattice parameters observed for different stoichiometries prepared in air (see Chapter 6, page 97).

2. Structure of Ce-doped SrTiO_3 :

- (a) Lattice parameters decreased with increasing cerium content when prepared in air using an A-site deficient stoichiometry. This suggested that cerium was incorporated on the A-site as Ce(III).
- (b) XRD data would suggest that Ce-doped SrTiO_3 was cubic, with the space group $Pm\bar{3}m$. Neutron powder diffraction, however, showed additional peaks which could not be indexed according to a cubic space group. It was determined that oxidised Ce-doped SrTiO_3 was most likely tetragonal, similar to that observed in La-doped SrTiO_3 [150]. Rietveld refinements, where the occupancy of the Ce was allowed to fluctuate, showed that cerium resides predominantly on the A-site.
- (c) TEM-EELS data also corroborates these results and, although the data was collected from samples with a low cerium content, it appears from EELS measurements that cerium was in the +3 oxidation state.
- (d) Examination of the Ti-L and O-K EELS edges also showed some interesting features, but without more data no definite conclusions can be drawn.
- (e) Thermal expansion coefficients were found to match that of CGO and YSZ, displaying values of between 10-12 p.p.m.K⁻¹. HT-XRD measurements also gave similar results.

3. Electrical conductivity and oxygen transport in Ce-doped SrTiO_3 :

- (a) The electrical conductivity in air increases with cerium doping but not to a level where it could be used as an electrode material.

- (b) In air, the resistivity is dominated by the grain boundaries, as it is in other titanate perovskites.
- (c) Under low $p(\text{O}_2)$, the conductivity increases significantly and eventually becomes metallic when heavily reduced. The conductivity mechanism appears to be similar as for other donor-doped titanates.
- (d) Oxygen partial pressure dependent measurements in this work show significant hysteresis. Often they do not obey ideal rules in terms of the slope of the $p(\text{O}_2)$ -dependent conductivity; this is thought to be due to slow equilibrium kinetics in dense bar samples.
- (e) Slow equilibrium kinetics may occur for two reasons. Firstly, the change in donor compensation mechanism between high and low $p(\text{O}_2)$ requires a significant amount of cation diffusion. This has shown to be extremely slow at temperatures below $\sim 1000^\circ\text{C}$. Secondly, the oxygen diffusion in these samples has also been shown, in this research and in the literature, to be very slow. The combination of these two factors results in slow equilibrium and the difficulty in obtaining meaningful $p(\text{O}_2)$ -dependent conductivity data.
- (f) In addition to the slow oxygen diffusion kinetics, the level of oxygen lost is relatively small. This results in a very small chemical expansion between high and low $p(\text{O}_2)$, which affords Ce-doped SrTiO_3 very high redox stability.

Overall, Ce-doped SrTiO_3 shows some very promising properties for electrode materials. The results of this research show that Ce-doped SrTiO_3 is very similar in almost every respect to other donor-doped SrTiO_3 , such as Nb, La and Y-doped materials.

Much of this research was devoted to obtaining reproducible results. This was found to be very difficult, as one set of samples prepared in a nominally identical fashion often resulted in significantly different results. As we have demonstrated (and some other authors have pointed out) true equilibrium in these materials can be very difficult to achieve in practice. There are large variations in reported electrical properties in the literature. Reported results need to fully explain the measurement conditions and the thermal history of the sample so that the data sets can be meaningfully compared.

8.2 Future work

Ce-doped SrTiO_3 has shown many of the required properties needed for fuel cell applications (such as high electronic conductivity, redox stability and good thermal expansion match to commonly used electrolyte materials such as YSZ and CGO). There are many interesting avenues for additional work on this material, ranging from examination of the fundamental defect chemistry to its application as a practical electroceramic. Below we will outline some areas in which we think additional work should focus.

1. A more thorough examination of the Sr-Ce-Ti-O phase diagram is required to fully understand the relationships in this system. A closer examination of the properties around the cerium solubility limit ($\sim 40\text{mol}\%$) is also recommended; there may be interesting properties as observed in La-doped SrTiO_3 .
2. A better understanding of the fate of second phases under reducing and oxidising conditions is needed.
3. Given the very slow equilibrium times in these materials it would be best to measure the $p(\text{O}_2)$ -dependent electrical properties at temperatures above 1000°C (which may cause practical experimental difficulties, but could help the understanding of the donor-doped materials). In combination with this, the chemical diffusion coefficient could be established via electrical conductivity relaxation measurements.
4. Isotopic ion exchange experiments over a range of temperatures and under moist atmospheres would be useful. An understanding of the origin of the unusual depth profiles we observed in this study (and why they did not obey the diffusion equation) is required. Examining the use of catalytically active materials during isotopic exchange, such as Pt or YBCO, to improve the oxygen surface exchange is also recommended.
5. Given the dual defect regimes in these materials and the likelihood of a second phase forming, an examination of what phases are least detrimental to fuel cell performance should be undertaken - for example, to identify the reason why an

A-site deficient sample (which should contain second phase) shows significantly higher conductivity compared to a nominally stoichiometric phase. A TEM study would be useful to examine if and where the second phase TiO_2 is formed, and what its role is in the electrical and ionic conductivity.

6. Only a handful of samples were used for EELS and neutron diffraction measurement. A more complete study of the nature of the crystal structure by temperature-dependent and composition-dependent neutron diffraction measurements would allow phase changes (e.g cubic - tetragonal) to be identified. A more detailed study of the Ti(III)/Ti(IV) relationship using EELS would also be useful.
7. Most important of all, in the context of this thesis, is the measurement of the fuel cell properties. Due to some practical problems and time constraints, this could not be achieved in this research. However, given the similarity of Ce-doped SrTiO_3 with La and Nb-doped SrTiO_3 , it would be expected that satisfactory cell performance could be achieved given the correct conditions. Sulfur tolerance and redox testing could also be performed.

In summary, Ce-doped SrTiO_3 represents a potentially useful new anode material for SOFC. Given its similarity with other donor-doped titanates, which have been demonstrated as working electrode materials, we would expect reasonable performance from Ce-doped SrTiO_3 . In addition, the slow reduction kinetics in these materials would mean an improvement in performance during cell operation as the electronic conductivity improved. Successful fuel cell application of the donor-doped titanates has been demonstrated when incorporated in an all-ceramic composite. We would suggest that this is the most likely strategy for the successful application of this material.

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