New Ionic and Mixed Conducting Materials for Fuel Cell Applications

by

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"One day hydrogen and oxygen, which together form water, will be used either alone or together as an inexhaustible supply of heat and light"

"Water is the coal of the future"

Jules Verne 1874
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In loving memory of D.E.S.
Abstract
The project has dealt with the synthesis and characterisation of new materials for use in solid oxide fuel cells. In terms of potential electrolytes we have been studying a range of apatite based materials. High oxide ion conductivity has been recently reported in the apatite phases $\text{La}_{10-y}\text{M}_y\text{O}_{26+z}$ ($\text{M} = \text{Si, Ge}$). Preliminary work focused on the preparation and characterisation of single phase samples of previously reported phases, e.g. $\text{La}_{9.33}\text{(Si/Ge)}_6\text{O}_{26}$ and $\text{La}_8\text{A}_2\text{(Si/Ge)}_6\text{O}_{26}$ ($\text{A} = \text{alkaline earth}$). Neutron diffraction studies revealed significant disorder within the oxygen channels for systems showing high oxide ion conductivity, namely non-stoichiometric systems containing either cation vacancies, e.g. $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$, or excess oxygen, e.g. $\text{La}_9\text{Sr}\text{Si}_6\text{O}_{26.5}$. Compositions containing excess oxygen showed the highest conductivities, e.g. $0.01 \text{ S cm}^{-1}$ at $800 \degree \text{C}$ for $\text{La}_9\text{Sr}\text{Si}_6\text{O}_{26.5}$. Conversely, fully stoichiometric systems, e.g. $\text{La}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$, showed poor oxide ion conduction, which appears to be associated with oxygen ordering within the channels. A range of doping studies followed in order to optimise the oxide ion conductivity, i.e. $\text{La}_{9.33+y/3}\text{Si}_6-x\text{M}_x\text{O}_{26}$ ($\text{M} = \text{Al, B, Ga}$) and $(\text{La}/\text{M})_{10-x}\text{Si}_6\text{O}_{26+y}$ ($\text{M} = \text{Mg, Ca, Sr, Ba}$). The sample $\text{La}_3\text{BaSi}_6\text{O}_{26.5}$ showed the highest conductivity, with a value of $6 \times 10^{-3} \text{ S cm}^{-1}$ at $500 \degree \text{C}$, which is significantly higher than that of YSZ at this temperature ($1 \times 10^{-3} \text{ S cm}^{-1}$). This sample is therefore a highly promising candidate material for use as an electrolyte in intermediate temperature SOFCs ($500 \degree \text{C} - 700 \degree \text{C}$), as well as other technological applications. Similar studies were performed for samples with germanium in place of silicon. High oxide ion conductivity was observed for these systems, although germanium volatility was identified as a significant problem in these cases.

In terms of cathode materials research has involved the preparation of a range of perovskite type phases based on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO). The compositions tested were of formula type $\text{YSr}_2\text{Cu}_3-x\text{M}_x\text{O}_{7-y}$ ($\text{M} = \text{Ga, Co, Fe}$), and the results indicated that these samples were not promising candidates as replacement cathode materials since, they all showed only moderately high conductivity. Furthermore, the phases were shown not to be chemically compatible with most current or prospective electrolyte materials, with significant impurity phases found to be produced when the electrolyte and cuprate were heated together at SOFC operating temperatures ($900 \degree \text{C} - 1000 \degree \text{C}$).
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<td>Alkaline Fuel Cell</td>
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<tr>
<td>ANL</td>
<td>Argonne National Laboratory</td>
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<tr>
<td>ASR</td>
<td>Area Specific Resistivity</td>
</tr>
<tr>
<td>BOP</td>
<td>Balance of Plant</td>
</tr>
<tr>
<td>CCSL</td>
<td>Cambridge Crystallography Subroutine Library</td>
</tr>
<tr>
<td>CGO</td>
<td>Ce_{0.9}Gd_{0.1}O_{1.95}</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined Heat and Power</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>ERC</td>
<td>Energy Research Corporation</td>
</tr>
<tr>
<td>EVD</td>
<td>Electrochemical Vapour Deposition</td>
</tr>
<tr>
<td>FCE</td>
<td>Fuel Cell Energy</td>
</tr>
<tr>
<td>FCV</td>
<td>Fuel Cell Vehicle</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier Transform</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width Half Max</td>
</tr>
<tr>
<td>GE</td>
<td>General Electric</td>
</tr>
<tr>
<td>GSAS</td>
<td>General Structure and Analysis Software</td>
</tr>
<tr>
<td>HRPD</td>
<td>High Resolution Powder Diffraction</td>
</tr>
<tr>
<td>IFC</td>
<td>International Fuel Cells</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium-Tin Mixed Oxide</td>
</tr>
<tr>
<td>LCCF</td>
<td>La_{0.6}Ca_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}</td>
</tr>
<tr>
<td>LSCo</td>
<td>La_{0.6}Sr_{0.4}CoO_{3-δ}</td>
</tr>
<tr>
<td>LSCFe3</td>
<td>La_{0.84}Sr_{0.16}Co_{0.7}Fe_{0.3}O_{3}</td>
</tr>
<tr>
<td>LSCFe7</td>
<td>La_{0.84}Sr_{0.16}Co_{0.3}Fe_{0.7}O_{3}</td>
</tr>
<tr>
<td>LSCN</td>
<td>La_{0.8}Sr_{0.2}Co_{0.8}Ni_{0.2}O_{3-δ}</td>
</tr>
<tr>
<td>LSF</td>
<td>La_{0.8}Sr_{0.2}FeO_{3}</td>
</tr>
<tr>
<td>LSFC</td>
<td>La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3}</td>
</tr>
<tr>
<td>LSFN</td>
<td>La_{0.7}Sr_{0.3}Fe_{0.8}Ni_{0.2}O_{3-δ}</td>
</tr>
<tr>
<td>LSGM</td>
<td>La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-0.5(x+y)}</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>LSM</td>
<td>Lanthanum Strontium Manganate (La$<em>{0.8}$Sr$</em>{0.2}$MnO$_{3-x}$)</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten Carbonate Fuel Cell</td>
</tr>
<tr>
<td>MS</td>
<td>Manhattan Scientific</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>NECAR</td>
<td>New Electric Car</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric Acid Fuel Cell</td>
</tr>
<tr>
<td>P&amp;W</td>
<td>Pratt &amp; Whitney</td>
</tr>
<tr>
<td>PEM</td>
<td>Polymer Electrolyte Membrane</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Polymer Electrolyte Membrane Fuel Cell or Proton-Exchange Membrane Fuel Cell</td>
</tr>
<tr>
<td>RC network</td>
<td>Resistive Capacitive Network</td>
</tr>
<tr>
<td>SCF</td>
<td>SrCo$<em>{0.8}$Fe$</em>{0.2}$O$_{3-\delta}$</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>SUV</td>
<td>Sport Utility Vehicle</td>
</tr>
<tr>
<td>SWPC</td>
<td>Siemens Westinghouse Power Corporation</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethoxysilane</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>TPB</td>
<td>Three-Phase Boundary</td>
</tr>
<tr>
<td>UK</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>US</td>
<td>United States (of America)</td>
</tr>
<tr>
<td>UTC</td>
<td>United Technologies Corporation</td>
</tr>
<tr>
<td>YBCO</td>
<td>YBa$_2$Cu$<em>3$O$</em>{7-x}$</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttria Stabilised Zirconia $(Y_2O)<em>{0.08}(ZrO_2)</em>{0.92}$</td>
</tr>
</tbody>
</table>
Chapter 1.0: Introduction

The world’s fossil fuel reserves are gradually becoming exhausted and increasingly expensive to extract. In addition the dire consequences of worldwide pollution and global warming are well documented. Therefore the requirement for more efficient, renewable and environmentally friendly sources of energy is increasingly becoming more urgent.

Fuel cells are a possible solution to the world’s energy supply and pollution problems. They are quiet and highly efficient devices, converting chemical energy into electrical energy from the electrochemical reaction between oxidising agents, e.g. oxygen, and fuel materials, e.g. hydrogen gas and hydrocarbons (methane, methanol etc). They negate the requirement for dirty and wasteful combustion processes. Indeed the electrochemical oxidation of hydrogen (H₂/O₂) can occur theoretically at high efficiencies (83 % at 25 °C).¹ Solid Oxide Fuel Cells (SOFCs) are of particular interest to fuel cell manufacturers and researchers because the high temperature of operation (1000 °C) means that they can potentially utilise either hydrocarbons or hydrogen gas as fuel material, and also negates the need for expensive noble metal catalysts. The world’s natural gas resource is plentiful and hydrogen gas is a potentially renewable resource through the cracking of water using solar radiation. SOFCs are solid state devices, eliminating a number of the problems associated with liquid electrolytes, such as corrosion and flooding. SOFCs offer fuel efficiencies of up to 55 %, increasing to 80 % efficiency, if the surplus heat energy generated is utilised (combined heat and power systems).

Another advantage of SOFCs is that they can generate power at source. Localised power generation potentially eliminates the use of power grids and the associated transmission losses (up to 1/3 of the power generated by power stations), especially in remote areas. Localised pollution that presently surrounds existing fossil fuel powered stations will be eliminated, as will the visual impact of unsightly power pylons. Furthermore, there is growing concern regarding the health issues of people located in the proximity of electricity pylons. Localised power generation using SOFCs would also help to eliminate this problem. It should be noted, however, that
the SOFCs running on hydrocarbon fuels will themselves produce pollution \((\text{CO}_2 \, (g))\), but because of the higher efficiency the levels are significantly lower.

The main problem with existing SOFCs is the very high temperature of operation, \(1000 \, ^\circ\text{C}\), owing to limitations in the existing electrode and electrolyte materials employed by SOFC developers. Although the high temperature operation gives benefits as outlined above, it also causes problems in terms of sealing the cell and cell degradation. These problems could be overcome by lowering the temperature of operation to between 500 °C and 800 °C, and this is the aim of the project. To achieve this, we are aiming to develop new electrolyte and cathode materials with improved properties at lower temperatures.

Over the last few decades there have been a number of useful review papers on fuel cell topics published.\(^1\)\(^-\)\(^8\) A number of less technical reviews have appeared in periodicals such as ‘Scientific American’ and ‘New Scientist’ magazine,\(^9\)\(^-\)\(^13\) which supply a good overview of the field. A number of web sites are also available, such as Fuel Cells 2000 and Fuel Cells Today, which are useful sources for current information on the technological and commercial status of fuel cells. Another useful resource is provided by the Fuel Cell Handbook, published by the US Department of Energy.\(^14\) More recently, Boudghene, Stambouli and Traversa \textit{et al.} have provided a review on the environmental aspects of SOFCs.\(^15\)

1.1 How Fuel Cells Work

The different types of fuel cell all have the same basic design and mode of operation. The fuel cell is essentially a simple device consisting of anode and cathode electrodes sandwiching an electrolyte. The electrolyte is a special material that permits the migration of ions \((\text{H}^+, \text{O}^2-, \text{OH}^-\text{or CO}_3^{2-})\), but is devoid of any electronic conduction.

Fuel cells and batteries both operate by means of an electrochemical reaction. Fuel cells differ from batteries in so far as, in the former the fuel and oxidant are delivered
to the cell electrodes and the cell will continue to operate as long as fuel and oxidiser continue to be delivered to the cell, degradation of the cell components notwithstanding. However, in batteries the fuel and oxidiser form part of the electrodes, and thus there is a fixed amount of chemical energy in these electrodes. Once this energy is used up, the battery is either disposed of or recharged.

1.1.1 Operation in the Case of Proton Conducting Electrolytes

The fuel, typically hydrogen gas, is delivered to the anode where it is oxidised. The electrons flow through an external electrical circuit, the load, to the cathode, whereas the protons diffuse through the electrolyte to the cathode. The oxidant, typically oxygen gas, is delivered to the cathode where it is reduced. The electrons from the external circuit combine with the oxygen and the protons to form water. The electrodes usually contain a catalyst, typically platinum metal, to increase the rate of electrochemical reaction. This is especially the case if the cells are operating at relatively low temperature, such as in polymer electrolyte membrane fuel cells (PEMFCs) and phosphoric acid fuel cells (PAFCs).

Anode reaction: \( 2H_2 \rightarrow 4H^+ + 4e^- \)

Cathode reaction: \( O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \)

Overall reaction: \( 2H_2 + O_2 \rightarrow 2H_2O + \text{electrical energy} \)

1.1.2 Operation in the Case of Oxide Ion Conducting Electrolytes

The oxidant, typically oxygen gas, is delivered to the cathode where it is reduced by the electrons from the external circuit, to form oxide ions. The oxide ions diffuse through the electrolyte to the anode where they combine with the fuel, typically hydrogen gas, to form water. Electrons are liberated from this oxidation and flow through the load to the cathode. Note that in the case of proton conducting electrolyte, the \( H_2O \) is generated at the cathode, whereas for an oxide ion conducting electrolyte,
it is generated at the anode. A schematic diagram of the operation of a solid oxide fuel cell is shown in figure 1.1.

Cathode reaction: \( \text{O}_2 + 4e^- \rightarrow 2\text{O}^{2-} \)

Anode reaction: \( 2\text{O}^{2-} + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O} + 4e^- \)

Overall reaction: \( 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{electrical energy} \)

Figure 1.1. Simplified schematic of a solid oxide fuel cell.

The electrical resistance of the electrolyte can affect the efficiency of a fuel cell. Heat energy is lost, as a consequence, owing to \( I^2R \) power losses in the electrolyte and electrodes of a fuel cell. Thus, the higher the resistance the higher the losses. In addition, any electron migration across the electrolyte will short-circuit the cell, reducing electron flow in the external circuit. Therefore, ideally, the electrolyte (oxide ion conductor or proton conductor) should have no electronic conduction.
1.2 Types of Fuel Cell

There are five main types of fuel cell in existence at present; and each type is classified according to the type of electrolyte used. Details of cell components and operating conditions are summarised in table 1.1, and a summary of fuel cell operation is shown in figure 1.2.

Table 1.1. Fuel Cell Types Compared.¹⁰

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Alkaline Fuel Cell</th>
<th>Proton Exchange Membrane</th>
<th>Phosphoric Acid</th>
<th>Molten Carbonate</th>
<th>Solid-Oxide</th>
</tr>
</thead>
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<tr>
<td><strong>Operating Temp. / °C</strong></td>
<td>70</td>
<td>80</td>
<td>200</td>
<td>650</td>
<td>800-1000</td>
</tr>
<tr>
<td><strong>Charge Carrier</strong></td>
<td>Hydroxide</td>
<td>Proton</td>
<td>Proton</td>
<td>Carbonate</td>
<td>Oxide Ion</td>
</tr>
<tr>
<td><strong>Reformer</strong></td>
<td>External</td>
<td>External</td>
<td>External</td>
<td>Internal or External</td>
<td>Internal or External</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>Potassium Hydroxide</td>
<td>Polymer membrane</td>
<td>Phosphoric acid</td>
<td>Alkali metal Carbonate</td>
<td>Yttria Stabilised Zirconia (YSZ)</td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td>Pt or Ni</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel</td>
<td>Ni-YSZ</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td>Pt or Ni</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel</td>
<td>Lanthanum Strontium Manganate (LSM)</td>
</tr>
<tr>
<td><strong>Efficiency / %</strong></td>
<td>60</td>
<td>40-50</td>
<td>40-50</td>
<td>60+</td>
<td>60+</td>
</tr>
</tbody>
</table>
1.2.1 The Alkaline Fuel Cell

The alkaline fuel cell (AFC) uses either an aqueous solution of sodium hydroxide or potassium hydroxide as the electrolyte, and these cells operate at less than 100 °C. AFCs are fuelled on hydrogen gas, with \( \text{O}_2 \) as the oxidant. Both should be \( \text{CO}_2 \) free to prevent solid carbonate build up in the electrolyte. Carbonate build up needs to be avoided because it lowers the output voltage by blocking the electrode/electrolyte interface and decreasing the efficiency of the cell. The electrodes usually consist of a carbon support with platinum or nickel for the catalyst. The corrosive nature of the electrolyte created many engineering challenges during their development, but these have largely been overcome.
1.2.2 The Phosphoric Acid Fuel Cell

The phosphoric acid fuel cell (PAFC) uses an orthophosphoric acid (phosphoric (V) acid, H$_3$PO$_4$) electrolyte, with an operational temperature of around 200 °C. PAFCs can be fuelled on hydrogen gas that contains carbon dioxide impurity, because acidic electrolytes are resilient to carbonate build up in the electrolyte. The oxidant can be either pure oxygen or air. PAFC technology has been around the greatest length of time and is available commercially (>100 kW systems). A number of organisations around the world are selling and developing PAFCs, including ONSI, a subsidiary of United Technologies, who had installed approximately 170 systems that are fuelled on natural gas, in the late 1980s and 1990s. Some of their systems have been operating for tens of thousands of hours. PAFCs have found themselves niche markets such as in landfill sites, wastewater treatment plants, food processing plants, where waste methane gas can be used for energy recovery. PAFCs are also used where uninterrupted power generation is a necessity. PAFCs have also been used to power city buses. However, PAFCs are unlikely to catch on in the passenger vehicle market, owing to their long warm up time. The overall efficiency of PAFC systems can be improved if the excess steam is captured and the energy harnessed for other uses such as heating a house or running a steam turbine. Steam turbines can run efficiently owing to the high temperature of the evolved steam. This type of system is often referred to as a combined heat and power, CHP, unit.

1.2.3 The Molten Carbonate Fuel Cell

The molten carbonate fuel cell (MCFC) requires an operating temperature of around 650 °C. The electrolyte is molten potassium lithium carbonate. MCFCs are fuelled with a mixture of hydrogen gas and carbon monoxide gas. The fuel gas mixture is prepared by means of the catalytic steam reformation of methane, from natural gas. Methane gas is reacted with steam at a temperature of 800 °C and a pressure of 40 atm in the presence of a nickel catalyst:
The overall efficiency of MCFC systems can be improved if operated as a CHP unit. The corrosive nature of the electrolyte, however, leads to component failure especially near full loading. Indeed the Energy Research Corporation (ERC), Danbury, Connecticut, US, installed a 2 MW MCFC plant in Santa Clara in California that only operated for 3000 hours and rarely produced more than 1 MW of electricity.

1.2.4 The Solid Oxide Fuel Cell

The solid oxide fuel cell (SOFC) uses ceramic materials for the electrolyte and electrodes. Currently, yttria stabilised zirconia (YSZ) is favoured for the electrolyte, Ni-YSZ cermet for the anode and lanthanum strontium manganate, LSM, for the cathode. These cells operate at high temperature, typically between 800 °C and 1000 °C. SOFCs can be fuelled on a mixture of hydrogen gas and carbon monoxide gas, prepared by the steam reformation of methane gas from natural gas as described earlier. The high temperature operation of SOFCs negates the need for expensive catalysts but does create problems in terms of cell degradation and sealing. The overall efficiency of SOFC systems can be improved if the waste heat energy is harnessed for use in other systems such as running a steam turbine or to heat water and living areas.

Raymonde Gorte and his team from the University of Pennsylvania, Philadelphia, have reported running SOFCs directly on hydrocarbon fuels, without the need for fuel reformation. Gorte replaced the anode material, a Ni-yttria-stabilised zirconia cermet with copper and ceria circumventing the problem of carbon formation on Ni destroying the catalytic efficiency of the cell.\(^6\)

There are \(\approx 40\) companies worldwide developing SOFC technology. In 1998 Siemens acquired Westinghouse Power Generation, thus creating one of the largest
companies developing SOFCs. Other companies involved in SOFC development include SOFCo, Ztek Corporation, Rolls Royce and McDermott.

1.2.5 The Polymer Electrolyte Membrane Fuel Cells

The polymer electrolyte membrane fuel cell (PEMFC), also known as proton-exchange membrane cell, uses a semi-permeable polymer membrane material for the electrolyte, such as DuPont’s Nafton®. The semi-permeable polymer membrane allows the migration of protons but inhibits the passage of electrons. It was discovered recently that Gore-Tex could be used to strengthen these membranes. The electrodes usually consist of a carbon support with platinum loading for the catalyst, and ruthenium is used as a co-catalyst to prevent carbon monoxide poisoning the catalyst.\textsuperscript{10,12}

At the present time eighty-five companies worldwide are working on PEMFCs including Ballard generation Systems, Burnaby, US. Ballard intend to have 250 kW units available commercially this year.

1.3 Fuel Cells: Past, Present and Future

Useful all round information with day by day headlines on fuel cell technologies can be obtained from the ‘FuelCell Works’ and ‘The Hydrogen and Fuel Cell Investor’ web sites.

Fuel cells have traditionally been used for niche applications. They were used onboard the Gemini and Apollo spacecraft back in the 1960s and 1970s, including the Apollo 11 spacecraft used in the mission that pioneered man landing on the moon. In recent times fuel cells have been utilised onboard NASA’s space shuttles. However, fuel cell technology has not yet entered the mass market, such as in the production of zero emission vehicles and localised household electricity generating apparatus.
The concept of fuel cells has been around since its accidental discovery by Welsh physicist William Grove in 1839. Grove was investigating the electrolysis of water using platinum electrodes, when he observed a reversal of polarity to the applied current flow to the cell when the electricity supply was switched off. The platinum electrodes in Grove’s ‘gas battery’ were catalysing the reaction between hydrogen and oxygen, the products of the electrolysis reaction, to form water with the liberation of electrical energy. The basic principle of fuel cell operation is fundamentally the same today as it was in Grove’s original gas battery. Fifty years later two chemists, Ludwig Mond and Carl Langer coined the term ‘fuel cell’ to describe their similar electrochemical device, which utilised a porous non-conductor to contain the electrolyte. An engineer from Cambridge University called Francis Thomas Bacon, descendant of the 17th century philosopher Francis Bacon, began working on alkaline fuel cells (AFCs) in 1932. In 1959 he built the first practical device, a stack of 40 AFCs, capable of generating 5kW of electrical energy. Allis-Chalmers, a farm equipment manufacturer from Milwaukee, US, pioneered the first fuel cell powered vehicle. His 20-horsepower tractor contained a stack of 1008 AFC cells capable of generating 15 kW. The power density (power output per unit volume) of these stacks was high. However, these cells had their operational limitations. The hydrogen fuel and the oxygen, supplied as compressed gases to these cells, had to be extremely pure because any traces of carbon dioxide gas would form a solid carbonate by reacting with the electrolyte, thus clogging up the cell pores, and reducing the efficiency of these cells. These cells also needed to be heated to 150 °C before they performed properly.

Research focused on AFCs, during the 1960s, in spite of the highly corrosive nature of the electrolyte. AFCs were cheaper to produce than the PEMFCs owing to the high content of platinum metal required for catalysis in the latter. Phosphoric acid fuel cells (PAFCs) were also researched owing to their operational advantage of being able to run on impure hydrogen gas, produced from the reformation of methanol.
In 1983 the Canadian department of National Defence commissioned Ballard research of Vancouver, Canada, to develop a low cost PEMFC that could run on contaminated gases. Ballard significantly reduced the amount of platinum metal catalyst used. They prevented any carbon monoxide impurity in the hydrogen gas from poisoning the catalyst by adding a ruthenium co-catalyst. These early cells used Nafion® membrane for the electrolyte, or a similar, but more effective membrane manufactured by Dow Chemical. Nafion® is the trade name for a perfluorinated polymer with perfluorosulphonic acid side groups manufactured by DuPont. Ballard’s continued refinement of these PEMFCs proved successful and they began to supply stacks of cells in 1987.

Ballard, now renamed Ballard Power Systems, continued to improve the PEMFC, increasing the power density from 70 kW m\(^{-3}\) in 1989 to 1.8 MW m\(^{-3}\) in 1997. Progress has been relatively slow since there are significant engineering problems associated with manufacturing stacks of fuel cells. Hydrogen and oxygen gases have to be supplied efficiently to the anode and cathode respectfully of each cell in the stack. In addition, the hydrogen and oxygen gases must be kept separate. Effective cooling is also required to prevent the electrodes from overheating and the product water must be efficiently removed from the cells to prevent flooding of the electrodes.

### 1.3.1 Fuel Cells in Space

Willard Thomas Grubb, a chemist working for the General Electric company (GE), Schenectady, New York State, US, used an ion-exchange membrane, a sulphonated polystyrene resin, as an electrolyte; Grubb patented the polymer electrolyte membrane fuel cell in 1955. GE expressed little interest in Grubb's design initially, because it still required the fuel and oxidant gases to be of high purity. GE expressed more interest in Grubb's design when the space race began in the late 1950s, because it was realised that spacecraft would require reliable power sources.
Leonard Niedrach, also working for GE, devised a way of depositing the platinum catalyst onto titanium gauze, which he then attached to the polymer membrane. GE developed the ‘Grubb-Neidrach fuel cell’ under contract to NASA, and this cell was used in the Gemini space programme. Pratt & Whitney (P&W) of what is now called United Technologies Corporation (UTC), from Connecticut, US, modified Bacon’s AFC to reduce its weight. The resultant cell had a longer working life than the PEMFC used on the Gemini space programme, so these AFCs were used for the Apollo space programme for the moon missions, and subsequently 12 kW AFC units were used in the space shuttle missions. The water by-product of the electrochemical reaction is used onboard the space shuttle for drinking.

1.3.2 Submarines and Submersible Craft

Another niche for fuel cell technology is in submarine applications. Ballard Power Systems have developed an 80 kW PEMFC, fuelled by methanol, for such purposes. International Fuel Cells, IFC, have also produced a 30 kW AFC (KOH) unit, supplied with H₂ and O₂ for the Lockheed Deep Quest vehicle, which is designed to operate to depths of 1500 m.

1.3.3 Fuel Cells in Vehicles

Automotive vehicle manufacturers are showing a great deal of interest in fuel cells for mass-market applications. The energy conversion efficiency of fuel cells is greater than that of the internal combustion engine, which averages 15 % or may reach 35 % under ideal operating conditions. This is partly due to the fact that fuel cells do not have to idle when a vehicle is stationary, unlike combustion engines in vehicles.

The large motor manufacturers began to show an interest in fuel cells in 1993 when Ballard unveiled their pioneering fuel cell powered bus. Ballard and Daimler-Benz, now DaimlerChrysler, collaborated to produce a series of prototype fuel cell vehicles
(FCVs) known as the NECAR (New Electric Car) series. DaimlerChrysler also plan to pioneer the commercial availability of fuel cell powered buses that run on compressed hydrogen. They have supplied 30 vehicles to a number of cities across Europe and Iceland, each capable of carrying up to 70 passengers, with a range of up to 300 km and a top speed of 80 km h⁻¹, and are close to going into mass production. The NECAR 5, fuelled by hydrogen, has just completed a 3000-mile endurance test across the US. The first production car based on the A-class is due to go on the market in 2004. Ballard are very influential in the automotive market and have supplied fuel cells to DaimlerChrysler, Ford, Daewoo, General Motors, Honda, Hyundai, Mazda, Nissan, Volkswagen, and Volvo.

In 1997 Ballard further collaborated with Daimler and Ford to form two new jointly owned specialist companies: XCellsis who integrate fuel systems with cell stacks to produce fuel cell engines, and Ecostar who supply electrically powered trains complete with monitoring and control systems. In 1999 Ballard teamed up with the fuel companies Arco, Shell, and Texaco, the Californian Air Resources Board and the Californian Energy Commission to form the Californian Fuel Cell Partnership. They plan to have 60 FCVs, including 20 buses, running by the end of 2003.

Other partnerships between companies that develop fuel cells and those that produce vehicles for the mass market include one between UTC Fuel Cells, Nissan and Renault, who have teamed up to develop fuel cells for vehicles using ambient-pressure PEMFC technology. UTC fuel Cells have also announced the formation of a partnership with Hyundai to develop the ‘SUV demonstrator program’ which aims to install a 75 kW fuel cell system into their new Santa Fe sport utility vehicle (SUV). General Motors, Volkswagen, Volvo, Chrysler, Nissan and Ford are also planning to build prototype PEMFC units, fuelled by hydrogen, methanol or petrol.¹⁸

Research into fuel cells is also underway in this country. Zevco is a British company that specialise in commercialising AFCs for use in vehicles and marine applications. In 1998, Zevco revealed their Millennium Taxi based on the London black cab. Zevco has more recently supplied a fuel cell powered van to Westminster Council.
They are developing a cobalt catalyst in order to replace platinum metal catalysts in AFCs, and so reduce the production costs.

Toyota Motor Corporation are developing fuel cell hybrid vehicles, the HCFV series. The Honda FCX has become the first fuel cell vehicle in the world to receive government certification. It is powered by a Ballard 78 kW PEMFC unit, fuelled on hydrogen. More information is available about fuel cell powered vehicles from the relevant manufacturers web sites.

The high cost of platinum metal has been a particular financial barrier to the commercialisation of fuel cells. Ballard Power Systems, in conjunction with Johnson Matthey, have developed a ‘supported catalyst system.’ Tiny particles of platinum metal, 2 nm in diameter, bonded to carbon particles, are made into an ink and printed onto the electrode material. This new process has reduced the cost of electrode production dramatically. However, should fuel cell powered vehicles ever go into mass production, the requirements for platinum will be huge and this will be likely to push worldwide platinum prices up even higher. Therefore, this particular problem still has to be resolved.

Another significant problem with commercialisation of fuel cell powered cars is that there is currently no infrastructure for the supply of H₂ gas at petrol stations. However, liquid fuels such as methanol, petrol or synthetic paraffin can be converted into hydrogen gas and carbon dioxide gas by means of catalytic reformation with steam. 1st generation fuel cells could therefore run on these liquid fuels until the necessary infrastructure for the supply of hydrogen has been established.

### 1.3.4 Fuel Cells as Stationary Power Units

The development of fuel cell technologies has brought us closer in time to the reality of cost effective and reliable localised power generation. Fuel cells, installed as stationary power units, with delivery capacities ranging from several hundred kW to MW of electrical power, may well be used to power a range of domestic and
commercial utilities including houses, apartment blocks, hotels, hospitals, small businesses and factory units. The larger fuel cells are also suited to power generation for grid systems. These systems can be fuelled by natural gas or gasified coal. Deregulation and demonopolisation of the electricity supply industry in the US and in the UK has, in some cases, resulted in increasingly long distances between electricity suppliers and users, which could be eliminated by using stationary units.

Fuel cells operate relatively cleanly and silently. Their widespread distribution, replacing existing fossil fuel powered generating plants, would help reduce the amount of localised pollution associated with fossil fuel powered generating plant. Fuel cells also have the advantage that they are less likely to be put out of operation by storms and calamities. It is noteworthy that fuel cells have been employed in place of other power generating sources for a variety of unusual reasons. A 200 kW fuel cell unit was installed at the police substation in New York, US, in order to eliminate the expensive task of laying underground power cables beneath Central Park. The First National Bank of Omaha, Nebraska, US, has installed four 200 kW fuel cells as its main power source, because it requires ultra-high reliability, since even brief interruptions to its credit card transaction processes can be costly.

High temperature fuel cells can run at efficiencies approaching 80%, especially with the recovery of waste heat energy (combined heat and power system), and can be manufactured from relatively cheap materials, because they do not require the use of expensive noble metal catalysts. Furthermore, high temperature fuel cells such as MCFCs and SOFCs can potentially be fuelled from a diversity of hydrogen-rich sources, e.g. ammonia, natural gas, petroleum distillate, liquid propane, gasified coal, and renewable sources including biomass and hydrogen gas produced by geothermal, solar and wind plants. The use of these fuel cells as cost effective and reliable stationary units is likely to occur once the problems associated with present materials have been overcome. A fuel cell of around 45 kW generating capacity is adequate for a large domestic house or a small commercial application, such as a laundry. Fuel cells, capable of generating up to several hundred kW of electrical power, could potentially be used to power large commercial establishments.
United Technologies Fuel Cells, UTC Fuel Cells, have developed a 200 kW PAFC unit, marketed as the PC25™. This unit is fuelled by natural gas and has been used for a number of applications, including hospitals, hotels, manufacturing sites and wastewater treatment plants, to provide a range of services, including backup, uninterrupted power supply and as an independent power source. UTC Fuel Cells sold 23 of these units in 2001, and have announced the planned installation of a number of units across North and South America. UTC Fuel Cells also have a joint agreement with Burderus Heiztechnic to develop fuel cells for the European residential market.  

Ballard Generation Systems have developed a 250 kW PEMFC system, fuelled on natural gas, of which they are currently in the process of installing and testing 9 units.

The products of Fuel Cell Energy, FCE, include 250 kW DFC®, 300 kW, 1.5 MW and 3MW MCFC units. They have received orders for a number of installations, especially for their 250 kW DFC® unit. Interestingly, one of these units is to supply power to a brewery outside Tokyo in Japan. It will be fuelled by a methane based gas produced by digesting the brewery effluent. Similarly, they are to supply a 1 MW DFC® unit to a wastewater treatment plant in Washington, which will be fuelled by a methane-rich gas supplied by an anaerobic digestion of the effluent.

Siemens Westinghouse Power Corporation, SWPC, is the leader in the field of SOFCs and has developed a range of prototype cells that are in operation, and is expecting to market 220 kW, 100 kW and 25 kW SOFC systems, based on their tubular design, by the end of this year. SWPC also plan to market a 250 kW cogeneration system, operating at atmospheric pressure. SWPC favour the use of SOFC/gas turbine hybrid systems and plan to market a 0.5 MW version in the future. Efficiencies in the range 60% to 70% are obtainable using such hybrid systems.

To demonstrate reliability SWPC have run a 25 kW system for more than 9000 hours using a variety of fuels, including natural gas, diesel and jet fuel at the National Fuel Cell Research Centre at Irvine, California. A 250 kW system with CO₂ capture
technology is to be supplied to Norske Shell on Norway. The system is intended to demonstrate the economical recovery of CO₂, which can be stored underground, or used for farming or agricultural purposes.¹⁴

1.3.5 Portable Fuel Cells

Miniature fuel cells have been developed that could be used to run small electronic items such as laptop computers or mobile phones. The ‘micro fuel cell’ runs on a mixture of methanol and water. It can be mass-produced by means of a lithographic process that prints the electrodes and catalysts onto a polymer film. Such Micro Fuel Cells are currently capable of an output power more than three times greater than that of standard lithium batteries, with a potential capability of up to thirty times greater.

Manhattan Sciences, MS, is collaborating with the battery and electronic industry to develop the Micro Fuel Cell further. MS also owns the rights to the fuel cell technology developed by NovArs. NovArs are a German Company who specialise in high current/low voltage applications such as power tools and wheel chairs. MS are developing the HYDROCYCLE™; a fuel cell powered bicycle, for which the initial testing is now complete. They hope to storm the Asian market with this invention, since this market is more amenable to new inventions. NovArs has applied for patent protection on the PEMFC based power unit for this technology in key markets around the world.¹⁹

Ballard Generation Systems have also developed a 1.2 kW portable PEMFC module, which is being marketed as the Nexa™. They are also developing a 1 kW co-generation system for the Japanese market.
1.4 Solid Oxide Fuel Cells

This project is concerned with the development of new materials for SOFCs, and so the important characteristics of the materials used for such fuel cells will now be discussed in more detail. The essence of an SOFC is that it is a solid state device whose function relies on the efficient reaction/passage of appropriate gases, ions and electrons across solid state materials. The choice of components for these systems is crucial in that they must not only perform well as individual items, but must also be compatible with the other components of the cell. Each of the major cell components will be covered in turn following a brief introduction into ionic conduction.

1.4.1 Fast Ion Conduction

An ionic conductor is any material capable of electrical conduction by means of the migration of ions through its structure. Most solids are poor ionic conductors owing to high activation energies for ionic migration and/or an insufficient number of defect sites available to facilitate ion migration. The solids that do conduct ions well are known as fast ion conductors. The conductivities of fast ion conductors generally fall into the range of $10^{-3}$ to $10^{1}$ S cm$^{-1}$, at the particular temperature in question. These materials are referred to as solid electrolytes if they only display ionic conduction. If however, these materials also display electronic conduction then they are referred to as mixed conductors.

All crystalline solids contain defects that fall into two categories, intrinsic defects and extrinsic defects. Intrinsic defects are integral to the crystal lattice structure and do not change the overall composition. They fall into two categories, Schottky defects and Frenkel defects. Schottky defects are sympathetic anion and cation vacancies that occur together in order to preserve charge neutrality. Frenkel defects occur in one sublattice when either cations or anions are located in interstitial, non-regular, lattice sites leaving the normal site vacant. Frenkel defects usually involve the displacement of cations into interstitial sites owing to the relatively smaller ionic radius of cations compared to anions.
The creation of vacancies incurs a cost in terms of a decrease in lattice energy ($\Delta H$).
This decrease in lattice energy is compensated by an increase in entropy ($\Delta S$),
associated with the increased disorder within the crystal structure. Increasing the
overall temperature of the system makes the creation of additional defects even more
thermodynamically favourable ($-T\Delta S$), by means of an increase in the Gibbs free
energy ($\Delta G$), $\Delta G = \Delta H - T\Delta S$.

The characteristics of fast ion conduction can be illustrated by the situation in NaCl.
In NaCl, cation vacancies, due to Schottky defects, will facilitate the migration of
Na$^+$ ions. However, the low number of such defects, due to the high lattice energy,
means that NaCl is a poor cation conductor. The conductivity does increase
dramatically when the temperature of the crystal approaches the melting point owing
to the introduction of a high degree of disorder within the crystal. The melt is itself a
good ionic conductor because of the mobility of all the ions.

Inserting foreign ions into the crystal lattice structure, e.g. by means of doping,
creates extrinsic defects and increases ionic conductivity. Doping CaCl$_2$ into NaCl
according to the composition Na$_{1-2x}$Ca$_x$Cl gives one extra Na vacancy for every Ca
ion introduced in order to preserve charge neutrality. Even so, the conductivity of
such a system is still relatively low. To explain this, it is important to consider the
activation energy, $E_a$, for migration of ions through the lattice. In NaCl the Na$^+$ ions
follow a curved pathway through the crystal lattice that incurs the lowest activation
energy. They leapfrog their way past the Cl$^-$ ions, avoiding the direct route between
two Cl$^-$ ions, thus circumnavigating the most sterically hindered route. Even so, the
activation energy is high, and so the conductivity of NaCl is low, except at very high
temperatures. Therefore for high ionic conduction, we require a large number of
defects and low activation energy for defect migration.
The ionic conduction properties of solids often show Arrhenius type dependence, and can be related to the equation:

$$\sigma = A \exp(-E_a/RT)$$

Where $A$ = pre-exponential factor

- $R$ = gas constant (JK$^{-1}$)
- $T$ = temperature (K)
- $E_a$ = activation energy (J)
- $\sigma$ = Conductivity (S cm$^{-1}$).

A refinement on the equation above introduces a further temperature dependence:

$$\sigma T = A' \exp(-E_a/RT)$$

Plotting log ($\sigma T$) vs. 1000/T or log $\sigma$ vs. 1000/T will give straight-line graphs, from which the activation energy can be calculated.

In this project we are concerned with oxide ion conduction in solids, and so we shall now discuss typical structures showing good oxide ion conduction.

### 1.4.2 Ionic Conduction in the Fluorite Structure

There are a number of crystalline materials with the fluorite type structure that display good anionic conductivity ($F^-$, $O^{2-}$). PbF$_2$ is a good example of a $F^-$ ion conductor, demonstrating a conductivity of $\approx$ 5 S cm$^{-1}$ at 500 °C. The structure comprises a cubic array of $F^-$ ions with half of the body centre positions filled with Pb$^{2+}$ ions. Ionic conductivity is facilitated by means of Frenkel defect formation. $F^-$ anions move into vacant body centre positions leaving some of the anion sites vacant, thus aiding the conduction of $F^-$ ions.

Zirconia (ZrO$_2$) is an example of a good oxide ion conductor, the properties of which have been known for over a century. ZrO$_2$ adopts the cubic fluorite structure at high
temperatures. The cubic fluorite structure can be stabilised at low temperatures by doping with aliovalent ions such as Ca and the rare earth elements. Doping with these elements also introduces oxide ion vacancies. Consequently these stabilised zirconias demonstrate high oxide ion conductivities. The conductivity of \((\text{Y}_2\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}\), otherwise known as YSZ, is \(\approx 0.1\ \text{S cm}^{-1}\) at 1000 °C, and this is the currently favoured electrolyte for SOFCs. Oxide ion conductivity can be improved by doping with ions that have a similar ionic radius to Zr. If ZrO₂ is doped to a level of between 8 % and 12 % with Sc₂O₃, then higher oxide conductivity is observed. The oxide ion conductivity of \((\text{Sc}_2\text{O}_3)_{0.1}(\text{ZrO}_2)_{0.9}\) is \(\approx 0.1\ \text{S cm}^{-1}\) at 800 °C. If the zirconia is doped with Sc₂O₃ to levels higher than 12 %, the oxygen vacancies tend to aggregate to form defect clusters, resulting in a decrease in oxide ion conductivity.

Fluorite materials based on CeO₂ doped with rare earth metals are also known to display higher oxide ion conductivity than YSZ. These materials will be discussed in detail later in this chapter.

\(\text{Bi}_2\text{O}_3\), otherwise written as \(\text{BiO}_{1.5}(\text{vacancy})_{0.5}\), adopts the fluorite structure and contains intrinsic oxide ion vacancies. \(\text{BiO}_{1.5}(\text{vacancy})_{0.5}\), adopts a \(\delta\) phase above 750 °C.²¹ The \(\delta\) phase is the best oxide ion conductor known, almost two orders of magnitude greater than YSZ, because the oxide ion vacancies are disordered in this high temperature phase. The oxide ion conductivity is believed to be enhanced by the high polarisability of the \(\text{Bi}^{3+}\) ion. The \(\delta\) phase can be stabilised at room temperature, by doping with \(\text{Y}_2\text{O}_3\) and annealing below 700 °C, although this phase is thought to be metastable owing to an observed gradual decrease in oxide ion conductivity with time. \((\text{Bi}_2\text{O}_3)_{0.75}(\text{Y}_2\text{O}_3)_{0.25}\), displays a conductivity of \(1.3 \times 10^{-2}\ \text{S cm}^{-1}\) at 500 °C. Unfortunately, phases containing Bi display some electronic conductivity under reducing conditions owing to the partial reduction of \(\text{Bi}^{3+}\), rendering them useless as materials for electrolytes in SOFCs.
1.4.3 Ionic Conduction in the Perovskite Structure

Perovskites have the general formula ABO₃ (A is a large cation and B is a small cation). The A and O cations are arranged as a cubic close packed structure with the B cations occupying a quarter of the octahedral holes. O²⁻, H⁺ and Li⁺ conduction have been observed in perovskite phases. A number of perovskite phases display good oxide ion conductivity at high temperatures when vacancies have been introduced into the structure by means of suitable doping. Perovskites with the formula ABO₂.₅ are known to form the brownmillerite structure, in which the oxide ion vacancies become ordered. The brownmillerite structure contains alternate layers of octahedral and tetrahedral B cations. This ordering of vacancies lowers the conductivities of such compounds. For example Ba₂In₂O₅ displays only moderate oxide ion conductivity below 900 °C. However, increasing the temperature to above 900 °C results in an order-disorder transition. This increase in disorder results in an increase in oxide ion conductivity of over an order of magnitude. Thus Ba₂In₂O₅ displays an oxide ion conductivity of ≈ 0.1 S cm⁻¹ at 900 °C. There are a number of useful articles covering the subject of electrolyte materials in the literature including a review paper by Morgensen and Skaarup et al. which covers the main aspects.

Perovskite phases that display oxide ion conductivity will also display proton conductivity, although one form of conductivity is likely to be dominant over the other. Doped Sr and Ba Cerates display the best proton conductivity, where the Ce sites are partially substituted with trivalent rare earth metals, e.g. ACe₁₋ₓMₓO₃₋ₓ/₂ (A = Sr, Ba; M = rare earth, e.g. Y, Yb, Nd).

Perovskite materials based on LaGaO₃ show high oxide ion conductivities, which will also be discussed later in this chapter.

1.4.4 Stack Configurations

There are two major design concepts followed by the majority of companies: the planar, or the tubular, the latter of which has been developed extensively by Siemens.
Westinghouse Power Corporation. These stack designs are covered in detail by the 6th edition of the Fuel Cell Handbook, and different manufacturing techniques are discussed by Minh et al. Other designs are also under consideration, including the monolithic design favoured by the Argonne National Laboratory, USA. The Co-fired SOFC Electrode-Electrolyte-Electrode Membrane Rolls, the “SOFCoRoll”, which is under development at the University of St Andrews in Scotland, and the Sulzer-Helix HXS 1000 premier, were featured at the Fuel Cell World conference in Lucerne, Switzerland in July of last year. The essence of the Sulzer-Helix design is a “compact disc” type planar configuration incorporating a radial gas distribution system.

1.4.5 Planar Stacks

The configurations of a single cell for the planar design are shown in figure 1.3. Planar stacks are categorised according to the nature of the support. YSZ electrolyte supported stacks are used for high temperature operation. The electrolyte is ≥ 100 μm in thickness and is produced typically by the tape casting process. The anode, 50 μm in thickness, and the cathode, 500 μm in thickness, are applied subsequently either by screen-printing or by plasma spraying.

![Diagram of planar fuel cell 'short stack'](image-url)
More recently, in an attempt to lower the operating temperature, Ni/YSZ anode supported cells are under development. In this case the thickness of the anode is ≈ 1.5 mm, the YSZ electrolyte thickness is ≈ 30 μm, with a cathode thickness of 50 μm. These systems can employ ferritic steel interconnects, thus improving fracture resistance and tolerance to thermal stress and reducing production costs.

1.4.6 Tubular Stacks

The configuration of the tubular design is shown in figure 1.4. The cell components are supported on a LSM cathode (2mm thick), which is produced by an extrusion/sintering process. The YSZ (8 mol % Y2O3) electrolyte is deposited onto the cathode to a thickness of between 30 μm and 40 μm by electrochemical vapour deposition, EVD. The Ni/YSZ cermet anode is deposited as a slurry and “EVD fixed” to a thickness of ≈ 150 μm. “EVD fixed” means that an additional layer of ZrO2 is deposited by EVD to fix the nickel anode to the electrolyte. This process is, however, an expensive one, and a cheaper process such as plasma or liquid spraying is being sought. The doped lanthanum chromite interconnects are deposited by plasma spraying to a thickness of ≈ 100 μm.
Figure 1.4. Tubular fuel cell design.
1.4.7 Balance of Plant

There are a number of equipment items, peripheral to the fuel cell itself, which are necessary for cell operation. These items are termed the "Balance of Plant" (BOP), several of which Steele et al. has identified as receiving minimal interest, in terms of research, such as fuel processing units, heat exchangers and pumps etc. This is despite the fact that BOP items often lead to cell failure, and can prove less reliable than the stack configuration itself. Steele et al. has also identified that power conditioning systems, such as d.c./a.c. converters and control systems require further development.¹

1.4.8 Electrolyte Materials

There are a number of important criteria that need to be considered when choosing an electrolyte material for use in an SOFC. The material needs to be a good oxide ion conductor at the desired operating temperature, in order to facilitate the efficient passage of oxide ions from the cathode to the anode. Ideally, there must be no electronic conductivity, which would short-circuit the cell and cause a drop in power density. In terms of oxide ion conduction, Steele et al. suggests that the electrolyte should not contribute more than 0.15 Ω cm² to the total cell area specific resistivity (ASR), and the conductivity should exceed 10⁻² S cm⁻¹ at the temperature of operation.¹ It follows, that it is important to keep the electrolyte thickness to a minimum, in order to minimise the resistive losses. Another important feature is that electrolyte materials must be stable at the fuel cell operating temperature under oxidising and reducing conditions owing to the porous nature of the electrodes allowing fuel and oxidant gases to come into contact with the electrolyte. Furthermore, an electrolyte must also have good mechanical properties at the desired working temperature, and not react with the cathode or anode.
1.4.9 Yttria Stabilised Zirconia

Yttria-stabilised-zirconia, YSZ, meets the criteria stated above, but is only a good oxide ion conductor at elevated temperatures, 800 °C to 1000 °C.\(^{31}\) YSZ achieves an ASR value of 0.15 \(\Omega\) cm\(^2\) and conductivity of \(10^{-2}\) S cm\(^{-1}\) at 700 °C, with a electrolyte thickness of 0.0015 cm (where \(\sigma = L/\text{ASR} = 0.0015/0.15\)).\(^{1}\) The thermodynamic properties of YSZ have been reviewed by Yokokawa \textit{et al.}\(^{32}\) Unfortunately, YSZ exhibits interfacial reactions when used in conjunction with LSM as a cathode material, which is of significant concern at these high operating temperatures,\(^{33}\) the details of which will be discussed later.

In the case of YSZ-based planar electrolyte supported systems, the electrolyte thickness generally ranges between 100 \(\mu\)m and 200 \(\mu\)m. It is possible to produce thinner layers, between 10 \(\mu\)m and 50 \(\mu\)m in thickness,\(^{34,35}\) however, the minimum practical thickness for dense impermeable films is between 10 \(\mu\)m and 15 \(\mu\)m.\(^{1}\) It is difficult to produce films thinner than 1 \(\mu\)m without the formation of pinholes or cracks, through which the oxidant and fuel gasses can mix, thus lowering the power density of the cell.\(^{36}\) Steele \textit{et al.} has considered the theoretical and practical limitations on the thickness of an electrolyte material. He has determined that below a certain thickness, 1 \(\mu\)m in the case of YSZ,\(^{1}\) that the surface exchange of oxide ions, and not their diffusion, becomes the predominant factor.\(^{37}\) Consequently, further reduction in electrolyte thickness does not lead to any improvement in conductivity. It therefore seems unlikely that YSZ will be a suitable candidate as an electrolyte material in an intermediate temperature fuel cell.
1.4.10 Anode Materials

B. C. H. Steele et al (1990) has identified ideal criteria for the properties of future anode materials: 38

1. Good electronic conductivity, preferably over $10^2$ Scm$^{-1}$ at anode operating potentials (0.7-0.9V). Probably n-type materials are preferable.

2. Predominant anion lattice disorder to enhance oxygen diffusion coefficients and possibly protonic conductivity.

3. High values for oxygen surface exchange kinetics.

4. Fabrication of adherent films with minimal processing problems.

5. Compatibility with the solid electrolyte substrate.


At the present time manufacturers developing SOFCs use a Ni-YSZ cermet as the anode material, 39 because it is relatively cheap to produce and readily catalyses the oxidation of hydrogen. Unfortunately, the competitive cracking of hydrocarbon fuels leads to carbon build up on the anode, and so poisons the anode catalyst. This is a major problem with using a Ni-YSZ cermet as the anode material. 40 This indeed prevents its use in cells where internal reforming of the fuel is required, and so negates the possibility of supplying methane directly as a fuel into SOFCs. Also, any sulphur present in the fuel (natural gas contains significant levels of sulphur) will react with the nickel in the anode to form nickel sulphide, and so also poison the catalyst. A further problem with a Ni-YSZ cermet is that the effective surface area of the electrode is reduced over time, due to sintering of the nickel in the anode at the high operating temperature.

Methane, and other hydrocarbons found in natural gas, can, however, be reformed prior to use with high-pressure steam by means of the following reaction scheme either internally or externally to the cell:
The third reaction scheme above liberates carbon and must be avoided by not allowing the steam pressure of the system to drop too low. External fuel reformation is an expensive process and it is therefore desirable to try and develop an SOFC that can reform fuel internally without poisoning the anode.\textsuperscript{41}

There are a number of problems associated with designing a fuel cell capable of internal fuel reformation. In addition to the catalyst poisoning outlined above, a significant problem is one of temperature gradients across the cell. This is because the reformation reaction is an endothermic one, whereas, the catalytic oxidation of hydrogen is an exothermic one.

In terms of alternative anodes, doped SrTiO\textsubscript{3} materials have also been investigated, as have a number of other oxide materials.\textsuperscript{42-47} However, none of the phases investigated so far have met all of Steele’s criteria. The quest to discover a material that will meet Steele’s criteria will be quite a challenge owing to the range of oxygen partial pressures experienced at the anode.

1.4.11 Cathode Materials

The selection criteria for alternate cathode materials is similar to those put forward by Steele for alternative anode materials; the main difference being that cathodes experience higher oxygen partial pressures and tend to exhibit p-type conductivity. Materials that readily adsorb oxygen molecules, promote oxidative dissociation into \( O^2^- \), and allow readily the transport of oxide ions into the electrolyte phase, are necessary requirements for efficient cathode operation in SOFCs. The pathways for the catalytic reduction of oxygen at the cathode/solid electrolyte interface have been under consideration for more than 25 years.\textsuperscript{48} The different reaction pathways at the cathode/solid electrolyte interface are shown below in figure 1.6.\textsuperscript{49}
Figure 1.6. The different reaction pathways at the cathode/solid electrolyte interface.

The reaction pathway $R_1$ depicts the direct reaction of $O_2(g)$ with the surface of the electrolyte. $R_2$ depicts dissociative-adsorption of $O_2(g)$ followed by surface diffusion towards the three-phase boundary, TPB, between the electrolyte, electrode and gas. $R_3$ depicts the initial surface reaction of $O_2(g)$ dissolution and diffusion of oxide anions through the electrode towards the cathode/electrolyte boundary. $R_2$ and $R_3$ will be the most significant of the three reaction pathways.

Another important feature is that they have a porous microstructure to allow efficient gas dispersion within the cathode. Furthermore, they must be stable in oxidising conditions at the temperature of fuel cell operation, often where a significant water vapour pressure is present, and crucially must show chemical and mechanical compatibility with the cell environment.

A number of materials have been investigated for potential use as cathode materials in SOFCs. There are a number of useful articles on cathode materials in the literature including a review paper by Mogensen et al., which covers the main factors controlling the performance of SOFCs, and more recently a review paper by A.J. McEvoy et al.
Following on from Nernst's initial work on solid electrolytes\textsuperscript{51} Baur et al. established in the 1930's that a fuel cell operating at high temperatures was necessarily a solid state device.\textsuperscript{52, 53} Baur initially used iron oxide as a cathode material owing to its potential to meet the above criteria. Also, redox activity could be promoted by using iron, catalysing the cathodic reaction. Unfortunately, $\text{Fe}_2\text{O}_3$ is the stable phase under cell operating conditions and is near insulating in nature. Therefore, other potential cathode materials had to be sought. Tannenberger and van den Berghe et al. evaluated Indium-tin mixed oxide, ITO, as a potential cathode material. ITO is essentially a glassy material and is impervious to gas: oxygen has to therefore permeate along the grain boundaries of the dendritic structure in order to reach the electrochemically active cathode/electrolyte interface.\textsuperscript{54} The same group also looked into the possibility of using lanthanum/strontium based perovskite materials containing either cobalt or chromium as cathodes, the latter of which is now used as an interconnect material in SOFCs. It was not until the 1980's that lanthanum strontium manganate, LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$), was identified as a cathode material, and is still the cathode material favoured by manufacturers to date.\textsuperscript{55}

\subsection*{1.4.12 Lanthanum Strontium Manganate}

LSM is a derivative of $\text{LaMnO}_3$, where Sr has been partially substituted into the La sites. LSM has been chosen for the cathode role in SOFCs because of its good electronic conductivity, good thermal expansion matching with YSZ and ready catalysis of the reduction of oxygen.\textsuperscript{56} Lanthanum manganate, $\text{LaMnO}_3$, adopts the perovskite structure, where manganese cations occupy octahedral sites and the lanthanum cations occupy 12 co-ordinate sites. In LSM, strontium occupies sites in the lanthanum sub-lattice, and a proportion of the manganese (III) is oxidised to manganese (IV) to maintain charge balance. Doping with strontium therefore increases electronic conductivity owing to an increase in the concentration of Mn$^{4+}$.

With regard to the electronic nature, LSM is a p-type semiconductor, the conductivity of which is enhanced by the presence of strontium ($100 \text{ S cm}^{-1}$ at 950 °C).\textsuperscript{6} The inclusion of strontium into lanthanum manganite also ensures that the
thermal expansion coefficient has a similar value to that of YSZ, thus avoiding the possibility of splintering at the electrode/electrolyte interface region when cycling the fuel cell between ambient and working temperatures.

An important factor to be considered when choosing a cathode material is any possible reaction between the cathode and the electrolyte. Although some chemical interaction between electrolyte and electrode is required to ensure proper adhesion, too much reaction can lead to the formation of other thermodynamically stable phases, which might be insulating in nature, and therefore detrimental to the operation of the cell. Lau and Singhal et al. have shown that stabilised zirconia reacts with LSM to form $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{SrZrO}_3$, which are insulating in nature.\(^{33}\) These observations have been verified by Mitterdorfer and Gauckler et al. using nano-scale imaging techniques.\(^{57}\) The effect of cell morphology at the YSZ-LSM interface region on cell operation is an important one, the details of which will be discussed briefly in the next few paragraphs.

There is a relationship between the geometry of an electrode and its resistance, and this relationship is bias-dependent (polarisation resistance). In the cathodic region (close to equilibrium) the resistance is proportional to the inverse of the electrode area. However, measurements taken without bias show that the resistance is proportional to electrode thickness, indicating that oxygen reduction is associated with a pathway through the bulk of the LSM cathode ($R_3$). Conversely, in the anodic region the resistance becomes proportional to the inverse of the three-phase boundary length, indicating that oxygen reduction is associated with a surface pathway ($R_2$).\(^{58}\)

Under such conditions of charge transfer, there is a drop in potential difference (overpotential) across the YSZ/LSM interface which can, according to the Nernst equation, be related to a reduced oxygen activity and $\rho(\text{O}_2)$ in this region. In-situ X-ray diffraction studies of LSM cathodes under operating conditions reveal that there is an associated lattice expansion, corresponding to an oxygen loss.\(^{59}\)

Polarisation effects on charge transfer at the YSZ-LSM interface represent the most significant losses in SOFC systems and are affected by the fuel cell operating history, as studied by Takahashi and Iwahara et al.\(^{60}\) Polarisation losses have been studied
more recently by Jiang and Love et al. Their findings suggest that the morphology of the YSZ-LSM interface is an important factor and that the initial high polarisation is related to the initial presence of species such as MnO$_x$ and in particular SrO on the surface of the electrode. Interestingly, they further suggest that these losses decrease with fuel cell use. Indeed, related work indicates that La$_2$Zr$_2$O$_7$ dissolves and reforms into the parent lattices under fuel cell operation. La$_2$Zr$_2$O$_7$ formation can be inhibited at the production stage by utilising compounds at the interface region that are deficient in lanthanum content thus restricting the initial formation. Polarisation effects have also been observed with ITO-YSZ interfaces, but these could be kept to a minimum by introducing a transition metal to the interface region in order to introduce mixed conductivity and delocalise oxygen reduction. A similar approach has been used by other workers to enrich the electrode/electrolyte region by deposition with other redox-active species such as iron, manganese and cerium, using techniques such as sputtering, pyrolysis of a salt solution, ion implantation. It is desirable to keep the number of layers down to a minimum because each additional one incurs more interfaces regions, and thus more potential losses, as well as adding to processing time and production costs.

Composite cathodes have been under consideration for a number of years. They comprise a porous outer region, which is made of LSM, and acts as a current collector, and a dense inner region, which is comprised of a YSZ/LSM composite. It is the interface region between the composite and the current collector that is believed to contain the active sites for oxygen reduction. Due to the correlation between microstructure and electrode performance, employing low sintering temperatures for the current collector, 1150 °C, results in low density and small particle size, which maintains an active triple phase boundary layer, and thus low polarisation losses and a ready pathway for oxygen diffusion. Composites of YSZ and (La/Sr)MnO$_3$ have demonstrated lower polarisation losses than simply using LSM, essentially by maximising the TPB area.

Removing the dependence of the cathode on the TPB length per unit area would simplify cathode production and increase cell efficiency by lowering the overpotential losses. This can be potentially achieved by using a mixed conductor for the cathode material. The cathode material now will display R3 type behavior, where the reaction is no longer
limited to the TPB, with oxygen reduction occurring on the cathode surface and oxide anions now able to pass through the cathode to the electrolyte.

There is still a need to discover new mixed conducting materials for use in cathodes. Research has been directed towards perovskite phases containing Co and Fe, e.g. LCCF (La$_{0.6}$Ca$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$-$\alpha$),$^{73}$ La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$M$_{0.2}$O$_3$, (where M = Co, Mn, Cr, Fe, or V),$^{74}$ LSCFe7 (La$_{0.84}$Sr$_{0.16}$Co$_{0.3}$Fe$_{0.7}$O$_3$) and LSCFe3 (La$_{0.84}$Sr$_{0.16}$Co$_{0.7}$Fe$_{0.3}$O$_3$)$^{56}$ Ruthenium perovskites and pyrochlores have also been looked at as materials for cathodes in SOFCs, although these are likely to be too expensive.$^{75}$

### 1.4.13 Interconnect Materials

LaCr(Mg)O$_3$ and La(Ca)CrO$_3$ based materials are predominantly used as interconnects in high-temperature SOFCs, although they exhibit problems related to \( \rho(\text{O}_2) \) expansion, owing to the chemical potential gradient between the cathodic and anodic environments of a cell, which can lead to structural failure.$^{76}$

Due to the high fabrication costs of such interconnect materials, other cheaper systems are being sought. One example is the Siemens Cr/Fe (95/5) alloy – stabilised with 1 \% Y$_2$O$_3$, although this suffers Cr$_2$O$_3$ deposition at the cathode/ electrolyte interface, by means of the migration of gaseous CrO$_2$(OH)$_2$ and CrO$_3$ species, leading to poisoning of the cathode.$^{77}$

### 1.4.14 Alternative Materials for Intermediate Temperature Fuel Cells

SOFCs were originally intended for use as high power stationary units owing to the fragile nature of the ceramic components. There is nowadays an interest by developers to diversify from the traditional high power/temperature units and to develop smaller and more versatile units that can be used for lower power applications, such as auxiliary power units for the automotive industry and as power sources for individual homes. Interestingly, Boeing are developing a unit that will power a light aircraft, and they are also considering using them as auxiliary power
units. A significant number of the problems identified for YSZ-based SOFC systems could be eliminated, or at least minimised, by lowering the temperature of operation. For example, expensive ceramic and alloy based interconnects and auxiliary plant, e.g. pipe connections, could be replaced by cheaper and more reliable stainless steel based components. Thermal mismatch and interfacial reaction would also be less of a problem, thus eliminating the problems identified due to thermal cycling. Operating temperatures can potentially be reduced by the use of thin layers of electrolyte, but these introduce associated production problems. Another alternative is the design of improved electrolyte materials, and to this end, electrolyte materials that possess high oxide ion conductivity at intermediate temperatures, $\approx 500 \degree C - 750 \degree C$, are under development.

Fluorite phases based on CeO$_2$, doped with rare earth metals, display higher conductivities than doped zirconia. A major drawback, however, with ceria based electrolytes is that Ce$^{4+}$ ions can be reduced to Ce$^{3+}$ under fuel rich conditions when operating at high temperatures. This introduces some electronic conductivity into the electrolyte, and thus a partial short circuit across the cell. A consequence of a short circuit is that large quantities of fuel would be consumed under low load conditions. The enthalpy of reduction for CeO$_{2-x}$ is large, $\approx 10 \text{ eV/mol } O_2$, as established by Bevan and Kordis et al. Although, Ross and Benjamin et al. consider that the electronic conduction is too high for ceria based electrolytes at 700 $\degree C$. Steele et al. have established that at low operating temperatures (500 $\degree C$) this problem becomes negligible. Steele considers the Ce$_{0.9}$Gd$_{0.9}$O$_{1.95}$ composition (CGO) to be optimal, and suggests that it is possible to achieve conductivities of $10^{-2}$ S cm$^{-1}$ at 500 $\degree C$, satisfying the target ASR of 0.15 $\Omega$ cm$^2$ using a 15 $\mu$m thick electrolyte.

An initial major difficulty with ceria based electrolytes was the development of compatible cathode materials. However, cathodes have now been developed that can function effectively at temperatures as low as 500 $\degree C$, with minimal overpotentials. Suitable sealant materials have also been developed for use with ceria based fuel cell systems, but the composition of these are largely proprietary; they are, however, generally glass/ceramic based. Researchers at the Argonne
National Laboratory, ANL, have been investigating La$_{1.2}$Sr$_x$Co$_{1.2}$Fe$_y$O$_{3-x}$ based perovskite systems such as La$_{0.5}$Sr$_{0.2}$Fe$_{0.8}$Co$_{0.2}$O$_3$ (LSFC) and La$_{0.8}$Sr$_{0.2}$FeO$_3$ (LSF) for use as cathode materials with CGO based electrolytes. The ASR of LSCF and LSF are 0.3 $\Omega$ cm$^{-2}$ and 0.1 $\Omega$ cm$^{-2}$ respectively at 850 °C, with the ASR for LSF remaining below 1 $\Omega$ cm$^{-2}$ at 750 °C. Studies at ANL of low temperature stacks utilising CGO electrolytes show relatively low power densities, 125 mW cm$^{-2}$, at intermediate temperatures, 650 °C, compared to cells with zirconia based electrolytes, 600 mW cm$^{-2}$, operating at high temperature, 800 °C to 1000 °C. There is evidently a lot of room for improvement before fuel cells based on doped-ceria electrolytes will become a viable proposition.

Perovskite systems based on doped lanthanum gallate, LaGaO$_3$, where strontium occupies some of the La sites, and Mg occupies some of the Ga sites with the general formula La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-\delta}$ (LSGM) have been identified as good oxide ion conductors by Ishihara et al. Compositions such as La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.85}$ display oxide ion conductivity as high as $\approx$ 0.1 S cm$^{-1}$ at 850 °C, thus offering the prospect of lower temperature fuel cell operation. Low temperature fuel cell operation has indeed been demonstrated using this electrolyte by Ishihara et al. A single phase composition for LSGM has been optimised, La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{2.85}$, and shown to have an oxide ion conductivity of 0.15 S cm$^{-1}$ at 800 °C. With the optimisation of the oxide ion conductivity of this phase, research has been directed towards suitable electrode materials for use with it. Huang et al. have studied La$_{0.6}$Sr$_{0.4}$CoO$_{2-\delta}$, LSCO, a mixed ionic/electronic conducting material, for use as a cathode material with LSGM. They have found that gallium and cobalt can inter-diffuse across the interface boundary, enhancing the diffusion of oxide ions across the interface without the formation of insulating impurity phases. They suggest further, that mixed ionic and electronic conductors containing iron or nickel can also be used without degradation of performance. Unfortunately, LSCO has a larger thermal expansion coefficient than LSGM and so is still unsuitable as a cathode material. The same group have studied a range of other potential perovskite cathode materials, La$_{0.85}$Sr$_{0.15}$MnO$_3$ (LSM), La$_{0.7}$Sr$_{0.3}$Fe$_{0.8}$Ni$_{0.2}$O$_{3-\delta}$ (LSFN),
La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Ni$_{0.2}$O$_{3-δ}$ (LSCN) and SrCo$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (SCF) and found that electrode resistance decreases with improved catalytic activity in the order LSM < LSFN < LSCO < LSCN < SCF. LSFN is the only material out of the range tested, which shows a compatible thermal expansion coefficient. Although, the performance of LSFN is better than that of LSM as a cathode material, the overpotential losses are still considered to be far too high. Therefore, other suitable cathode materials need to be sought. Another serious problem with lanthanum gallate based electrolytes is the vaporisation of Gallium at high temperature under reducing conditions, along with the diffusion of transition metal cations along the grain boundary regions. Indeed, the exact nature of these electrolytes is often unclear owing to the presence of species such as SrLaGa$_3$O$_7$ and La$_4$Ga$_2$O$_9$ in the grain boundary regions.

1.5 The Project

1.5.1 Electrolyte Materials

As discussed previously there is an urgent need for the development of new electrolyte materials for use in SOFCs, so as to achieve lower temperature operation. In this respect we have been studying apatite-based materials for potential use as electrolyte materials in fuel cells.

Apatite phases, general formula type $A_{10-x}(BO_4)_6O_{22+y}$, ($A =$ rare earths, alkaline earths, alkali metals, Pb, Bi, Mn; $B =$ Si, Ge, V, P, S, B etc) are being investigated for their potential role as electrolyte materials. High oxide ion conductivity has been recently reported in the apatite phases La$_{10-y}$M$_6$O$_{22}$ (M = Si, Ge). Indeed the Ge analogue has been reported to exhibit oxide ion conductivity higher than YSZ, where Sr is partially substituted onto the La site. One of the key aspects of these apatite phases is the wide range of substitutions available, offering huge potential to optimise the oxide ion conductivity in these interesting systems. There are reports in the literature of a range of similar apatite type phases; Nd$_{9.33}$Si$_6$O$_{26}$, Pr$_{9.33}$Si$_6$O$_{26}$,
NaLa$_9$Ge$_6$O$_{26}$, LiLn$_9$Si$_6$O$_{26}$ (where Ln = Nd, Sm, Eu, Gd, Dy), and Eu doped Ca$_2$La$_8$Si$_6$O$_{26}$, thus demonstrating some of the diversity available.

Figure 1.7 shows the structure of the general apatite-type oxide $A_{10}(BO_4)_6O_2$. The structure consists of isolated BO$_4$ tetrahedra with the ‘A’ cations located in both 7 co-ordinate and 9 co-ordinate cavity sites. Oxide ions occupy channels running through the structure. Oxide ion conduction is presumed to occur within these oxide ion channels. Interestingly, calcium hydroxyapatite is a phosphate based apatite material, with the formula $Ca_{10}(PO_4)_6(OH)_2$, which is found commonplace in nature as a major structural component of teeth and bone.

Figure 1.7. The general apatite, $A_{10-x}(BO_4)_6O_2$ structure, viewed approximately along the [001] direction.

(Tetrahedra = BO$_4$, dark and light grey spheres = A, white spheres = O).
Preliminary work focused on the preparation and characterisation of single-phase samples of previously reported phases, e.g. La$_{9.33}$(Si/Ge)$_6$O$_{26}$ and Ln$_8$A$_2$(Si/Ge)$_6$O$_{26}$ (Ln = rare earth and A = alkaline earth). This work included structural studies to gain a better understanding of the oxygen channels in these materials. This was followed by doping studies, e.g. La$_{9.33+x/3}$(Si/Ge)$_{6-x}$M$_x$O$_{26}$ (M = Al, B, Ga). The aim was to gain a qualified understanding of these materials so that new compositions could be designed with optimal oxide ion conductivity.

1.5.2 Cathode Materials

In addition to the work on apatite electrolytes, research in this project has also targeted the preparation of a range of phases of formula type YSr$_2$Cu$_{3-x}$M$_x$O$_{7-y}$ (M = Ga, Al, Co, Fe, S, P, B) to investigate their potential role as cathode materials for SOFCs. There is a wide range of possible substitutions and modifications available within this general system, which offers tremendous scope for tailoring a phase with the required cathode properties.

The perovskite type phase YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) is a superconductor below 93 K, and has been reported to express high oxide ion conductivity and high electronic conductivity at temperatures in excess of 300°C, raising the prospect of using this material as a cathode in SOFCs. There are, however, a number of problems associated with using YBCO as a cathode material. YBCO degrades, decomposes and reacts with YSZ substrate at temperatures above 900 °C. Furthermore there is electrochemical decomposition at low current densities (20 mA cm$^{-2}$).106

The structure of YBCO is shown below in figure 1.8. The main problem with the stability is associated with the Cu 1 site. The Cu 1 atom has square planer co-ordination in the oxygen rich phase (x $\approx$ 0). Oxygen is lost from around the Cu 1 sites at high temperature, particularly under reducing conditions, e.g. Ar(g) or N$_2$(g). Cu 1 is reduced to Cu$^+$ and adopts linear co-ordination. Further oxygen loss will then lead to decomposition.
The instability of the Cu 1 site can be potentially reduced by the substitution of other cations, e.g. Al, Ga, and transition metals, or oxyanions, e.g. SO$_4^{2-}$ and BO$_3^{3-}$, into the Cu 1 site. Thermal stability can also be improved by substituting Sr for Ba to give the range of phases with the general formula YSr$_2$Cu$_{3-x}$M$_x$O$_{7-y}$ (M = Ga, Al, Co, Fe, S, P, B).$^{107-110}$

Interestingly the parent compound YSr$_2$Cu$_3$O$_{7-x}$ can only be synthesised under high pressures.$^{111}$ This is probably related to strain around the Cu 1 site in YSr$_2$Cu$_3$O$_{7-x}$ due to displacement the oxygen atoms surrounding the Cu 1 site, in order to maintain the Cu-O bond distances at reasonable values. It is possible however, to remove the strain out of this system by doping the Cu 1 site with a small amount of another ion as outlined above. Doping the Cu 1 site completely with Ga, formula YSr$_2$Cu$_2$GaO$_7$, results in ordering of the Ga tetrahedra and doubling the unit cell in the ‘c’ direction.$^{112}$ The structure of YSr$_2$Cu$_2$GaO$_7$ is shown below in figure 1.9.

Figure 1.8. The structure of YBa$_2$Cu$_3$O$_{7-x}$. 
Figure 1.9. The structure of YSr$_2$Gu$_2$GaO$_7$.

The work in this area involved the synthesis of a range of materials, and investigation of their conductivities as well as their chemical compatibility with potential SOFC electrolyte materials.
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2.1 Standard Solid State Reactions

The traditional way in which to prepare ceramic materials, such as perovskites and apatites, is to use the ‘standard solid state route’. The starting compounds are mixed and ground together, to form a fine powder, and then fired at high temperatures, typically >800 °C, for a number of hours or even days. Intermediate regrinding is often required between firings.

For example, the preparation of the apatite $\text{La}_6\text{Sr}_2\text{Si}_6\text{O}_{26}$ is carried out at 1350 °C:

$$4\text{La}_2\text{O}_3 (s) + 2\text{SrCO}_3 (s) + 6\text{SiO}_2 (s) \rightarrow \text{La}_6\text{Sr}_2\text{Si}_6\text{O}_{26} (s) + 2\text{CO}_2 (g).$$

This method of product compound preparation is relatively easy. However, this method is not without its drawbacks. This is because the difference in structure between reactants and products is often considerable. Major structural reorganisation, involving the breaking and making of many bonds, and counter ion migration is required for complete product formation. The greater the structural similarity between product compound and reactants, the less structural reorganisation is necessary. Consequently, nucleation and ion diffusion occur more readily between similar structures than dissimilar structures. Crystal defects, such as vacancies, aid the diffusion process owing to relatively free passage within their location. Counter ion diffusion between reactant particles can also be a difficult and energy intensive process. High surface area contact between grains aids this diffusion process. Growth of product layer occurs on the surface of the reactants as a consequence of counter ion diffusion. Ions have to migrate through this layer in order for complete product formation. The smaller the particle size, the less counter ion diffusion is necessary.

Although this method is easy to perform and mostly effective, it is disadvantaged by the high energy input, owing to the high temperatures required, and the lengthy reaction times. Furthermore any impurities, such as unreacted starting materials, that have not been eliminated through regrinding and reheating will be present in the product materials. A further disadvantage is that volatile materials such as alkali
metal oxides can be lost during the reaction, owing to the high temperatures involved. Using excess reactants and or sealing the reactants in a tube can help overcome this problem.

Finally high temperature synthesis leads to the formation of the most thermodynamically stable product phase. However, metastable phases can sometimes be produced owing to slow kinetics, where product compounds are not necessarily in their most thermodynamically stable state. Some inorganic phases are only stable at low temperatures and therefore have to be synthesised using different routes. In this project, all samples were prepared by the standard solid state reaction route.

2.1.1 Other Routes to the Preparation of Solid State Compounds

There are a number of other methods available to the solid state inorganic chemist for synthesis, and these are discussed briefly in the following paragraphs.

2.1.2 Co-precipitation

Co-precipitation is used when a high degree of homogenisation and small particle size is required, such as for investigations involving small particle size, e.g. the synthesis of ZnFe₂O₄ spinel. This method of synthesis is however rarely used currently because problems can arise if there is a difference in solubility and/or precipitation rate between reactant components, leading to incorrect reactant ratios, or an inhomogeneous mixture.
2.1.3 Sol-Gel Synthesis

Sol gel synthesis incorporates low temperature synthesis with small particle size and homogeneity of product compounds. Gels can be prepared by adding water to a solution of metal alkoxides. For example, $\text{La}_{10}\text{Si}_{6}\text{O}_{27}$ can be prepared using stoichiometric quantities of tetraethoxysilane (TEOS) and $\text{La}_2\text{O}_3$, dissolved in an aqueous solution of ethanol, acetic and nitric acid. This process starts with a homogenous solution of all the cationic ingredients. Providing the correct conditions of pH and concentration have been selected, an amorphous translucent gel is eventually produced, in which none of the crystalline phases has precipitated out. To obtain the final product, the gel is then fired at the appropriate high temperature, removing any volatile fractions trapped in the gel pores. This method is widely used when lower temperature synthesis or control of particle size is required. A disadvantage of this method is that is generally an expensive and time-consuming process.

2.1.4 Hydrothermal Synthesis

Hydrothermal synthesis involves using water at high pressure and temperatures between 100 - 250 °C. Elevated temperatures increase the rate of reaction, and the water acts as a pressure-transmitting medium. Furthermore, reactions occur within the liquid/vapour phases owing to the partial solubility of the reactants in the pressurised water. This method of synthesis is ideal for the production of phases that are unstable at high temperature, such as zeolites.
2.2 The Powder Diffraction Experiment

X-ray powder diffraction is a useful and readily available technique for identifying new phases and checking sample purity. It is very useful for the simple fingerprint characterisation of crystalline materials, but can also be used to determine crystallographic structures by using profile refinement techniques. Neutron powder diffraction, although not so readily available as X-ray powder diffraction, is a very useful and complimentary technique for analysing crystallographic structures, particularly the accurate location of light atoms amongst heavy atoms.

2.2.1 The Theory of Diffraction

The Laue equation, $a \sin \phi = n\lambda$ (where $a =$ atom separation, $\phi =$ diffraction angle and $\lambda =$ wavelength), is one of two traditional methods for interpreting signal data collected from a diffraction experiment. This method is the mathematically correct way to account for the diffraction of radiation by crystal lattices, but it is complicated to use. This is because crystals are three dimensional arrays, and so three Laue equations have to be satisfied simultaneously for diffraction to occur, i.e.

$$a_1 \sin \phi_1 = n\lambda; \quad a_2 \sin \phi_2 = n\lambda; \quad a_3 \sin \phi_3 = n\lambda.$$

Another approach, which is used extensively nowadays, is based on Bragg’s law. This method is much more straightforward and easier to use, and considers the crystal structure as being composed of a series of semi-reflective planes, where the angle of incidence is equal to the angle of diffraction. Successive planes diffract transmitted X-rays.
Figure 2.1. Derivation of Bragg's law.

It can be seen from figure 2.1 that incident beams 1 and 2, which are monochromatic, are diffracted by planes A and B respectively to become diffracted beams 1' and 2'. Beams 1' and 2' are in phase giving constructive interference when distance x y z is equal to a whole number of wavelengths. In other words, the Bragg condition has now been satisfied. The perpendicular distance between A and B is related to the distance x y z by the equations:

\[ x \cdot y = y \cdot z = d_{hkl} \sin \theta_{hkl} \quad \text{and} \]

\[ x \cdot y \cdot z = 2d_{hkl} \sin \theta_{hkl}. \]

Since this distance must be an integer number of wavelengths for constructive interference to give a diffraction peak, i.e.

\[ x \cdot y \cdot z = n\lambda, \]

then we can write:

\[ 2d_{hkl} \sin \theta_{hkl} = n\lambda \quad \text{(Bragg's Law),} \]

Where it is normally assumed that \( n = 1 \).

For other angles of incidence where the Bragg condition is not met, i.e.
destructive interference will occur and the diffracted waves will cancel out. Since crystal lattices comprise thousands of planes, any deviation from the Bragg angle beyond more than a few 10ths of a degree will result in complete destructive interference.

2.2.2 The Generation of X-Rays

X-rays are electromagnetic waves with wavelengths of the order of 1 Å ($1 \times 10^{-8}$ cm). They can be produced by bombarding matter with high energy particles. In the case of X-ray diffraction experiments, high-energy electrons (40 keV) are used to bombard typically a metal target (e.g. Cu). The result of this collision is the generation of a continuous spectrum of X-rays, known as Bremsstrahlung. Contained within this spectrum there are a number of sharp peaks of high intensity X-rays. The source of these peaks is from the X-ray emission of 2p or 3p electrons relaxing into vacant positions in the 1s shell of a target nucleus. These vacancies in the 1s shell arise from the interaction with the high energy electrons, which results in electrons being ejected from these positions. X-ray emissions due to transitions from 2p to 1s and 3p to 1s are known as $K_\alpha$ and $K_\beta$ lines respectfully. $K_\alpha$ transitions occur more readily than $K_\beta$ and are therefore the ones selected for use in X-ray diffraction experiments. The $K_\alpha$ signal takes on the form of a doublet $K_{\alpha 1}, \lambda = 1.54051$ Å and $K_{\alpha 2}, \lambda = 1.54432$ Å for Cu X-radiation. This splitting is a result of the fact that the 2p electron may be in one of two possible spin states, and so a different wavelength will be observed for each one. This splitting is, however, only usually observed clearly at diffraction angles greater than $2\theta = 35^\circ$. The $K_\alpha$ signal is separated from the Bremsstrahlung and $K_\beta$ by using, commonly a crystal monochromator (typically the Ge (111) plane), or for older instruments a foil filter (Ni in the case of Cu X-rays) placed in front of the source.
2.2.3 The X-ray Powder Diffraction Experiment

The crystalline sample is ground into a fine powder and placed onto the sample holder where it is levelled and placed in the machine. The powdered sample contains many thousands of small crystals, all (ideally) randomly distributed, ensuring that for a given diffraction there are a number of lattice planes orientated at the Bragg angle to the X-ray source at any one time.

A monochromatic X-ray beam is focused onto the surface of the sample and the diffracted beam is then refocused and recorded.

Diffracted beams can be focused and collected by a number of means. Originally they were focused onto a strip of photographic film, employing Debye-Scherrer and Guinier focussing methods. Nowadays however, moveable detectors are used; typically a scintillation counter, or for older instruments a Geiger counter.

Optical focussing techniques cannot be used to focus X-ray beams. Therefore, use is made of the geometry of a circle in order to get convergence of the resultant X-ray beam.
Figure 2.2. Theorem of a circle used to focus X-rays.

Figure 2.3. Focussing geometry of a diffractometer.
The arcs $X C Y$, $X C' Y$ and $X C'' Y$ form part of the circumference of a circle. They are subtended from the same points, $X$ and $Y$, on the circumference of the circle; therefore the angles of these arcs are all equal (Figure 2.2).

If point $X$ is the monochromatic X-ray source, $(S)$, $Y$ is the receive slit of a detector, $(F)$, and the sample is placed between points $C'$ and $C''$ then the incident beam will be diffracted and refocused at the receiver (Figure 2.3).

With traditional powder diffractometers the sample moves through $\theta^\circ$ and the detector moves through 20$^\circ$, in order to keep the detector in focus and the sample tangential to the focusing circle. However, this system does have some inherent problems, e.g. the sample falling out of the holder at high angles. Consequently new systems have been developed where the sample remains fixed in order to overcome the problems. In these theta-theta systems, the source and detector are both moved through $\theta$, ensuring focusing geometry is maintained throughout the range of Bragg angles collected. The diffractometer used for this work is a Seiffert XRD3003TT theta-theta diffractometer. It utilises Euclidean focusing geometry, which is shown in figure 2.4.

![Diagram of focusing geometry of a Seiffert theta-theta diffractometer.](image_url)
2.2.4 Neutron Diffraction

Chadwick et al first discovered neutrons, in 1932, and Mitchell and Powers later showed, in 1936, that crystals could diffract them.

The neutron is a fundamental particle with zero electrical charge. It has a mass of $1.675 \times 10^{-27}$ kg, a spin of $\frac{1}{2}$ and consequently a magnetic moment of $-1.913$ nuclear magnetons. The wavelength, $\lambda$, is described by the de Broglie equation:

$$\lambda = \frac{h}{mv},$$

where $h$ = Plank’s constant,

$m$ = mass and

$\nu$ = velocity.

2.2.5 Production and Use of Neutrons

There are two different methods employed for neutron diffraction experiments; constant wavelength neutron diffraction and time of flight neutron diffraction. An advantage of the constant wavelength experiment is that it reveals greater detail at large d-spacings. Conversely, the time of flight experiment is advantaged by giving greater detail at small d-spacings.

Constant wavelength neutron diffraction is analogous to X-ray diffraction as it uses fixed $\lambda$ and $\theta$ is varied. Neutrons for diffraction are required to have wavelengths of similar values to the interatomic $d$-spacings, $\lambda \approx 1 \text{ Å}$. Nuclear reactors are suitable sources for such neutrons. A distribution of neutron velocities is emitted from the reactors, which follows a Maxwellian curve. Neutrons of the appropriate wavelength can then be selected for diffraction using a crystal monochromator. However, neutron beams emitted from nuclear reactors are generally of low intensity, making neutron collection times long in duration.
Time of flight neutron diffraction, typically involves the process of proton spallation to produce an intense beam of neutrons. An advantage of time of flight neutron diffraction over constant wavelength neutron diffraction is that neutron collection times are far shorter owing to the increased intensity of the beam. In this work time of flight neutron diffraction was employed, and this will now be discussed in more detail.

2.2.6 Proton Spallation

At the ISIS neutron source Rutherford Appleton Laboratory the method of proton spallation is used to give a high flux pulsed neutron beam. This method entails bombarding a heavy metal element, usually tantalum, with a beam of high-energy protons, (500-8000 M eV). The heavy metal nuclei are disrupted, yielding a high return in neutrons, approximately 25 neutrons per proton (Figure 2.5).

![Proton spallation](image)

Figure 2.5. Proton spallation.
2.2.7 Time of Flight Neutron Diffraction

The de Broglie equation can be used to show that \( \lambda \) changes inversely with neutron momentum:

\[
\lambda = \frac{h}{mv}; \quad \lambda (\text{Å}) = 3.956/v(\text{mm} \text{ µs}^{-1}).
\]

The flight time of such neutrons, \( t \), can be measured electronically. Thus for a flight path of length, \( L \):

\[
\lambda = \frac{ht}{mL}; \quad \lambda (\text{Å}) = 3.956 \frac{t(\text{µs})}{L(\text{mm})}.
\]

In the time of flight method this expression is used and neutrons are collected as a function of elapsed time following each pulse (Figure 2.6).

![Figure 2.6. Schematic layout of a pulsed neutron source neutron powder diffractometer.](image)

The sample, S, is positioned directly in the path of the incident neutron beam. A detector is located at a fixed angle, \( 2\theta \), from the sample recording neutron arrival as a function of time of flight. The distance travelled by the neutrons, \( L \), is equal to the distance between the moderator and the detector, \( D \), \((L_0 + L_1)\).

Equation \( \lambda = \frac{ht}{mL} \) can be combined with Bragg's law to give the following:

\[
d = \frac{ht}{2mL \sin \theta}; \quad d (\text{Å}) = \frac{1.987t(\text{µs})}{L(\text{mm}) \sin \theta}.
\]
The time of flight data collected can therefore be plotted directly against a scale in d-spacing to give the neutron diffraction profile for the sample under examination.

In powder diffraction experiments the crystals contained within the powdered sample are randomly orientated. As with X-ray diffraction experiments the incident beam is scattered over the complete range of diffraction angles. However, the angle $2\theta$ is fixed for time of flight neutron diffraction experiments, and diffractions at this fixed angle have different values of $\lambda$ dependent on the d-spacing involved. Consideration of Bragg's law, $\lambda = 2d \sin\theta$, shows that in the time of flight method, $\theta$ is fixed and $\lambda$ is varied, in contrast to traditional diffraction experiments where $\lambda$ is fixed and $\theta$ is varied.

The resolution of time of flight powder diffractometers improves with increased flight path length. This can be explained as follows: the neutrons have to be slowed down by the moderator in order to possess the correct range of wavelengths suitable for diffraction. There is, however, an element of uncertainty in the length of the flight path, dependent on their point of emission from the moderator, which is typically 5 cm long. This is known as the full-width-at-half-maximum (FWHM) fractional flight path uncertainty. The relationship between $L$, $t$, and $d$ is linear, therefore:

$$\frac{\Delta L}{L} = \frac{\Delta t}{t} = \frac{\Delta d}{d} (\text{moderator}) = \frac{0.034}{L (\text{meters})}$$

From this relationship it can be seen that the uncertainty is reduced with increasing flight path length. Thus the Polaris diffractometer at ISIS has a flight path of $\approx 12$ m, with an uncertainty of $\frac{\Delta d}{d} \approx 3 \times 10^{-3}$, whereas the HRPD diffractometer has a flight path of approximately 100 m, with an uncertainty of $\frac{\Delta d}{d} \approx 3 \times 10^{-4}$. Therefore the former instrument has a poorer resolution than the latter. For our experiments, the high resolution powder diffractometer (HRPD) was used, so that any subtleties (e.g. minor monoclinic distortion) in the crystal structure could be identified.
One problem of employing a longer flight path is that there is lower neutron intensity at the sample, due to absorption of neutrons by the waveguide. A further problem is that of frame overlap, which occurs when fast neutrons from one pulse overtake slow neutrons from the previous pulse. This problem is usually only apparent for long neutron flight paths, and such cases require the use of rotating beam choppers between frame exposures. These choppers can be set to allow only 1 in 2, 1 in 3 etc. pulses through, and so eliminate this problem.

2.2.8 Miller Indices

Simple crystalline structures can be considered to comprise layers (or planes) atoms which are stacked to form a three dimensional structure. In some cases these layers relate directly to the unit cell, e.g. where a row of atoms might correspond to a unit cell side. It is very important, however, not to confuse planes of atoms with the concept of lattice planes. Lattice planes are a concept, and do not necessarily correspond to rows of atoms, especially in more complex structures. They are defined by the unit cell parameters, and provide a reference point from which the position of atoms in the crystal structure can be identified.

A lattice plane can be characterised in three dimensions by the use of Miller indices. They describe the points at which a lattice plane intersects the ‘a’, ‘b’, and ‘c’ axis of a unit cell. They are identified by the use of three integers, one for each unit cell axis, each of which is the reciprocal of the fraction at which the lattice plane intersects the unit cell axis.
Figure 2.7. Lattice planes for the (222) plane.

Figure 2.7. shows the situation for the (222) plane. In this case the plane intersects the ‘a’, ‘b’ and ‘c’ axis at a value of $1/2$, which correspond to $h$, $k$ and $l$ values of 2, 2, and 2 respectively, and has a Miller index of (222). This set of planes is therefore referred to as the (222) plane.

For orthogonal systems, where $\alpha = \beta = \gamma = 90^\circ$ the Miller indices can be related to the unit cell ‘a’, ‘b’ and ‘c’ parameters in the following way:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2},$$

where $d$ is the interplanar $d$-spacing, $h$, $k$ and $l$ are the Miller indices, and ‘a’, ‘b’ and ‘c’ are the respective unit cell parameters.

In the case of a hexagonal unit cell (commonly observed for apatite systems), where $a = b \neq c$, $\alpha = \beta = 90^\circ \gamma = 120^\circ$, the Miller indices can be related to the unit cell as follows:
\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}. \]

### 2.2.9 Systematic Absences

Bragg's law only defines a minimum condition where constructive interference might occur - it does not state however that diffraction will occur. In reality the symmetry of the crystal lattice plays an intrinsic role in determining if a diffraction peak will be observed. Certain peaks will be absent from a diffraction pattern, if, for example, the lattice type is non-primitive, or if aspects of space symmetry, such as a screw axis, are present. In the case of the cubic \( \alpha \)-Fe structure, which has a body centred lattice (I), a diffraction experiment shows the diffraction from the (100) plane to be systematically absent, whilst the diffraction from the (200) plane is present. The reason for this is that the body centred atom is located midway between the (100) planes (Figure 2.8), and consequently diffracts incident radiation \( 180^\circ \) out of phase relative to the corner atoms, resulting in zero overall intensity. Diffraction peaks are present in a profile for the (200) diffraction because all atoms involved are located in the (200) planes (Figure 2.9).

![Figure 2.8. (100) planes in \( \alpha \)-Fe.](image)
2.2.10 Preferred Orientation

The X-ray diffraction experiment assumes a completely random distribution of crystallites. The intensity of diffraction peaks can therefore be affected if the crystals tend to pack in a specific manner. This can happen, especially if the crystals are needle or plate-like in shape. This effect leads to peaks that are disproportionately high or low in intensity according to sample orientation. This effect can be kept to a minimum by using a rotating sample holder.

2.2.11 Peak Multiplicities

The intensity of a diffraction is proportional to the number of atoms contributing towards it. The number of Miller planes contributing towards a specific diffraction also affects its intensity. For example, in a cubic material the (100), (010) and (001) diffractions all have the same \(d\)-spacing. Consequently, diffractions from all these planes contribute to the same peak. In single crystal diffraction each Miller plane can be analysed separately, thus avoiding the situation of peak multiplicities.
2.2.12 Form Factors: The X-ray Diffraction Experiment

Different atoms will scatter X-rays to differing degrees, and this scattering is defined by the atomic form factor. The value of this depends on both the diffraction angle and atomic number. The intensity of X-rays scattered is proportional to the number of electrons present in an atom, and hence increases with atomic number. As a consequence, scattering from heavy atoms dominates a diffraction profile in an X-ray diffraction experiment. The angle dependence takes the form of \( \frac{(\sin \theta)}{\lambda} \).

These factors can be explained as follows. For an X-ray diffraction experiment, diffraction occurs due to the effect of Thompson scattering. The interaction of X-ray photons with the electron density of an atom initially involves a transfer of energy from the incident photon to the atom. The target atom acts as a secondary emission source, where a second X-ray photon is emitted, the nature of which is coherent to the incident photon. The scattering will thus depend on the electron density of the atom and hence increases with increasing atomic number. The electron density of an atom is not, however, a point charge. Electrons are distributed over the atom, the diameter of which is similar in magnitude to the wavelength of the incident X-ray. The range of interaction is therefore \( \approx 1 \text{ Å} \), and interference occurs between X-rays scattered from different parts of the atom, owing to the different path lengths. Partial destructive interference can then occur between X-rays diffracted by different parts of the same atom. This effect is proportional to the diffraction angle, hence the term \( \frac{(\sin \theta)}{\lambda} \). In a diffraction experiment the intensity of scattered X-rays therefore decreases significantly with increase in \( 2\theta \) value.

2.2.13 Form Factors: The Neutron Diffraction Experiment

A significant difference between an X-ray diffraction experiment and a neutron diffraction experiment is that, in the latter experiment, diffraction occurs due to an interaction between the incident neutron and the atomic nucleus, rather than by
interaction with the electron cloud. Exceptions to this rule occur when atoms possess a magnetic moment. In such circumstances the spin or orbital magnetic moments of the electrons interact with the neutrons, owing to the neutron’s spin magnetic moment. This useful property can be used to investigate magnetic structures.

Since neutrons interact with the nucleus, diffracted neutron radiation is not affected by a fall off in intensity with increasing atomic number. For neutron experiments there is no simple relationship between atomic number and scattering intensity. Indeed, different isotopes of the same element will have different scattering factors, e.g. hydrogen and deuterium. In addition, there is no fall-off in intensity with increasing angle. Consequently, neutron diffraction experiments can reveal much more information at shorter d-spacings than X-ray diffraction experiments.

Neutron diffraction techniques are often used to complement X-ray diffraction studies, in order to obtain accurate information about the positions of light atoms, such as hydrogen, lithium and oxygen, which is of extreme importance for understanding the oxide ion conduction in the systems studied in this project.

In this work we were interested in looking for subtle differences in the oxygen sublattice of the apatite structure and therefore neutron diffraction studies were performed. The crucial thing for our systems is that the neutron scattering factor for oxygen is of a similar value to that of lanthanum, and so unlike with X-rays the neutron scattering is not dominated by the positions of the lanthanum atoms. Consequently, the oxygen positions can be identified accurately.

Another important consequence of the fundamental difference between the two techniques is that X-ray diffraction only effectively reveals an electron density map. The atom positions then have to be inferred from this. The atom positions can therefore be less well defined than for neutron diffraction. This can be especially so for systems where there is a large degree of polarisation of the electron clouds. In comparison neutron diffraction reveals the positions of nuclei directly. Interestingly, a combination of the two studies on a given system may reveal details of electron polarisation.
So far, a number of advantages of neutron diffraction over X-ray diffraction have been outlined. Unfortunately, compared to X-ray diffraction, neutron diffraction is a very expensive technique, and usually requires a reasonably large quantity of powdered sample (≈ 5 g) and long data collection times.

### 2.2.14 Structure Factors

In order to fully explain the scattering from an atomic array or a crystal the ‘structure factor’, $F_{hkl}$, must be considered. This is a relationship, which defines the form factor for a particular atom type, the Miller indices for the diffraction peak and the fractional coordinates for each atom. The relationship between these contributors is similar in the case of either neutron or X-ray radiation (with the relevant form factor).

$$F_{hkl} = \frac{N}{\sqrt{\sin(h_{\mathbf{x},r} + k_{\mathbf{y},r} + l_{\mathbf{z},r})}},$$

or

$$F_{hkl} = \frac{N}{\sqrt{\sin(h_{\mathbf{x},r} + k_{\mathbf{y},r} + l_{\mathbf{z},r})}} \exp \left(2\pi \left(h_{\mathbf{x},r} + k_{\mathbf{y},r} + l_{\mathbf{z},r}\right)\right).$$

Where $f_r$ = form factor for atom $r$;

$h$, $k$ and $l$ = Miller indices for the diffraction peak,

and $x_r$, $y_r$ and $z_r$ = fractional coordinates for atom $r$.

The intensity of a particular diffraction peak is proportional to the square of the structure factor.
2.2.15 Temperature Factors

In addition to the dependence on the position of the atoms in the crystal, the scattering intensity of diffracted radiation can be reduced and background scattering increased due to the effect of atomic thermal vibrations. The higher the temperature, the higher these factors will be, and they can be quantified in the diffraction experiment. High temperature factors can sometimes be an indication of a displacement of atoms from their ideal site in the structure.

2.2.16 Structural Analysis of Powder Diffraction Data

Single crystal diffraction is the preferred experiment if structural information on a system is required. Unfortunately, it is often difficult or impossible to prepare crystals suitable for this experiment. In most cases powder samples are more readily available, and powder diffraction experiments therefore more commonly performed.

There are two possible methodologies available for refining structural data from powder diffraction experiments. These are the integrated intensity and the Rietveld refinement, the essence of which are described below.

The integrated intensity method is the traditional method used and involves reducing the pattern to a set of integrated intensities (line data), where \( \sum F^2_{hkl} \) represents a summation in the case of overlapping diffractions. This method, however, becomes impractical for structures with low symmetry, where peak overlap is severe.

The Rietveld refinement technique is the most common method applied to obtain structural solutions from powder diffraction experiments.\(^9\)\(^10\) The essence of a Rietveld refinement is that a model structure is fitted to the entire experimental diffraction profile. The simple approach to this method assumes the profile to be the sum of suitably shaped peaks centred at the respective Bragg diffractions. This method is more effective than the integrated intensity method and represents the available intensity data more accurately, rather than just fitting the intensity maxima.
Refinement techniques involve curve fitting and least squares methodologies. The intensity of each data point is considered in the calculation. Consequently, diffraction optics, instrument geometry and second phases can be taken into consideration, in order to give a more accurate characterisation of a sample structure.

The Rietveld methodology involves adjusting the parameters of an initial crystal model in such a way as to minimise the following function:

$$ \sum_i w_i \left[ Y_i(\text{obs}) - \left( \frac{1}{c} \right) Y_i(\text{calc}) \right]^2, $$

where $Y_i(\text{obs})$ and $Y_i(\text{calc})$ are respectively the observed and calculated profile intensities, $w_i$ is the least-squares weight and $c$ is the scale factor.

The parameters to be refined are dependent on the crystal structure, or on the characteristics of the diffractometer, particle size, and effects due to preferred orientation.

The asymmetry, which occurs due to the fact that the sample has a finite height, and cannot therefore be considered as just a point on the axis of the diffractometer, can also be corrected for. This correction is particularly necessary for peaks occurring at low Bragg angles.

It is possible to carry out Rietveld refinements using desktop computers. There are several software packages capable of refining X-ray and neutron diffraction data, such as GSAS (General Structure and Analysis Software) and FULLPROF. However, in this work structural refinement of the neutron data was performed by the Rietveld method using program TF15LS based on the Cambridge Crystallography Subroutine Library (CCSL).

It is imperative to state that the Rietveld refinement method is not capable of uniquely assigning intensities of diffraction peaks to Bragg diffractions, nor is this method capable of resolving overlapping peaks. Forehand knowledge, in terms of a
realistic starting model, is required before a refinement can begin; details of space group, unit cell and starting atom positions are therefore prerequisite.

2.2.17 R-Factors

The accuracy of a fit using Rietveld analysis can be quantified in terms of Residual factors (R-factors), of which there are four used in common practice:

1. Profile R factor ($R_p$)
2. Weighted R factor ($R_{wp}$)
3. Intensity or Bragg R factor ($R_I$)
4. Expected R factor ($R_E$)

These can be defined as follows:

$$R_p = \frac{\sum_i |Y_i(\text{obs}) - Y_i(\text{calc})|}{\sum_i Y_i(\text{obs})}$$

Where $Y$ = intensity of the point on the powder diffraction profile,

$$R_{wp} = \left[ \frac{\sum_i |Y_i(\text{obs}) - Y_i(\text{calc})|^2}{\sum W_i Y_i^2(\text{obs})} \right]^{1/2}$$

$W$ = weighting factor.

$$R_I = \sum_h \left| I_h(\text{obs}) - \frac{1}{c} I_h(\text{calc}) \right| \sum_h I_h(\text{obs}).$$

where $I$ = peak intensity.
$R_f$ is useful in quantifying the structural fit because it is related to the area contained within the peak and not related to the peak shape.

$$R_E = \left( \frac{N - P + C}{\sum W_i Y_i (obs)^2} \right)^{1/2},$$

Where $N =$ number of observations,

$P =$ number of variables and

$C =$ number of constraints.

Another indication to the accuracy of a refinement is the value of $\chi^2$, and is determined using the following equation:

$$\chi^2 = \left( \frac{R_{wp}}{R_E} \right)^2.$$

In the case of an ideal refinement $R_{wp}$ and $R_E$ should be identical in value. A $\chi^2$ value of $< 4$ is normally taken as a good fit. There are however a number of factors that can influence the value of $\chi^2$. As a consequence, $\chi^2$ should not be used on its own as a guide to refinement accuracy. It is important to compare observed and calculated profiles at each refinement stage in order to check progress, and to determine refinement strategy.

Indeed it should be noted that $R$ values can sometimes appear artificially high in value. This can be due to a number of reasons. These include short counting times, which leads to problems such as large statistical error in the background and poor peak separation etc. The use of specialist equipment such as cryostats or furnaces might also add to the background contribution. These factors should be taken into consideration in elucidating the quality of the fit.
2.3. Fourier Transform Infrared Spectroscopy

2.3.1 Vibrational Spectroscopy

Infrared (IR) spectroscopy can provide important information regarding the nature of energies of molecular vibrations in a variety of materials including solids, liquids and gases. These molecular vibrations are usually associated with pairs of bonded atoms, e.g. C-H, Pt-Cl and C=O.

A diatomic molecule can be described as a harmonic oscillator, with frequency, $f$, and modelled as two spherical masses $m_1$ and $m_2$ interconnected by a weightless spring, with a force constant $k$ (Figure 2.10).

![Figure 2.10. Mechanical model of a diatomic molecule.](image)

The motion of this harmonic oscillator can be described by the equation:

$$v = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}},$$

Where $v$ is measured in wavenumbers ($\text{cm}^{-1}$),

$k$ is measured in Newton's per meter ($\text{N m}^{-1}$), and

$\mu$ is the reduced mass, measured in kilograms (kg) and

$c$ is the velocity of light $2.998 \times 10^{10}$ m s$^{-1}$

The transitional energy ($E$) is the energy difference between the vibrational ground state ($v = 0$) of a molecule and the first excited vibrational level ($v = 1$). This
transition in energy level is referred to as a fundamental and its value is quantised
\[ E = hf = \hbar \nu, \]

Where \( E \) is the energy in Joules, J,

\( f \) is the frequency in Hz and

\( h \) is Plank's constant, \( 6.6 \times 10^{-34} \text{ J s}^{-1} \).

The simple harmonic oscillator model is, however, only an approximation. The quantum mechanical model provides a more realistic representation:

\[ E_v = \left( v + \frac{1}{2} \right) \frac{\hbar}{2\pi} \sqrt{\frac{k}{\mu}} \quad (v = 0, 1, 2, \ldots) \text{ abbreviated to } E_v = \left( v + \frac{1}{2} \right) hf, \]

Where \[ \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = f. \]

The energy for the fundamental transition \( (v = 0 \rightarrow v = 1) \) is consistent with \( E = hf = \hbar \nu \). However, the main difference between the quantum mechanical and simple harmonic oscillator models is that in the latter model the molecule still possesses a zero-point energy:

\[ E_0 = \frac{1}{2} hf \]

In reality, the vibrational modes of molecules are not strictly harmonic. The separation in energy levels between \( v = 0 \rightarrow v = 1 \) and \( v = 1 \rightarrow v = 2 \) etc. are not equal: the simple harmonic oscillator is too much of an approximation. The upper levels close-in increasingly with increasing vibrational quantum number \( v \).

The anharmonicities for molecules cover a range from \( \approx 1 \text{ cm}^{-1} \) for heavy atoms to about \( \approx 230 \text{ cm}^{-1} \) for light ones.
2.3.2 Infrared Spectroscopy

The vibrational energies for molecules can be determined from their IR spectra. Such spectra result from absorption of IR radiation by the molecular bonds for the fundamental transitions from the ground state to the first level ($\nu = 0 \rightarrow \nu = 1$).

The selection rule for IR spectroscopy is $\Delta \nu = \pm 1$, where $+1$ means absorption and $-1$ means emission. This rule is not always adhered to because of the anharmonic nature of many vibrations, leading to the inclusion of overtones and combinations in the spectra.

Incident infrared radiation in the region $4000 - 30 \text{ cm}^{-1}$ will be absorbed by a molecule, when it matches that of one of the molecules vibrational modes: IR radiation is absorbed by a molecule providing the frequency of the applied alternating electric field matches that of the oscillating dipole. All molecules, with the exception of homonuclear diatomic molecules such as $\text{O}_2$, possess some vibrational modes that result in a change in dipole moment and will therefore have a characteristic IR absorption spectrum. The amount of absorption is dependent upon the probability of the associated transition occurring, which is dependent on the change in dipole moment.

An important observation about IR spectroscopy is that many chemical groups, e.g. C-H, C=O, C-N and C-C absorb IR radiation of characteristic frequency. The concept of group frequencies follows from these observations and is the foundation of this technique as a major analytical tool for qualitative identification of chemical compounds.

The most common type of IR spectrometer available today is the Fourier transform (FT) IR spectrometer. The FT-IR spectrometer works on the principle of the Michelson interferometer. A beam of IR radiation is split into two and passed through an optical system, and then recombined to produce an interference pattern. Beam splitting is achieved by means of an optical substrate, positioned at $45^\circ$ to the incident beam, which transmits one part of the beam and simultaneously diffracts the remainder. A schematic diagram of a FT-IR spectrometer is shown in figure 2.11.
The transmitted beam 2, \( B_2 \), is diffracted back towards the beam splitter by moving mirror \( M_2 \), whereas beam 1, \( B_1 \), is diffracted back towards the beam splitter by the fixed mirror, \( M_1 \). The two diffracted beams combine constructively or destructively, dependent on the position of \( M_2 \). The resulting interferogram is transformed by means of a mathematical process to produce an IR spectrum (Figure 2.11).

It takes only a fraction of a second to scan a sample. However, a complete IR spectrum will often comprise a number of co-added scans, typically 32, interferograms. The type of spectrometer used in this work was a FT-IR spectrometer PE 2000FTIR, using Nicolet 510P software.

![Schematic diagram of FT-IR spectrometer](image)
2.4 Four Probe D.C. Resistance Measurements

Two independent techniques can be used to determine conductivity values; their choice of use is dependent on the resistance of the system under test. A.C. impedance spectroscopy is the preferred technique, and is used to determine the conductivity of samples where the resistivity of the sample is relatively high (≈ 10⁷ to 10² Ω cm), as might be typical of a solid electrolyte. This technique was therefore employed to characterise the oxide ion conductivity of the apatite systems, and is discussed in detail in the next section. If the resistivity of the sample is low (< 10² Ω cm), as might be typical of a metal or a good semiconductor, then the 4 probe d.c. technique is preferred. This technique was used in this work to determine conductivity values for the cuprate systems, and is discussed in this section.

Four electrodes are attached to the sample pellet and a current is applied to the outer electrodes with the voltage across the inner two electrodes being measured.

The conductivity is calculated taking into account the geometric dimensions of the pellet and the current and voltage data using the following equations:

\[ R = \frac{V}{I}, \]

where \( R \) = resistance (Ω),

\[ V = \text{voltage (V)} \]

\[ I = \text{current (A)}; \]

\[ \sigma = \frac{1}{R} \times \frac{L}{A}, \]

where \( L \) = distance between the electrodes (cm) and

\[ A = \text{cross sectional area of the pellet (cm²)}. \]
In addition to conductivity measurements with varying temperature, conductivity measurements are also made at different oxygen partial pressures, $\rho(O_2)$, using an intrinsically sealed vertical furnace (figure 2.12). Typically, conductivities are measured initially in going from oxidising to reducing conditions, where nitrogen gas is allowed to pass slowly into the system. The sample would then be held under a $N_2$ atmosphere for at least 15 hours, in order for the system under test to equilibrate fully, prior to any measurements being taken in the reverse direction (from reducing to oxidising). The $N_2$ flow is then shut off and oxygen allowed to leak back naturally into the system over a period of approximately 24 hours. A YSZ sensor is used to determine the oxygen partial pressure. This effectively behaves as a concentration cell, and the oxygen partial pressure can be determined, using the Nernst equation for gases, from the sensor reading obtained:

$$\Delta E = \frac{RT}{nF} \ln \left( \frac{\rho(O_2)^n}{\rho(O_2)^i} \right),$$

where $\Delta E = $ measured voltage across the sensor (V),

$R =$ gas constant (8.314 J mol$^{-1}$K$^{-1}$),

$T =$ temperature (K),

$n =$ number of transferred electrons (4 for the process $O_2 + 4e \rightarrow 2O^{2-}$),

$F =$ Faraday constant (96485.56 C mol$^{-1}$),

$\rho(O_2)^n =$ oxygen partial pressure in air (0.21 bar) and

$\rho(O_2)^i =$ oxygen partial pressure experienced by the sample.

This equation can be rearranged, to give the following, from which the oxygen partial pressure can be calculated:
\[ \rho(O_2)' = \frac{\rho(O_2)^u}{\exp\left(\frac{\Delta E_nF}{RT}\right)} \]

A plot of log σ against log \( \rho(O_2) \) can be used to determine if the conductivity of the system under test shows any oxygen dependence. If the conductivity is dominated by the migration of oxide ions, i.e. the material is an oxide ion conductor; the plot should be a flat response across the \( \rho(O_2) \) range, because there should be no dependence with the oxygen partial pressure. A change in conductivity with \( \rho(O_2) \) is usually indicative of electronic conduction. If the slope of the graph is positive we have a p-type conductor, if however the slope is negative then we have an n-type conductor.
Figure 2.12. Schematic diagram of $\rho(O_2)$ test rig.
2.5 A.C. Impedance Spectroscopy

A.C. impedance spectroscopy is a very powerful technique that is routinely used for the characterisation of ionic conduction in ceramic electrolyte materials.\(^\text{17}\) It is the study of the variation of the impedance of the sample under test as a function of the frequency of the applied voltage. A.C impedance techniques have been used to characterise solid electrolytes since the mid 1960's.\(^\text{18,19}\) Bauerle et al. pioneered the analysis of polarisation in 1969 with his work on yttria-zirconia systems.\(^\text{20}\) Impedance spectroscopy can be used to characterise the bulk conductivity of ceramic materials without having to perform complex analysis of data involving polarisation phenomena; electrolyte polarisation is avoided by using a low amplitude high frequency source.\(^\text{21}\) The a.c. characteristics of the system under test are obtained by measuring the responses of the system to the application of a broad frequency sweep of sinusoidal signals, typically \(10^2 - 10^7\) Hz. It is possible to characterise different domains within the sample, including the d.c. characteristics for the sample. Usually the spectrum will comprise two distinct features, in the form of semicircles, each of which can be assigned to specific domains within the system under test. These are referred to as the “bulk” and “grain boundary” regions of the material, which represent the intragrain and the intergrain regions respectively. It is therefore often possible to determine the bulk, grain boundary and total (bulk + grain boundary) conductivity of the system. The depth of sintering can also be qualified and the extent of electronic conductivity determined. The main drawback with this technique is the correct interpretation of the data. The electrode-sample system can be represented by an “equivalent circuit”, the nature of which is often unclear at the start of the experiment. This equivalent circuit contains resistive, \(R\), and capacitive, \(C\), components, connected either in series or parallel “RC networks”, or a combination of the two. Unfortunately, the semicircles are not always very well resolved and, in these cases it is only possible to determine reliably the total conductivity. Examination of temperature dependence on conductivity reveals information on activation energies and ion transport mechanisms.\(^\text{22}\)
All conductivities reported here were made using a Hewlett Packard 4192A Impedance analyser. Pellets (1.6 cm in diameter and ≈ 0.1 cm in thickness) for each sample (using an initial mass of ≈ 1 g) were obtained by pressing powders in a die set at 6000 kg cm\(^{-2}\) followed by sintering at elevated temperature (1150 °C to 1700 °C) in order to obtain dense sample pellets. Both sides of the pellets were then coated with Pt paste to act as electrical contact for the measurements, and heated to 850 °C for 30 minutes to ensure bonding of the platinum to the pellet. The experimental set up is shown below in figure 2.13.

Figure 2.13. Schematic of the a.c. impedance test rig used in this study.
2.5.1 Theory of A.C. Impedance

When a sinusoidal a.c. voltage is applied across a load there is a general equation that can be used to express the value of instantaneous voltage, \( v \) (Volts, V), at any instant in time \( t \) (seconds, s) after the start of the cycle; this equation is as follows:

\[ v(t) = V_{\max} \sin \omega t, \]

where \( V_{\max} = e.m.f.(V) \) and \( \omega = 2\pi f \) (angular velocity, rad s\(^{-1}\)) \((f = \text{frequency in Hertz, Hz})\).

The instantaneous current flow, \( i \) (Amperes, A), in this circuit will have a similar waveform which can be described by the equation below which gives the value of the instantaneous current at any instant in time after the start of the cycle,

\[ i(t) = I_{\max} \sin \omega t. \]

Typically a range of sinusoidal a.c. voltages, \( v(t) \), increasing sequentially in frequency are applied to the system under test,

\[ v(t) = V_{\max} \sin \omega t \ (v(t) \text{ is a rotating vector with magnitude } V_{\max}). \]

The phase shift, \( \phi \), and amplitude of the resulting current can then be measured,

\[ i(t) = I_{\max} \sin(\omega t + \phi). \]

The applied voltage and the resultant current are in phase for a pure resistor. However, the current leads the voltage by 90°, i.e. \( \phi = \pi/2 \) radians, for a capacitor, and the current lags the voltage by 90°, i.e. \( \phi = -\pi/2 \) radians, for an inductor. The relationship between current, \( I \), and voltage, \( v \), phasors and as a function of \( \omega t \) are shown in figures 2.14 and 2.15 respectively.
Figure 2.14. The relationship between current, $i$, and voltage, $v$, phasors.

Figure 2.15. The variation of current, $I$, and voltage, $v$, as a function of $\omega t$. 
The capacitive and inductive components, referred to respectively as capacitive reactance \( (X_C) \) and inductive reactance \( (X_L) \), only impede current flow without contributing to any power \( (I^2R) \) losses; energy is stored and returned out of phase to the power supply. Reactances are functions of frequency:

\[
X_C = \frac{1}{2\pi f C} = \frac{1}{\omega C},
\]

where \( C \) is the capacitance measured in Farads (F), and

\[
X_L = 2\pi f L = \omega L,
\]

where \( L \) is the inductance measured in Henrys (H).

However, systems under test cannot generally be described in terms of pure resistance, capacitance or inductance; they are a combination of all these components. Resistive and capacitive effects tend to dominate an impedance spectrum at low frequencies. Self-inductance only tends to become a significant influence if test frequencies > 1 MHz are used.

\( X_C \) and \( X_L \) are a measure of the opposition to a.c. current flow by the capacitive and inductive components of the system under test. The current is related to the reactance as follows:

for a capacitor, where \( \phi = \frac{\pi}{2} \),

\[
I(t) = \frac{V_{\text{max}}}{X_C} \left[ \sin(\omega t + \frac{\pi}{2}) \right],
\]

and for an inductor,

\[
I(t) = \frac{V_{\text{max}}}{X_L} \left[ \sin(\omega t - \frac{\pi}{2}) \right].
\]
2.5.2 Complex Impedance

The impedance, $Z$, of a system is a vector quantity and is defined as the opposition to current flow in that system,

$$|Z| = \frac{v(t)}{i(t)}.$$  

In order to determine the magnitude of $|Z|$ and the phase angle $\phi$ it is convenient to plot the impedance in the complex plane. The complex impedance, $Z$, can be described by the combination of the complex conjugate, $Z^*$, real, $Z'$, and imaginary, $Z''$, quantities,

$$Z^* = Z' \text{ (real)} - jZ'' \text{ (imaginary)}.$$  

$Z'$ and $Z''$ respectively comprise the resistive, $R$, and reactive components of the sample: where reactance is a combination of capacitive and inductive components.

The plot of $Z'$ (real) against $Z''$ (imaginary) for a range of frequencies gives rise to an impedance spectrum called a Cole-Cole plot. These can be plotted using either Cartesian (x, y) or Polar ($|Z|$, $\phi$) coordinates: Such a plot is shown in figure 2.16. Important information can be inferred from these plots, in terms of electrical circuit elements, for the system under test.\textsuperscript{17,23}

In the case for Cartesian coordinates,

$$Z' = |Z| \cos \phi \text{ and}$$  

$$Z'' = |Z| \sin \phi,$$

In polar coordinates $|Z| = \left[(Z')^2 + (Z'')^2\right]^{1/2}$,

And $\phi = \tan^{-1}\left(\frac{Z''}{Z'}\right)$. 

100
2.5.3 Equivalent Circuits

The sample electrode system under test can be considered to comprise a combination of series and parallel resistive capacitive circuits (RC networks). The spectra for these network elements is discussed in detail below.

2.5.4 Ideal resistors

In the case of an ideal resistor, applying an oscillating voltage \( v(t) = V_o \sin \omega t \) across a pure resistance results in a current \( I \), which is in phase with the applied voltage.

\[
i(t) = \frac{[V_{\text{max}} \sin (\omega t)]}{R} = \frac{I_{\text{max}}}{R} \sin(\omega t)
\]

Therefore, the value \( I_{\text{max}} = \frac{V_{\text{max}}}{R} \) is independent of frequency. Consequently, the magnitude of the impedance is equal to the resistance: \( Z' = R \), which is represented in the complex impedance plane as a point distance \( R \) from the origin along the horizontal, \( Z' \), axis (Figure 2.17).
2.5.5 Ideal Capacitors

In the case of an ideal capacitor the current flow can be defined as

\[ i(t) = \frac{V_{\text{max}}}{\chi_c} \sin(\omega t + \frac{\pi}{2}) = \omega C V_{\text{max}} \sin(\omega t + \frac{\pi}{2}) \]

The flow of d.c. current through a capacitor is blocked because the current leads the voltage by \( \phi = \frac{\pi}{2} \) radians. The a.c. current flow is, however, proportional to the applied voltage. For an ideal capacitor the phase angle is \( \frac{\pi}{2} \) (irrespective of the frequency) and by definition the resistance is 0 \( \Omega \). The magnitude of the impedance is therefore exclusively related to the imaginary impedance component,

\[ |Z| = -j \chi_c = \frac{j}{\omega C}. \]

In order to plot the impedance in the positive quadrant the conjugate of the complex impedance is plotted.

\[ Z^* = (j \omega C)^{-1} \] (from \( |Z| = \frac{V_{\text{max}}}{I_{\text{max}}} \) and \( Z^* = Z' - jZ'' \)).
Consequently the magnitude of the impedance is represented by a vertical line along the imaginary – $Z''$ axis (figure 2.18).

![Complex impedance plot for an ideal capacitor.](image)

**Figure 2.18. Complex impedance plot for an ideal capacitor.**

### 2.5.6 Resistor and Capacitor in Series

An important consequence of a series $RC$ network is that the phase angle increases with frequency, where the total voltage across a series $RC$ network is equal to the sum of the voltage drop across the resistive and capacitive components.

$$V_{TOT} = V_R + V_C$$

It follows that, for a series circuit, the total impedance is defined as

$$Z_{TOT} = Z_1 + Z_2 + \ldots + Z_n$$

$$Z = R + \frac{1}{j\omega C}$$

$$Z = R - \frac{j}{\omega C}$$

Therefore $Z' = R$ and $Z'' = -\frac{1}{\omega C}$. 
As in the case of a pure capacitor the conjugate of the complex impedance is plotted,
\[ Z^* = R - (j \omega C)^{-1} = R + \frac{j}{\omega C}. \]

Consequently, the complex impedance plot consists of a vertical line at a distance \( R \) from the origin along the \( Z' \) axis (figure 2.19).

**Figure 2.19. Complex impedance plot for a series RC network.**

### 2.5.7 Resistor and Capacitor in Parallel

For parallel \( RC \) networks:
\[
\frac{1}{Z_{TOT}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \ldots + \frac{1}{Z_n}, \quad \text{as in the case for resistors in parallel.}
\]

Deriving an expression for \( Z^* \):
\[ Z_{TOT}^* = \left( \frac{1}{\sqrt{R}} + j \omega C \right)^{-1}, \]

Which on expansion gives,
where \( \frac{\omega RC}{[1 + (\omega RC)^2]} \) defines a Debye peak. The maximum height, \( Z'' = \omega RC \), occurs at \( Z' = R/2 \).

Consequently, the complex impedance plane plot takes the form of a semi-circle, where the maximum height is at \( R/2 \) and the intercepts occur along the \( Z' \) axis at point 0 \( (f \rightarrow \infty) \) and \( R \) \( (f \rightarrow 0) \) (Figure 2.20).

In conclusion, semi-circles in the complex impedance plots are indicative of parallel \( RC \) networks. This is typical for an electrolyte material.

**Figure 2.20.** Complex impedance plot for a parallel RC network.
2.5.8 Capacitance Values

It is possible to assign resistive and capacitive components to appropriate portions of the sample-electrode system under test. This is achieved by considering the magnitude of the capacitances of the system. A parallel plate capacitor can be defined as:

\[ C = \varepsilon_0 \varepsilon' A/l \]

Where \( \varepsilon_0 = \) permittivity of free space \((8.854 \times 10^{-14} \text{ F cm}^{-1})\)

\( \varepsilon' = \) permittivity of the dielectric between the two plates

\( A = \) surface area of the plates

\( l = \) distance between the plates

Maxwell's layered dielectric model (figure 2.21) assumes \( \varepsilon' \) to hold a constant value throughout the system under test. Typical capacitance values and their assignments are given in table 2.1.

Figure 2.21. Maxwell's dielectric model for an electrode-solid electrolyte interface and the electrolyte-electrolyte grain boundary.
Table 2.1. Typical capacitance values and their attributed phenomenon.

<table>
<thead>
<tr>
<th>Capacitance / $F$</th>
<th>Phenomenon attributed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-12}$</td>
<td>Bulk</td>
</tr>
<tr>
<td>$10^{-11}$</td>
<td>Minor - Secondary Phase</td>
</tr>
<tr>
<td>$10^{-11} - 10^{-8}$</td>
<td>Grain Boundary</td>
</tr>
<tr>
<td>$10^{-7} - 10^{-3}$</td>
<td>Sample-Electrode Interface</td>
</tr>
</tbody>
</table>

2.5.9 Typical Characteristics for an Ionic Conductor

Two parallel $RC$ networks in series with a capacitor can be considered as an equivalent representative of a ceramic ionic conductor under test conditions where the total impedance is given as:

$$Z_{TOT}^* = Z_b^* + Z_{gb}^* + Z_{dl}^*$$

The sample consists of two distinct regions, the intragrain (bulk) and the intergrain (grain boundary) regions represented by $(R_b, C_b)$ and $(R_{gb}, C_{gb})$ respectively; $C_{dl}$ is the double layer capacitance, which comes from the use of blocking electrodes, i.e. the vertical line in figure 2.22. In cases where conductivities are high the value of $C_{dl}$ is greater than an order of magnitude higher than the value for $C_{gb}$. Consequently at low frequencies $C_{dl}$ and $R_{gb}$ dominate the impedance spectrum, whereas at high frequencies $C_b$ and $R_b$ dominate.
Figure 2.22. Complex impedance plot for 2 parallel RC networks, representing the bulk and grain boundary regions of a solid electrolyte in series with a capacitor, representing the double layer capacitance.

2.5.10 External Reactive Contributions

There are a number of external reactive components that contribute towards the impedance spectrum. Some of these contributions are summarised in figure 2.23 below. These contributions are, however, difficult to quantify in practice, but it can be seen from the diagram that there are a number of possible series/parallel inductive/capacitive circuit combinations that could resonate within the applied test frequency spectrum. For example a series resonance condition between $L_1$ and $C_3$ would provide a low resistance path for the signal to earth.\(^{25}\) The effect of $L_1$ can be minimised by keeping the applied signal voltage to a minimum. $C_2$ and $C_3$ can be minimised by proper shielding of the test leads, up to the point of contact with the sample under test (figure 2.13), and $C_1$ can be minimised by keeping the distance between the electrodes to maximum value and the contact area to a minimum value.
In summary, a great deal of information can be obtained from the a.c. impedance spectrum. The greatest problem with this technique is the analysis of the data, especially when responses due to the individual components are not well resolved. Therefore great care is required in interpretation of the data.

2.6. Thermal Analysis

The physical and chemical properties of some compounds can be examined using thermal analysis techniques. The sample is maintained in a controlled and constant atmosphere for the duration of the experiment, and is monitored as a function of temperature. There are two main experimental techniques that can be employed; Thermogravimetric Analysis and Differential Thermal Analysis.
2.6.1 Thermogravimetric Analysis (TGA)

In this experiment the mass of the sample is monitored as a function of temperature where the rate of heating/cooling is controlled. This technique is often used to study decomposition, dehydration, oxidation and reduction processes.

2.6.2 Differential Thermal Analysis (DTA)

In this experiment the temperature of the sample is compared to a reference (usually alumina) as a function of temperature and/or time. This technique can detect endothermic or exothermic processes, and is often used to study phase changes and reactions. It should be noted however that this technique is not accurate enough to give quantitative analysis of heat capacities or enthalpies. For that aim, the method of differential scanning calorimetry (DSC) is used.
2.7. References

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Chapter 3.0: Preliminary Results, Observations and Discussion:
La$_{9.33}$Si$_6$O$_{26}$, La$_6$Sr$_2$Si$_6$O$_{26}$, La$_6$SrSi$_6$O$_{26.5}$ and La$_{9.33}$Ge$_6$O$_{26}$

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3.1 Introduction

The high oxide ion conductivity of La$_{9.33}$Si$_6$O$_{26}$ was confirmed prior to the commencement of doping studies. The value obtained was, however, lower than previously reported$^1$, because the pellet density achievable for this system, and indeed other silicate systems initially prepared by us, was comparatively low ($< 80 \%$ theoretical). This was due to the fact that the maximum sintering temperature that we could employ at the outset of the project was limited to 1500 °C with our existing furnace complement. Conductivity data reported in the literature was obtained on pellets sintered at temperatures between 1600 °C and 1700 °C. As a consequence the grain boundary contribution towards the conductivity was high. An a.c. impedance plot recorded at 400 °C for La$_{9.33}$Si$_6$O$_{26}$ is shown in figure 3.1. The total conductivity for these systems is therefore reported in this chapter owing to the difficulty in resolving respective semi-circles for bulk and grain boundary components from the recorded data, as has been reported by other groups.$^2$

![Figure 3.1. A.C. impedance plot for La$_{9.33}$Si$_6$O$_{26}$ (recorded at 400 °C).](image-url)
Samples containing germanium in place of silicon show enhanced oxide ion conductivity at high temperatures, 800 °C, compared to their silicon analogues, with values approaching that of YSZ. However, the germanium analogues also have high activation energies for the oxide ion conductivity, meaning that the conductivity decreases significantly with decreasing temperature. A large selection of samples were initially prepared and characterised and a selection of our initial results on conductivity measurements are shown in Table 3.1. Interestingly, samples containing nominal cation vacancies or excess oxygen, e.g. La$_{9.33}$Si$_6$O$_{26}$ and La$_9$SrSi$_6$O$_{26.5}$, appeared to show higher oxide ion conductivity, 800 °C, than nominally stoichiometric samples, e.g. La$_8$Sr$_2$Si$_6$O$_{26}$.

Table 3.1. Conductivity data for selected silicate and germanate apatite samples obtained at the outset of the project on pellets sintered at 1500 °C for 16 hours.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 800 °C / S cm$^{-1}$</th>
<th>Activation Energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{9.33}$Si$<em>6$O$</em>{26}$</td>
<td>$6.63 \times 10^{-4}$</td>
<td>0.81</td>
</tr>
<tr>
<td>La$_9$SrSi$<em>6$O$</em>{26.5}$</td>
<td>$4.14 \times 10^{-3}$</td>
<td>0.62</td>
</tr>
<tr>
<td>La$_9$Sr$_2$Si$<em>6$O$</em>{26}$</td>
<td>$1.56 \times 10^{-6}$</td>
<td>1.22</td>
</tr>
<tr>
<td>La$_{9.33}$Ge$<em>6$O$</em>{26}$</td>
<td>0.01</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Interestingly the X-ray diffraction profile for La$_{9.33}$Ge$_6$O$_{26}$ showed signs of peak broadening and the occurrence of extra peaks after sintering at 1500 °C, indicating either the presence of impurities, or a dramatic reduction in symmetry. Hexagonal La$_{9.33}$Ge$_6$O$_{26}$ could, however, be prepared by heating to 1150 °C. Figure 3.2 demonstrates the evolution of the X-ray profile with temperature, showing the introduction of peak broadening/extra peaks on heating to temperatures > 1150 °C.
Figure 3.2. X-ray diffraction profile for (a) La$_{9.33}$Ge$_6$O$_{26}$ heated to 1150 °C (b) La$_{9.33}$Ge$_6$O$_{26}$ heated at 1350°C and (c) La$_{9.33}$Ge$_6$O$_{26}$ heated to 1500 °C.

Initial work involved determining the rationale behind the conductivities observed for these systems in terms of their structural aspects, before commencement of doping studies in order to try and enhance their conductivity. It was particularly important to establish why systems with nominal cation vacancies or excess oxygen showed higher conductivities and lower activation energies than nominally stoichiometric systems. We also needed to identify why the germanium-based systems were better oxide ion conductors than their silicon-based counterparts. Furthermore, we needed to establish what was happening to the structure of the germanium-based systems on heating to high temperature, and to quantify this in terms of conductivity. One aim was to try to stabilise the hexagonal lattice for the germanium based systems to high temperature.
3.2 Structural Studies: A Powder Neutron Diffraction Study of the Oxide Ion Conducting Apatite Type Phases \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) and \( \text{La}_{8}\text{Sr}_2\text{Si}_6\text{O}_{26} \)

In order to rationalise these materials further we need to understand the relationship between structure and conductivity so that we can prepare new materials with improved conductivity. Particular attention has been focused in this respect on the silicon-based system, as high purity samples are more readily obtained for this system than the germanium-based analogue. We have found that the composition \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) showed high oxide ion conductivity as previously reported, whereas the conductivity of the sample with composition \( \text{La}_{8}\text{Sr}_2\text{Si}_6\text{O}_{26} \) was poor. One difference between the two samples is the presence of cation (La) vacancies in the \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) sample, although the oxide ion content is the same and nominally stoichiometric in both samples, meaning that the oxide ion channel sites are nominally full. In order to try to rationalise the difference in the conductivities and learn more about the structures of these interesting new oxide ion conductors, we have performed a powder neutron diffraction study on these two samples.

3.2.1 Sample Preparation and Data Collection

High purity \( \text{La}_2\text{O}_3 \), \( \text{SrCO}_3 \) and \( \text{SiO}_2 \) were used to prepare the samples \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) and \( \text{La}_{8}\text{Sr}_2\text{Si}_6\text{O}_{26} \). The dried starting materials were ground in the appropriate ratios and heated to 1300 °C for 16 hours. The samples were then reground and reheated to 1350 °C for a further 16 hours.

Time of flight powder neutron diffraction data were recorded on the diffractometer HRPD, ISIS, Rutherford Appleton Laboratory. Structure refinement was performed by the Rietveld method using program TF15LS based on the Cambridge Crystallography Subroutine Library (CCSL).\textsuperscript{4,5} Scattering factors of 0.827, 0.702, 0.4149, 0.5805 (all \( x 10^{-12} \text{cm} \)) were assigned to \( \text{La} \), \( \text{Sr} \), \( \text{Si} \), and \( \text{O} \) respectively.
3.2.2 Structural Determination

Three possible space groups were examined, P6\textsubscript{3} (no. 174), P6\textsubscript{3}/m (No. 177), and P-3 (No. 147) in accordance with previous studies of apatite-type structures. Initially only isotropic thermal parameters were employed (in order to aid convergence the thermal parameters for the (La1) and (La2) sites were constrained to be equal), and it was found that for both samples the space group P-3 gave the best fit: e.g. $R_{wp}$ for La\textsubscript{9.33}Si\textsubscript{6}O\textsubscript{26} = 6.83, 7.42 and 7.48 % for space groups P-3, P6\textsubscript{3} and P6\textsubscript{3}/m respectively ($R_e = 3.76 \%$). Therefore the space group P-3 was favoured. The apatite structure for La\textsubscript{9.33}Si\textsubscript{6}O\textsubscript{26} is shown in figure 3.3.

![Figure 3.3. The structure for La\textsubscript{9.33}Si\textsubscript{6}O\textsubscript{26}, viewed approximately along the [001] direction, showing La1, La2, La3 and O5 positions (Tetrahedra = SiO\textsubscript{4}.)](image)
In the case of La$_{0.33}$Si$_6$O$_{26}$, the refinement of the occupancy of the channel oxygen (O5) position suggested the presence of some vacancies ($\approx 10\%$) on this site. In order to confirm whether the sample was indeed oxygen deficient, or whether some of the oxygen atoms had been shifted off site, we searched for the presence of oxygen atoms at other sites in the channels. Initially, attempts were made to place oxygen atoms at the (0,0,0.5) site, the position generally occupied by large channel anions (e.g. Cl) in the apatite structure. Refinement of the occupancy of this site, however, indicated a zero occupancy. We then attempted to place oxygen atoms midway between the (0,0,0.25) and (0,0,0.5) site at (0,0,0.375). We allowed both refinement of the z coordinate and the occupancy (initial occupancy employed = 10\%) with the thermal parameter fixed as equal to that of the O5 site, and obtained a stable refinement with reduced R factors ($R_{wp}$ decreased from 6.83 to 6.73). The position of this site (O6) refined to (0,0,\approx 0.37) with an occupancy of 0.14(2). Attempts to refine a similar additional oxygen position for La$_8$Sr$_2$Si$_6$O$_{26}$ resulted in a refinement of the O6 position to (0,0,\approx 0.31), thus closer to the O5 position, with only a small occupancy of 0.04(2). In this case, however, there was no improvement in the structural fit ($R_{wp} = 5.32$ for both models), and so we favour the initial refinement with only the O5 channel site, as it has a lower number of variables.

The refinement of both samples showed quite high isotropic thermal parameters for the oxygen atoms (1.0 - 2.5$\text{Å}^2$), with higher values for the La$_{0.33}$Si$_6$O$_{26}$ sample. Therefore anisotropic thermal parameters were refined for the oxygen atoms.

The final refined structural parameters are given in tables 3.2 and 3.3, with observed, calculated, and difference neutron diffraction profiles in figures 3.4 and 3.5. Selected bond distances are given in tables 3.4 and 3.5.
3.2.3 Discussion

The conductivities of \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) and \( \text{La}_{8}\text{Sr}_2\text{Si}_6\text{O}_{26} \) are vastly different, with the former showing high oxide ion conduction and a low activation energy \( (\sigma = 6.63 \times 10^{-4} \text{ S cm}^{-1} \text{ at } 800 \, ^\circ\text{C}, \text{Ea} = 0.81 \text{ eV}) \), while for the latter the oxide ion conduction is rather low \((>2 \text{ orders of magnitude lower})\), and the activation energy is high \( (\sigma = 1.56 \times 10^{-6} \text{ S cm}^{-1} \text{ at } 800 \, ^\circ\text{C}, \text{Ea} = 1.22 \text{ eV}) \). Although the densities of the pellets are relatively low, less than 80\% theoretical, the densities of the pellets do not appear to be the reason for the conductivity difference, especially since the pellet density for \( \text{La}_{8}\text{Sr}_2\text{Si}_6\text{O}_{26} \) was higher than for \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) (74\% of the theoretical density for the former pellet compared to 67\% of the theoretical density for the latter). This was confirmed later by experiments on dense pellets (sintered at 1600 °C to 1700 °C, after the purchase of an 1800 °C furnace), as discussed in chapter 5.

In order to try to explain this difference we need to consider the structures of both these compounds.

Both samples are nominally stoichiometric in oxygen, and the refinements were in good agreement with this. A key difference between the two samples was found in the channel oxygen sites. For \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) a significant number \((\approx 14\%) \) of the oxygen atoms were displaced from the ideal (O5) site at \((0,0,0.25)\) to a new site (O6) at \((0,0,0.37)\) leading to Frenkel-type defects. In contrast incorporation of such an oxygen position for \( \text{La}_{8}\text{Sr}_2\text{Si}_6\text{O}_{26} \) produced no improvement of fit, and so in this sample the channel oxygens appear to be located essentially only in the O5 site. It is also interesting to note that for \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) the values for the thermal parameters \((B_{11}, B_{22}, B_{33})\) for O5/O6 indicate more anisotropy than for \( \text{La}_{8}\text{Sr}_2\text{Si}_6\text{O}_{26} \) with the values of \( B_{11} \) and \( B_{22} \) being essentially zero.

We can therefore propose that the higher conductivity and lower activation energy for oxide ion conduction for \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) is related to the observed disorder in the channel sites. We however need to rationalise why there should be disorder in the channels for \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) and not for \( \text{La}_{8}\text{Sr}_2\text{Si}_6\text{O}_{26} \). This may be related to the presence of a significant number of cation vacancies \((\approx 7\%)\) for the former (as
expected from the composition), which represents the other key structural difference between the two systems. These vacancies may result in structural distortions, which result in oxygen displacements from the (0,0,0.25) site. The thermal parameters of all the atoms in the case of La$_{0.33}$Si$_6$O$_{26}$ support this, in that they are larger than for La$_8$Sr$_2$Si$_6$O$_{26}$.

The cation vacancies are preferentially located on the (La1), and (La2) sites, which are the La sites furthest from the channel (O5, O6) oxygen atoms, and the number are in good agreement with that expected for the composition, La$_{9.24(3)}$Si$_6$O$_{25.96(5)}$. In the case of La$_8$Sr$_2$Si$_6$O$_{26}$, it is impossible to say for certain whether a small number of cation vacancies exist, due to the presence of both La and Sr in these sites. The refined composition is, however, in reasonable agreement within errors with that weighed out, i.e. La$_{6.9(3)}$Sr$_{3.1(3)}$Si$_6$O$_{26}$. It is interesting to note here that the Sr atoms are also located preferentially in the (La1) and (La2) sites. Thus there appears to be a preference for lower positive charges on these two sites, and this has also been seen in refinements of La$_5$NaSi$_6$O$_{26}$, Na being located on these sites.

A final point of interest is the large thermal parameters for the silicate oxygens. Of relevance to this is the fact that recently reported modelling studies suggest that the silicate tetrahedra play a significant role in the conduction process. The modelling results suggest that oxide ion conduction is aided by co-operative displacements of the silicate groups, effectively opening up the oxygen channels.
3.2.4 Summary

It appears as if these apatite systems have significant complexities in their structures, particularly within the channel oxygen sites. It appears as if the lower conductivity and higher activation energy in La$_8$Sr$_2$Si$_6$O$_{26}$ compared to La$_9.33$Si$_6$O$_{26}$ is due to the fact that the channel oxygen atoms are essentially ordered close to the ideal (0,0,0.25) sites in the former, while the latter contains significant oxygen displacements. It is possible that the reason for this difference is the presence of significant cation vacancies in La$_9.33$Si$_6$O$_{26}$.

Figure 3.4. Observed, calculated and difference neutron diffraction profiles for La$_9.33$Si$_6$O$_{26}$.
Figure 3.5. Observed, calculated and difference neutron diffraction profiles for La₈Sr₂Si₆O₂₆.

Table 3.2. Refined structural parameters for La₈.₃₃Si₆O₂₆.

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<thead>
<tr>
<th>Atom</th>
<th>Site</th>
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<th>y</th>
<th>z</th>
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<th>Site Occ.</th>
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<td>-0.0086(7)</td>
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<td>2/3</td>
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<td>1.51(6)</td>
<td>0.86(2)</td>
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<td>Si</td>
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<td>O1</td>
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<td>0.2572(9) *</td>
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</tr>
<tr>
<td>O2</td>
<td>6g</td>
<td>0.5942(2)</td>
<td>0.4722(2)</td>
<td>0.2522(9) *</td>
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</tr>
<tr>
<td>O3</td>
<td>6g</td>
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<td>0.2518(7)</td>
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<td>0.2569(7)</td>
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<td>O5</td>
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<td>0.00</td>
<td>0.245(3) *</td>
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<td>0.00</td>
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* Anisotropic Thermal Parameters

<table>
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<th>B₃₃</th>
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<td>2.5(1)</td>
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<td>-1.9(2)</td>
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<tr>
<td>O2</td>
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<td>2.3(1)</td>
<td>1.2(3)</td>
<td>0.8(2)</td>
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<tr>
<td>O3</td>
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<td>1.9(2)</td>
<td>-0.1(2)</td>
<td>-1.8(2)</td>
<td>0.6(3)</td>
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<td>O4</td>
<td>3.4(3)</td>
<td>1.4(2)</td>
<td>1.2(2)</td>
<td>0.8(2)</td>
<td>0.7(2)</td>
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<td>O5</td>
<td>-0.1(2)</td>
<td>-0.2(2)</td>
<td>3.0(2)</td>
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<td>0.0</td>
<td>-0.8(1)</td>
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<tr>
<td>O5</td>
<td>-0.1(2)</td>
<td>-0.2(2)</td>
<td>3.0(2)</td>
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Hexagonal, Space Group P-3 (No. 147); a = b = 9.7248(1) Å, c = 7.1895(1) Å
R₁ = 4.3%, Rₚ = 4.9%, Rₚₚ = 5.6%, Rₑ = 3.8%
Table 3.3. Refined structural parameters for La₉Sr₂Si₆O₂₆.

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<th>z</th>
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<th>Site Occ.</th>
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<td>0.79(3)</td>
<td>0.2(2)/0.8(2)</td>
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<td>1/3</td>
<td>2/3</td>
<td>0.5007(2)</td>
<td>0.79(3)</td>
<td>0.7(2)/0.3(2)</td>
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<td>0.2453(1)</td>
<td>0.2486(7)</td>
<td>0.61(2)</td>
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* Anisotropic Thermal Parameters

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<th>B₁₂</th>
<th>B₂₃</th>
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<tr>
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<td>1.7(2)</td>
<td>0.5(2)</td>
<td>0.4(2)</td>
<td>0.4(2)</td>
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<tr>
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Hexagonal, Space Group P-3; a = b = 9.7083(1) Å, c = 7.2377(1) Å,
R₁ = 3.2%, Rₚ = 4.3%, Rwpdb = 4.8%, Rₑ = 3.7%

Table 3.4. Selected bond distances for La₉₃₃Si₆O₂₆.

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<th>Bond Distance / Å</th>
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<td>2.565 [x3]</td>
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<td>La2-O3</td>
<td>2.840 [x3]</td>
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<tr>
<td>La3-O1</td>
<td>2.725</td>
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<td>La3-O2</td>
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<td>La3-O4</td>
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<td>La3-O5 (occupancy = 0.84)</td>
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Table 3.5. Selected bond distances for La₈Sr₂Si₆O₂₆.

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3.3 References

Chapter 4.0: An Investigation of the Synthesis and Conductivities of La-Ge-O Based Systems

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<th>Section</th>
<th>Page</th>
</tr>
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<td>136</td>
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<td>4.1.4 Summary</td>
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Chapter 4.0: An Investigation of the Synthesis and Conductivities of La-Ge-O Based Systems

4.1 Introduction

Most of the initial work on these apatite-type oxide ion conductors has focused on the Si based systems, despite reports of higher conductivities for Ge based systems, La$_{10-x}$Ge$_6$O$_{25+x}$. This is because of the complexities associated with the Ge based systems, with the exact nature of the conducting phase being unclear. In the initial paper on these systems, it was claimed that they were apatite-type, although the X-ray diffraction profiles showed significant broadening of peaks/extra peaks around the main apatite peaks. Subsequently the same group reported that these phases were in fact cation deficient La$_2$GeO$_5$ type, and presented a detailed investigation of the La$_{2-x}$GeO$_{5.5x/2}$ system. Oxide ion conductivity increased with increased Lanthanum deficiency up to a maximum value of $x = 0.39$ in La$_{2.05}$GeO$_{5.8}$, which corresponds to a composition La$_{9.66}$Ge$_{6.8}$O$_{26.5}$. The authors also reported strontium doping in this system, with the sample of composition La$_{1.5}$Sr$_{0.17}$Ge$_{6}$O$_{26}$ being reported as pure La$_2$GeO$_5$ type. This composition corresponds to the composition La$_9$SrGe$_6$O$_{26.5}$, for which the X-ray diffraction profile in the authors' previous paper suggested it being apatite-type, albeit with evidence of peak broadening. Indeed, the X-ray diffraction profile reported bore little resemblance to that expected for a La$_2$GeO$_5$ based system. From the data shown for low Lanthanum deficiencies, $x \leq 0.39$, the X-ray diffraction profiles were consistent with that expected for La$_2$GeO$_5$. While, for the higher values of $x \geq 0.45$, (and the highest conductivity samples), the profiles appear to resemble more closely that expected for an apatite-type system, albeit with the aforementioned extra peaks/peak broadening. There is therefore clearly some ambiguity regarding the nature of the conducting phase in the germanium based systems, and so to rationalise this we made a detailed study of this system. Attention has been principally focused on the composition La$_{9.33}$Ge$_6$O$_{26}$, as a direct comparison to the La$_{9.33}$Si$_6$O$_{26}$ system, which we have studied earlier.
We have successfully synthesised hexagonal La$_{9.33}$Ge$_6$O$_{26}$ apatite by firing at moderate temperature, 1150 °C - 1250 °C, and have examined the stability of this phase according to both synthesis temperature and heating time. We have also looked into the effect of sintering temperatures and sintering time on the oxide ion conductivity. In particular, data on the effect of extended sintering on this system at high temperatures, 1500 °C, has been collected.

For comparison we have also measured the oxide ion conductivities of other phases in the La-Ge-O phase diagram, i.e. La$_2$GeO$_5$ and La$_4$GeO$_8$.

### 4.1.1 Synthesis and Experimental

La$_{9.33}$Ge$_6$O$_{26}$, La$_2$GeO$_5$, and La$_4$GeO$_8$ were prepared using high purity La$_2$O$_3$ and GeO$_2$. The dried starting materials were ground together in stoichiometric proportions and fired for 14 hours at 1150 °C (La$_{9.33}$Ge$_6$O$_{26}$), 1400 °C (La$_2$GeO$_5$ and La$_4$GeO$_8$). The samples were reground and reheated for a further 14 hours at 1150 °C (La$_{9.33}$Ge$_6$O$_{26}$), 1500 °C (La$_2$GeO$_5$ and La$_4$GeO$_8$). Phase purity was examined using X-ray diffraction, which indicated single phase samples. FT-IR spectra for samples were run on a PE 2000 FTIR using Nicolet 510P software.

The conductivity measurements were made using a.c. impedance measurements. Pellets were prepared, as described in chapter 2, and sintered at 1150 °C (La$_{9.33}$Ge$_6$O$_{26}$), 1500 °C (La$_2$GeO$_5$ and La$_4$GeO$_8$) for 14 hours. Densities were ≈ 61 %, 78 %, 85 % of the theoretical for La$_{9.33}$Ge$_6$O$_{26}$, La$_2$GeO$_5$, and La$_4$GeO$_8$ respectively. In addition the La$_{9.33}$Ge$_6$O$_{26}$ sample was remeasured after sintering at 1350 °C for 20 hours and 1500 °C for 6 hours (approximate densities of the pellet in these cases were 72 % and 75 % of the theoretical respectively). Due to the general problem experienced in resolving bulk and grain boundary semicircles in these apatite-type oxide ion conductors, the conductivities reported represent total conductivities.
In order to examine the stability of the La$_{9.33}$Ge$_6$O$_{26}$ phase to long term sintering, a second sample was prepared and half was heated at 1250 °C for 4 weeks, with the other half heated at 1500 °C for 120 hours. The latter sample was examined by X-ray diffraction after 48 hours, before being reground and reheated for the remaining 72 hours. In both cases the sample was weighed before and after heat treatment to see if there was any mass lost.

### 4.1.2 La$_{9.33}$Ge$_6$O$_{26}$: Synthesis and Conductivity

It was shown that synthesis at 1150 °C resulted in the formation of La$_{9.33}$Ge$_6$O$_{26}$ with an X-ray diffraction profile typical of that expected for a hexagonal apatite cell. Refinement of the cell parameters gave the values $a = b = 9.913(4)$, $c = 7.282(4)$ Å, which, as expected, are larger than for the corresponding silicate phase, La$_{9.33}$Si$_6$O$_{26}$ ($a = b = 9.725(1)$, $c = 7.190(1)$ Å) due to the larger size of Ge. Heating to higher temperature (>1300 °C), however, resulted in broadening of the apatite peaks. This broadening of the peaks in the X-ray diffraction profile became more extreme at higher temperature, 1500 °C, for which distinct extra peaks around the nominal apatite peaks became resolved (figure 4.1). Noticeably, however, the (0,0,1) peaks appeared to remain sharp, and so this suggested that the hexagonal cell may have transformed to a monoclinic cell. However, attempts to refine the profile on a monoclinic cell have so far proved unsuccessful, as have attempts to fit the profile to two different apatite-type phases or an apatite-type phase and a La$_2$GeO$_5$ type phase. It should be noted that the changes in X-ray diffraction profile are irreversible and reheating at lower temperatures leads to no resultant change to the X-ray diffraction profile. It is clear, from the data, that the profile bears a much closer resemblance to apatite rather than La$_2$GeO$_5$ reported by Ishihara et al. Furthermore, recent work by Berastegui et al. has supported the conclusion that the highly conductive phase is indeed apatite type. The authors attribute the initial peak broadening to an incommensurate supercell, as a result of ordering within the apatite channels. It was also suggested that in the system prepared at high temperature (1500 °C), the phase
may be triclinic, although no cell was determined. However, Leon-Reina et al. have reported more recently that the structure synthesised at high temperature can indeed be attributed to a triclinic pseudoapatite phase.\textsuperscript{7}

![X-ray diffraction profile](image)

Figure 4.1. X-ray diffraction profile for (a) La\(_{9.33}\)Ge\(_6\)O\(_{26}\) heated to 1150 °C (b) La\(_{9.33}\)Ge\(_6\)O\(_{26}\) heated at 1350°C and (c) La\(_{9.33}\)Ge\(_6\)O\(_{26}\) heated to 1500 °C.
Figure 4.2 shows the IR spectra for samples heated at 1150 °C, 1350 °C, and 1500 °C as well as that of La$_2$GeO$_5$. As was the case for the X-ray diffraction profile, the IR spectra for the La$_{9.33}$Ge$_6$O$_{26}$ sample heated at the different temperatures are similar to one another, with a broad peak in the region 550-850 cm$^{-1}$ corresponding to the O-Ge-O stretching and deformation modes. The sample of La$_2$GeO$_5$ also showed IR absorption in this region, but there was a clear multiplet rather than a broad unresolved peak, suggesting again a difference between the La$_{9.33}$Ge$_6$O$_{26}$ samples and La$_2$GeO$_5$.

In addition to the change in the X-ray diffraction profile, there was also a significant change in the conductivity data between the pellet sintered at 1150 °C, 1350 °C, and 1500 °C (Figure 4.3, table 4.1). Specifically the activation energy for oxide ion conduction increased as the sintering temperature was increased. It should be noted that the conductivities reported represent total conductivities and so some of the changes observed may correspond to changes in the grain boundary contribution, rather than the bulk. For the samples sintered at 1150 °C and 1350 °C, there was also evidence for a reduction in the activation energy for oxide ion conduction at high
temperature (table 4.1, figure 4.3). It is interesting to note from the plot that the low temperature conductivity for the pellet sintered at 1150 °C is significantly higher than for that sintered at 1500 °C. This could also be related to grain boundary effects, although it would be predicted that the grain contribution should be higher at low sintering temperatures, and not lower as the results would suggest. However, of relevance to this discussion, it was also noticeable that the pellet sintered at 1500 °C became very brittle in comparison to the pellet sintered at low temperature. This suggests some significant changes occur to this system on high temperature sintering.

![Figure 4.3](image)

**Figure 4.3.** Plots of conductivity data for pellets of La$_{0.33}$Ge$_6$O$_{28}$ (nominal composition) sintered at (a) 1150 °C (14 hours), (b) 1350 °C (20 hours) and (c) 1500 °C (6 hours).
Table 4.1. Conductivity data for La$_{9.33}$Ge$_6$O$_{26}$ (nominal composition) sintered at different temperatures.

<table>
<thead>
<tr>
<th>Sintering Temp./ °C</th>
<th>Sintering Time / hours</th>
<th>Pellet Density / % of Theoretical</th>
<th>Conductivity at 800 °C / S cm$^{-1}$</th>
<th>Activation Energy / eV (Low Temp. / High Temp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1150</td>
<td>14</td>
<td>61.3</td>
<td>$3.14 \times 10^{-3}$</td>
<td>*0.95/0.80</td>
</tr>
<tr>
<td>1350</td>
<td>20</td>
<td>71.8</td>
<td>0.01</td>
<td>*1.11/0.57</td>
</tr>
<tr>
<td>1500</td>
<td>6</td>
<td>75.2</td>
<td>0.01</td>
<td>1.42</td>
</tr>
</tbody>
</table>

4.1.3 La$_{9.33}$Ge$_6$O$_{26}$: The Effect of Synthesis Temperature and Time

Two studies were performed to examine further the effect of synthesis temperature and specifically synthesis time on La$_{9.33}$Ge$_6$O$_{26}$. One sample was heated at 1250 °C for 4 weeks, while a second sample was heated at 1500 °C for a total time of 120 hours, with an intermediate regrind after 48 hours. The X-ray diffraction profile for both samples showed significant changes, particularly that of the second sample. In the case of the sample heated to 1250 °C, a broadening of the apatite-type peaks was observed, similar to the profile observed for synthesis at 1350 °C. The X-ray diffraction profile for the sample heated to 1500 °C was completely different, with the profile resembling that of La$_2$GeO$_5$ (Figure 4.4), although there is still possibly the presence of a small amount of apatite-type phase. For both samples a mass loss was observed after the heat treatment; 1 % for the sample heated at 1250 °C, and 3.5 % for the sample heated at 1500 °C. If we assume that this mass loss is due to loss of Ge, since this is the most volatile element, then the mass loss observed at 1500 °C would correspond to a change in composition from La$_{9.33}$Ge$_6$O$_{26}$ (La$_{1.33}$GeO$_{4.33}$) to La$_{10.56}$Ge$_6$O$_{27.83}$ (La$_{1.76}$GeO$_{4.64}$). Thus the composition of the sample is moving closer to that of La$_2$GeO$_5$ which is consistent with the change in X-ray diffraction profile to one that resembles La$_2$GeO$_5$, and also would help to partially explain the confusion on the Ge based system in the previous literature.
Figure 4.4. X-ray diffraction profile for (a) a sample with starting composition, \( \text{La}_{0.33}\text{Ge}_9\text{O}_{26} \), heated to 1500 °C for 120 hours and (b) \( \text{La}_2\text{GeO}_5 \).

This loss of Ge represents a significant problem in the potential use of these materials in SOFCs. Similar problems have been encountered for LaGaO\(_3\) based electrolytes, with loss of Ga at high temperatures, particularly under reducing conditions.\(^8,9\) Whether the loss of Ge is also increased under reducing conditions, as well as the exact mechanism of the loss needs to be examined. We can, however, propose that the initial process involves leaching out of GeO\(_2\),

i.e. \( \text{La}_{0.33}\text{Ge}_6\text{O}_{26} \rightarrow \text{La}_{0.33}\text{Ge}_{6-x}\text{O}_{26-2x} + \text{GeO}_2 \).

This GeO\(_2\) is then lost through volatilisation. Indeed there is possible evidence for this in the X-ray diffraction profile with a small peak at \( 2\theta \approx 26^\circ \) being observed, which corresponds to the main peak for GeO\(_2\). If this is the case, then it is possible that the high activation energy observed for the pellet sintered at 1500 °C is due to the deposition of germanium oxide in the grain boundary region of the pellet.
In order to examine what effect this large loss of Ge and transformation to a La$_2$GeO$_5$ type system had on the conductivity, a pellet of the sample heated to 1500 °C for 120 hours was pressed and sintered for a further 6 hours at this temperature before the conductivity was measured. The data for this sample, as well as for a sample of La$_2$GeO$_5$ are shown in figure 4.5. As can be seen the data for La$_2$GeO$_5$ and the La$_{9.33}$Ge$_6$O$_{26}$ sample heated for extended time at 1500 °C are similar and significantly lower than for an apatite-type system. Somewhat surprisingly, however, the activation energy for oxide ion conduction is actually lower for the La$_2$GeO$_5$ based systems (Tables 4.1 and 4.2), which may be due to a high grain boundary component for the apatite-type systems, as intimated above. This germanium loss in La$_{9.33}$Ge$_6$O$_{26}$ was subsequently confirmed by Berastegui et al.\(^6\)

Table 4.2. Conductivity data for La$_2$GeO$_5$, La$_4$GeO$_8$, and a La$_{9.33}$Ge$_6$O$_{26}$ sample sintered at 1500 °C for 120 hours.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Pellet Density / % of Theoretical</th>
<th>Conductivity at 800 °C / S cm$^{-1}$</th>
<th>Activation energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_4$GeO$_8$</td>
<td>85.0</td>
<td>2.15 × 10$^{-5}$</td>
<td>1.01</td>
</tr>
<tr>
<td>La$_2$GeO$_5$</td>
<td>78.2</td>
<td>1.62 × 10$^{-5}$</td>
<td>0.88</td>
</tr>
<tr>
<td>Sample of initial composition La$_{9.33}$Ge$<em>6$O$</em>{26}$ heated at 1500 °C for 110 hours</td>
<td>≈73.0</td>
<td>3.04 × 10$^{-5}$</td>
<td>1.09</td>
</tr>
</tbody>
</table>
Figure 4.5. Conductivity data for (a) La$_2$GeO$_5$ and (b) a sample with starting composition, La$_{9.33}$Ge$_6$O$_{26}$, heated to 1500 °C for 120 hours.

Since the results indicate that Ge is being lost at high temperatures, a further experiment was performed to try to limit this Ge loss. A sample of La$_{9.33}$Ge$_6$O$_{26}$ was prepared by synthesis at 1150 °C as before. Part of the sample was then pressed as a pellet, with the remaining powder being used to cover the pellet to try to limit the loss of Ge from the pellet. The pellet was then sintered at 1500 °C for 2 hours and the conductivity measured. The density of the pellet was 81 % of the theoretical and the conductivity at 800 °C was 0.03 S cm$^{-1}$ with an activation energy of 1.0 eV (with possible evidence for a reduction in activation energy at high temperature, (Figure 4.6). An inspection of the X-ray diffraction profile showed an apatite-type profile, with only slight evidence of peak broadening, suggesting a greatly reduced Ge loss. Significantly, the conductivity was the highest of all the samples measured.
Figure 4.6. Conductivity data for a pellet of La$_{8.33}$Ge$_6$O$_{26}$ sintered at 1500 °C for 2 hours with a protective layer of La$_{8.33}$Ge$_6$O$_{26}$ powder.

In order to complete the study of La-Ge-O based systems, the conductivity of La$_4$GeO$_8$ was also measured. The conductivity was rather low ($2 \times 10^{-5}$ Scm$^{-1}$ at 800 °C, $E_a = 1$ eV) (Figure 4.7) and attempts to introduce oxygen vacancies via reducing the La content according to the formula La$_{4-x}$GeO$_{8-3x/2}$ resulted in significant impurities.
Figure 4.7. Plot of conductivity data for La₄GeO₈.

4.1.4 Summary

We have shown that hexagonal apatite-type La₀.₃₃Ge₀.₄₂₆ can be prepared at moderate temperatures, 1150 °C, and shows high oxide ion conduction. Heating to high temperatures results in peak broadening, which increases with sintering temperature and time, such that it resolves into clear extra peaks. Prolonged heat treatment at high temperatures results in a large change in X-ray diffraction profile and the formation of a La₂GeO₅ type system. These changes have been attributed to loss of Ge at high temperatures, which is a significant problem for the potential use of these materials in SOFC’s. In contrast to the apatite-type system, conductivities for La₂GeO₅ and La₄GeO₈ are rather low, although activation energies are also quite low, and so further doping studies in these systems may be of interest.
4.2 References

Chapter 5.0: The Synthesis and Conductivities of the Alkaline Earth Doped Apatite Type Phases (La/M)$_{10x}$Si$_6$O$_{26+y}$
(M = Mg, Ca, Sr, Ba)

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Chapter 5.0: The Synthesis and Conductivities of the Alkaline Earth Doped Apatite-Type Phases \((\text{La/M})_{10-x}\text{Si}_6\text{O}_{26+y} (M = \text{Mg, Ca, Sr, Ba})\)

5.1 Introduction

The importance of cation and oxygen non-stoichiometry was established previously in an initial study of strontium doped systems, as discussed in chapter 3. In continuation of these studies we have examined the structure and conductivities of related systems in which a selection of other divalent cations have been doped onto the lanthanum site, the details of which are discussed in this chapter. We have prepared a range of new phases following the doping scheme \((\text{La/M})_{10-x}\text{Si}_6\text{O}_{26+y} (M = \text{Mg, Ca, Sr or Ba})\). In one series of samples oxygen stoichiometry was maintained, i.e. \(y = 0\), while the number of cation vacancies was varied. In another set of samples cation stoichiometry was maintained, i.e. \(x = 0\), in this case however the oxygen content has been varied above and below the stoichiometric \(O_{26}\). Finally samples stoichiometric in both cation and oxygen content were prepared and tested. The results support the previous conclusion of the importance of cation non-stoichiometry and/or oxygen excess for achieving high oxide ion conductivity in silicon based apatite systems.

5.1.1 Synthesis and Experimental

High purity \(\text{La}_2\text{O}_3\), \(\text{SiO}_2\), \(\text{MgO}\), \(\text{CaCO}_3\), \(\text{SrCO}_3\) and \(\text{BaCO}_3\) were used for sample preparation. The dried starting materials were ground in the appropriate ratios prior to the first heat treatment. Details of synthesis conditions are given below in table 5.1. Each sample was reground prior to subsequent heat treatments. Phase purity was checked for all samples after synthesis using powder X-ray diffraction.
Table 5.1. Synthesis conditions for (La/M)$_{10-x}$Si$_6$O$_{28+y}$ (M = Mg, Ca, Sr or Ba).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>1st Heat Treatment / °C (Duration / hours)</th>
<th>2nd Heat Treatment / °C (Duration / hours)</th>
<th>3rd Heat Treatment / °C (Duration / hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{9.67}$Si$<em>6$O$</em>{26.5}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
<td></td>
</tr>
<tr>
<td>La$_{8.67}$MgSi$<em>6$O$</em>{26}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
<td></td>
</tr>
<tr>
<td>La$_{8.67}$Mg$_2$Si$<em>6$O$</em>{26}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
<td></td>
</tr>
<tr>
<td>La$<em>{8.5}$Mg$</em>{1.5}$Si$<em>6$O$</em>{26.25}$</td>
<td>1300(12)</td>
<td>1350(16)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>La$_{9}$MgSi$<em>6$O$</em>{26.5}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
<td></td>
</tr>
<tr>
<td>La$<em>{7.5}$Ca$</em>{2.5}$Si$<em>6$O$</em>{25.75}$</td>
<td>1350(14)</td>
<td>1350(14)</td>
<td></td>
</tr>
<tr>
<td>La$_{8.67}$CaSi$<em>6$O$</em>{26}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
<td></td>
</tr>
<tr>
<td>La$_{8}$Ca$_2$Si$<em>6$O$</em>{26}$</td>
<td>1350(14)</td>
<td>1350(18)</td>
<td></td>
</tr>
<tr>
<td>La$<em>{8.5}$Ca$</em>{1.5}$Si$<em>6$O$</em>{26.25}$</td>
<td>1300(12)</td>
<td>1350(16)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>La$_{9}$CaSi$<em>6$O$</em>{26.5}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
<td></td>
</tr>
<tr>
<td>La$_{8.67}$SrSi$<em>6$O$</em>{26}$</td>
<td>1300(12)</td>
<td>1350(16)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>La$_{8}$Sr$_2$Si$<em>6$O$</em>{26}$</td>
<td>1350(14)</td>
<td>1350(14)</td>
<td></td>
</tr>
<tr>
<td>La$<em>{8.5}$Sr$</em>{1.5}$Si$<em>6$O$</em>{26.25}$</td>
<td>1300(12)</td>
<td>1350(16)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>La$_{9}$SrSi$<em>6$O$</em>{26.5}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
<td></td>
</tr>
<tr>
<td>La$<em>{7.5}$Ba$</em>{2.5}$Si$<em>6$O$</em>{25.75}$</td>
<td>1350(14)</td>
<td>1350(14)</td>
<td></td>
</tr>
<tr>
<td>La$_{8.67}$BaSi$<em>6$O$</em>{26}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
<td></td>
</tr>
<tr>
<td>La$_{8}$Ba$_2$Si$<em>6$O$</em>{26}$</td>
<td>1350(14)</td>
<td>1350(18)</td>
<td></td>
</tr>
<tr>
<td>La$<em>{8.5}$Ba$</em>{1.5}$Si$<em>6$O$</em>{26.25}$</td>
<td>1350(5)</td>
<td>1200(16)</td>
<td>1200(16)</td>
</tr>
<tr>
<td>La$_{9}$BaSi$<em>6$O$</em>{26.5}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
<td></td>
</tr>
</tbody>
</table>

Pellets were prepared for conductivity measurements as described in chapter 2. Sintering temperatures between 1500 °C and 1700 °C were employed in order to obtain dense pellets. Densities were determined to be > 90 % of the theoretical density after sintering, with the noteworthy exception of La$_{8.67}$SrSi$_6$O$_{26}$. Attempts at sintering La$_{8.67}$SrSi$_6$O$_{26}$ above 1500 °C resulted in brittle sample pellets, leading to difficulty in obtaining reliable conductivity data. Consequently the conductivity of a pellet sintered at 1500 °C was measured. The phase purity of each sample pellet used for conductivity testing was also examined using X-ray diffraction.
5.1.2 Cell Parameters

Details of cell parameter data are given in table 5.2. X-ray diffraction data indicated the successful preparation of single phase samples for a range of samples (La/M)\textsubscript{10-\textit{x}}Si\textsubscript{6}O\textsubscript{26+y} (M = Mg, Ca, Sr or Ba). Figure 5.1 shows the X-ray diffraction profiles for La\textsubscript{9.67}Si\textsubscript{6}O\textsubscript{26.5} and La\textsubscript{9}CaSi\textsubscript{6}O\textsubscript{26.5}, and figure 5.2 shows the X-ray diffraction profiles for La\textsubscript{9}SrSi\textsubscript{6}O\textsubscript{26.5} and La\textsubscript{9}BaSi\textsubscript{6}O\textsubscript{26.5}. The magnesium and calcium doped systems showed a decrease in unit cell size with increased dopant content, while the barium doped samples showed a corresponding increase in size. These variations are in line with expectations, since Mg\textsuperscript{2+} and Ca\textsuperscript{2+} are smaller than La\textsuperscript{3+}, whereas Ba\textsuperscript{2+} is larger. However, a close inspection of the variation of the unit cell parameters with dopant (M = Mg, Ca, Ba) content suggests some deviation from Vegard’s law at high dopant levels.

Table 5.2. Cell parameter data for (La/M)\textsubscript{10-\textit{x}}Si\textsubscript{6}O\textsubscript{26+y} (M = Mg, Ca, Sr or Ba).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Unit Cell Parameters / Å (Hexagonal Cell)</th>
<th>Unit Cell Volume / Å\textsuperscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a = b)</td>
<td>(c)</td>
</tr>
<tr>
<td>La\textsubscript{9}Si\textsubscript{6}O\textsubscript{26.5}</td>
<td>9.733(2)</td>
<td>7.193(2)</td>
</tr>
<tr>
<td>La\textsubscript{9.67}Mg\textsubscript{0.33}Si\textsubscript{6}O\textsubscript{26}</td>
<td>9.647(4)</td>
<td>7.092(3)</td>
</tr>
<tr>
<td>La\textsubscript{9}Mg\textsubscript{2}Si\textsubscript{6}O\textsubscript{26}</td>
<td>9.633(2)</td>
<td>7.058(2)</td>
</tr>
<tr>
<td>La\textsubscript{9}Mg\textsubscript{1}Ca\textsubscript{1}Si\textsubscript{6}O\textsubscript{26.33}</td>
<td>9.626(3)</td>
<td>7.044(3)</td>
</tr>
<tr>
<td>La\textsubscript{9}MgSi\textsubscript{6}O\textsubscript{26.5}</td>
<td>9.675(3)</td>
<td>7.096(3)</td>
</tr>
<tr>
<td>La\textsubscript{8}Ca\textsubscript{2}Sr\textsubscript{1}Si\textsubscript{6}O\textsubscript{26.75}</td>
<td>9.655(3)</td>
<td>7.147(3)</td>
</tr>
<tr>
<td>La\textsubscript{8.67}Ca\textsubscript{0.33}Si\textsubscript{6}O\textsubscript{26}</td>
<td>9.693(3)</td>
<td>7.176(3)</td>
</tr>
<tr>
<td>La\textsubscript{8}Ca\textsubscript{2}Si\textsubscript{6}O\textsubscript{26}</td>
<td>9.661(2)</td>
<td>7.155(2)</td>
</tr>
<tr>
<td>La\textsubscript{8}C\textsubscript{a}Sr\textsubscript{1}Si\textsubscript{6}O\textsubscript{26.33}</td>
<td>9.683(6)</td>
<td>7.163(5)</td>
</tr>
<tr>
<td>La\textsubscript{8}CaSi\textsubscript{6}O\textsubscript{26.5}</td>
<td>9.697(2)</td>
<td>7.175(2)</td>
</tr>
<tr>
<td>La\textsubscript{8}Sr\textsubscript{2}Si\textsubscript{6}O\textsubscript{26}</td>
<td>9.714(4)</td>
<td>7.220(3)</td>
</tr>
<tr>
<td>La\textsubscript{8}Sr\textsubscript{1}Ca\textsubscript{1}Si\textsubscript{6}O\textsubscript{26.33}</td>
<td>9.714(4)</td>
<td>7.235(3)</td>
</tr>
<tr>
<td>La\textsubscript{8}SrSi\textsubscript{6}O\textsubscript{26.5}</td>
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<td>7.226(1)</td>
</tr>
<tr>
<td>La\textsubscript{8.67}Ba\textsubscript{0.33}Si\textsubscript{6}O\textsubscript{26.75}</td>
<td>9.797(3)</td>
<td>7.343(3)</td>
</tr>
<tr>
<td>La\textsubscript{8}Ba\textsubscript{2}Si\textsubscript{6}O\textsubscript{26}</td>
<td>9.757(3)</td>
<td>7.275(3)</td>
</tr>
<tr>
<td>La\textsubscript{8}Ba\textsubscript{1}Si\textsubscript{6}O\textsubscript{26.5}</td>
<td>9.790(2)</td>
<td>7.331(2)</td>
</tr>
<tr>
<td>La\textsubscript{8}Ba\textsubscript{2}Sr\textsubscript{1}Si\textsubscript{6}O\textsubscript{26.33}</td>
<td>9.762(3)</td>
<td>7.307(3)</td>
</tr>
<tr>
<td>La\textsubscript{8}BaSr\textsubscript{2}Si\textsubscript{6}O\textsubscript{26.5}</td>
<td>9.757(3)</td>
<td>7.276(3)</td>
</tr>
</tbody>
</table>
Figure 5.1. X-ray diffraction profiles for (a) La_{9.67}Si_6O_{26.5} and (b) La_9CaSi_6O_{26.5}.

Figure 5.2. X-ray diffraction profiles for (a) La_9SrSi_6O_{26.5} and (b) La_9BaSi_6O_{26.5}.
Plots of unit cell volume as a function of dopant content \( x \) are given for each dopant in figures 5.3 to 5.5. Data for the following formula types were selected, La\(_{9.67}\)Si\(_6\)O\(_{26.5}\), La\(_9\)M\(_{Si_6}\)O\(_{26.5}\), La\(_{8.5}\)M\(_{1.5}\)Si\(_6\)O\(_{26.25}\), La\(_8\)M\(_2\)Si\(_6\)O\(_{26}\), and La\(_{7.5}\)M\(_{2.5}\)Si\(_6\)O\(_{25.75}\), corresponding to 0, 10, 15, 20 and 25 % dopant levels respectively. It should be noted that Vegard’s law does not strictly apply in this context because oxygen stoichiometry is not consistent across the range, while the undoped sample, La\(_{9.67}\)Si\(_6\)O\(_{26.5}\), contains cation vacancies. However, the plots shown do provide a useful qualitative comparison in this circumstance. In the schemes where \( M = Ca, \) or Ba the trends in unit cell volume appear to obey Vegard’s law for samples with dopant contents \( \leq 20 \% \), suggesting the successfully preparation of single phase samples in these cases. However, any subsequent increase in dopant content results in a reduced change in unit cell volume, suggesting that dopant levels cannot be increased significantly above 20 %. In the case of magnesium doping the solubility limit appears to be even lower since the change in unit cell volume only obeys Vegard’s for samples with dopant levels \( \leq 15 \% \). There was no evidence of impurities in the samples containing high levels of magnesium dopant by X-ray diffraction. However, it does not necessarily follow that none were present since any reflections from a magnesium rich impurity would be likely to be low in intensity, relative to the main apatite phase due to the lower scattering factor of magnesium compared to lanthanum. In the case of strontium doping, the trend in volume obeys Vegard’s law for samples with dopant levels \( \leq 20 \% \), showing a slight increase in unit cell size with strontium content. The X-ray diffraction profile for the system with a dopant level of 25 % revealed small but significant impurities. Consequently data for this system has been omitted from this discussion. These results suggest that there exists a solubility limit of \( \leq 20 \% \) for divalent cation doping on the lanthanum site for the synthesis conditions employed in this experiment. It is noteworthy that in the cases discussed above where the cell parameters are shown not to comply with Vegard’s law, e.g. La\(_8\)Mg\(_2\)Si\(_6\)O\(_{26}\), the true composition of the apatite phase is unknown. If these systems are deficient in dopant, and thus rich in lanthanum, then their compositions will tend towards oxygen excess.
Figure 5.3. Unit cell volume as a function of % magnesium content, $(\text{La/Mg})_{10-x}\text{Si}_6\text{O}_{26+y}$.

Figure 5.4. Unit cell volume as a function of % calcium content, $(\text{La/Ca})_{10-x}\text{Si}_6\text{O}_{26+y}$. 
Figure 5.5. Unit cell volume as a function of % barium content, (La/Ba)_{10-x}Si_8O_{26+y}.

### 5.1.3 Conductivity Data

In order to resolve bulk and grain boundary contributions sintering temperatures higher than 1500 °C were required. The total conductivity is however reported for La_{9.67}SrSi_6O_{26}, as it was only sintered at 1500 °C. Details of bulk conductivity data, quoted at 500 °C and 800 °C, are given in table 5.3. The plots of log (σ T) versus 1000 / T for La_{9.33}Si_6O_{26}, La_{8}Mg_2Si_6O_{26} and La_{9}MgSi_6O_{26.5}, are given in figure 5.6. The corresponding plots for La_{9.33}Si_6O_{26}, La_{8.67}CaSi_6O_{26}, La_{9}CaSi_6O_{26.5}, La_{9}Ca_2Si_6O_{26} and La_{7.5}Ca_2.5Si_6O_{25.75} are given in figure 5.7. The plots for La_{9.33}Si_6O_{26}, La_{8.67}SrSi_6O_{26}, La_{8}Sr_2Si_6O_{26} and La_{9}SrSi_6O_{26.5}, are given in figure 5.8, and the plots for La_{9.33}Si_6O_{26}, La_{8.67}BaSi_6O_{26}, La_{9}BaSi_6O_{26.5}, La_{8}Ba_2Si_6O_{26} and La_{7.5}Ba_2.5Si_6O_{25.75} are given in figure 5.9.
Table 5.3. Conductivity data for (La/M)$_{10-x}$Si$_6$O$_{26+y}$ (M = Mg, Ca, Sr and Ba), quoted at 500 and 800 °C (Conductivity data given are bulk values except in the case of La$_{6.67}$SrSi$_6$O$_{26}$ where total values are given).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 500 °C/S cm$^2$</th>
<th>Activation Energy /eV</th>
<th>Conductivity at 800 °C/S cm$^2$</th>
<th>Activation Energy /eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{9.33}$Si$<em>6$O$</em>{26}$</td>
<td>1.09 x 10$^{-4}$</td>
<td>0.74</td>
<td>2.02 x 10$^{-3}$</td>
<td>0.74</td>
</tr>
<tr>
<td>La$_{9.67}$Si$<em>6$O$</em>{26.5}$</td>
<td>1.28 x 10$^{-3}$</td>
<td>0.62</td>
<td>0.01</td>
<td>0.62</td>
</tr>
<tr>
<td>La$_{8.67}$MgSi$<em>6$O$</em>{26}$</td>
<td>3.64 x 10$^{-6}$</td>
<td>1.13</td>
<td>2.97 x 10$^{-4}$</td>
<td>1.13</td>
</tr>
<tr>
<td>La$_{8}$Mg$_2$Si$<em>6$O$</em>{26}$</td>
<td>8.90 x 10$^{-7}$</td>
<td>1.29</td>
<td>1.47 x 10$^{-4}$</td>
<td>1.29</td>
</tr>
<tr>
<td>La$_{9}$MgSi$<em>6$O$</em>{26.5}$</td>
<td>1.27 x 10$^{-5}$</td>
<td>1.07</td>
<td>8.12 x 10$^{-4}$</td>
<td>1.07</td>
</tr>
<tr>
<td>La$<em>{7.5}$Ca$</em>{2.5}$Si$<em>6$O$</em>{28.75}$</td>
<td>*</td>
<td>*</td>
<td>1.85 x 10$^{-7}$</td>
<td>1.85</td>
</tr>
<tr>
<td>La$_{8.67}$CaSi$<em>6$O$</em>{26}$</td>
<td>3.57 x 10$^{-5}$</td>
<td>0.86</td>
<td>1.5 x 10$^{-3}$</td>
<td>0.86</td>
</tr>
<tr>
<td>La$_{8}$Ca$_2$Si$<em>6$O$</em>{26}$</td>
<td>*</td>
<td>*</td>
<td>9.9 x 10$^{-7}$</td>
<td>1.62</td>
</tr>
<tr>
<td>La$_{9}$CaSi$<em>6$O$</em>{26.5}$</td>
<td>1.60 x 10$^{-3}$</td>
<td>0.71</td>
<td>0.02</td>
<td>0.71</td>
</tr>
<tr>
<td>La$_{8.67}$SrSi$<em>6$O$</em>{26}$</td>
<td>1.00 x 10$^{-4}$</td>
<td>0.73</td>
<td>1.54 x 10$^{-3}$</td>
<td>0.73</td>
</tr>
<tr>
<td>La$_{8}$SrSi$<em>6$O$</em>{26}$</td>
<td>*</td>
<td>*</td>
<td>5.64 x 10$^{-7}$</td>
<td>1.14</td>
</tr>
<tr>
<td>La$_{9}$SrSi$<em>6$O$</em>{26.5}$</td>
<td>1.19 x 10$^{-3}$</td>
<td>0.56</td>
<td>0.01</td>
<td>0.56</td>
</tr>
<tr>
<td>La$<em>{7.5}$Ba$</em>{2.5}$Si$<em>6$O$</em>{28.75}$</td>
<td>*</td>
<td>*</td>
<td>1.99 x 10$^{-7}$</td>
<td>1.89</td>
</tr>
<tr>
<td>La$_{8.67}$BaSi$<em>6$O$</em>{26}$</td>
<td>1.84 x 10$^{-4}$</td>
<td>0.63</td>
<td>1.68 x 10$^{-3}$</td>
<td>0.67</td>
</tr>
<tr>
<td>La$_{8}$Ba$_2$Si$<em>6$O$</em>{26}$</td>
<td>*</td>
<td>*</td>
<td>5.43 x 10$^{-7}$</td>
<td>1.21</td>
</tr>
<tr>
<td>La$_{9}$BaSi$<em>6$O$</em>{26.5}$</td>
<td>5.92 x 10$^{-3}$</td>
<td>0.59</td>
<td>0.05</td>
<td>0.59</td>
</tr>
</tbody>
</table>

* Conductivity too low to be measured

It can be seen for the calcium, strontium and barium doped systems that there is a distinct correlation between conductivity and stoichiometry. Conductivity values can be seen to decrease in the following order: Systems containing excess oxygen, i.e. La$_{9}$MSi$_6$O$_{26.5}$, > systems containing cation vacancies, i.e. La$_{8.67}$MSi$_6$O$_{26}$, >> fully stoichiometric systems, i.e. La$_{9}$M$_2$Si$_6$O$_{26}$, > systems containing oxygen vacancies, i.e. La$_{7.5}$M$_2$Si$_6$O$_{28.75}$ (* It should be noted from the previous discussion on cell parameters that it is thought that the solubility limit may have been exceeded in the case of these samples). Conversely, activation energy can be seen to increase in this...
order, consistent with the reduction in conductivity. These trends can be seen clearly in table 5.4, where conductivity data (800 °C) has been rearranged accordingly.

**Table 5.4. Conductivity data for (La/M)_{10-x}Si_6O_{26+y} (M = Ca, Sr and Ba), to show the effect of cation and oxygen non-stoichiometry on the conductivity of these systems at 800 °C** (Bulk values are quoted except in the case of La_{8.67}SrSi_6O_{26} where total values are quoted).

<table>
<thead>
<tr>
<th></th>
<th>Ba</th>
<th>Sr</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma / S \text{ cm}^{-1}$</td>
<td>$E_a / eV$</td>
<td>$\sigma / S \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>La_{7.5}M_{2.5}Si_{6}O_{25.75}</td>
<td>1.99 x 10^{-7}</td>
<td>1.89</td>
<td>1.85 x 10^{-7}</td>
</tr>
<tr>
<td>La_{8}M_{2}Si_{6}O_{26}</td>
<td>5.43 x 10^{-7}</td>
<td>1.21</td>
<td>5.64 x 10^{-7}</td>
</tr>
<tr>
<td>La_{8.67}MSi_{6}O_{26}</td>
<td>1.68 x 10^{-3}</td>
<td>0.67</td>
<td>1.54 x 10^{-3}</td>
</tr>
<tr>
<td>La_{9}MSi_{6}O_{26.5}</td>
<td>0.05</td>
<td>0.59</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Systems that contain cation vacancies are good oxide ion conductors with relatively low activation energies. However, the highest conductivities are observed in systems that contain excess oxygen. La_{9}BaSi_{6}O_{26.5} shows the highest conductivity out of all the systems tested, 0.05 S cm$^{-1}$ at 800 °C, and the sample also has a low activation energy, 0.59 eV. This might be related to unit cell size, owing to the larger size of Ba$^{2+}$ compared to the other M$^{2+}$ dopant ions. Indeed, related studies of Ln_{9.33}Si_{6}O_{26} (Ln = rare earth) show that oxide ion conductivity decreases, and activation energy increases, with reduction in the size of the rare earth.$^{1}$

The effect of a reduction in unit cell size on conductivity is apparent between undoped cation deficient and oxygen rich systems, and their related magnesium doped systems at 800 °C. In the case of cation deficient systems the conductivity for La_{9.33}Si_{6}O_{26} is 2.02 x 10^{-3} S cm$^{-1}$. This value is approximately an order of magnitude higher than for La_{8.67}MgSi_{6}O_{26} which showed a conductivity of 2.97 x 10^{-4} S cm$^{-1}$.

The data also shows that stoichiometric systems are poor oxide ion conductors with high activation energies, and oxygen deficient systems are worse still, and tend to have very high activation energies. La_{7.5}Ca_{2.5}Si_{6}O_{25.75} displays very poor oxide ion conductivity, 1.85 x 10^{-7} S cm$^{-1}$, although it should be noted that the solubility limit
might have been exceeded in this case. The conductivity recorded for this system is almost an order of magnitude lower than the conductivity recorded for La₈Ca₃Si₆O₂₆, and the activation energy was also very high, 1.85 eV. Indeed, it was not possible to determine conductivity data for any of the La₈M₂Si₆O₂₆ or La₇.₅M₂.₅Si₆O₂₅.₇₅ (M = Ca, Sr, and Ba) samples at 500 °C, because the conductivity of these systems was so poor at low temperatures.

In all cases conductivities increase significantly as a function of temperature. Interestingly however, the conductivities for La₈.₆₇MgSi₆O₂₆, La₉MgSi₆O₂₆.₅ and La₈Mg₂Si₆O₂₆ appear to converge at high temperature, their values being within an order of magnitude of each other at 800 °C, ≈ 10⁻⁴ S cm⁻¹. This convergence is apparent in figure 5.6. It is noteworthy that the conductivity for the nominally stoichiometric system, La₈Mg₂Si₆O₂₆, is several orders of magnitudes higher than for its calcium or strontium doped analogues (Table 5.3). The high conductivity observed for La₈Mg₂Si₆O₂₆ further suggests that this sample was not prepared as single phase, as suggested previously from the cell parameter data.

![Figure 5.6. Conductivity data for (a) La₉.₃₃Si₆O₂₆, (b) La₈.₆₇MgSi₆O₂₆, (c) La₉MgSi₆O₂₆.₅ and (d) La₈Mg₂Si₆O₂₆.](image)
Figure 5.7. Conductivity data for (a) $\text{La}_{9.33}\text{Si}_8\text{O}_{26}$, (b) $\text{La}_{8.67}\text{CaSi}_6\text{O}_{26}$, (c) $\text{La}_9\text{CaSi}_6\text{O}_{26.5}$, (d) $\text{La}_9\text{Ca}_2\text{Si}_6\text{O}_{26}$ and (e) $\text{La}_{7.5}\text{Ca}_{2.5}\text{Si}_6\text{O}_{25.75}$.

Figure 5.8. Conductivity data for (a) $\text{La}_{9.33}\text{Si}_8\text{O}_{26}$, (b) $\text{La}_{8.67}\text{SrSi}_6\text{O}_{26}$, (c) $\text{La}_9\text{SrSi}_6\text{O}_{26.5}$ and (d) $\text{La}_8\text{Sr}_2\text{Si}_6\text{O}_{26}$. 

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Figure 5.9. Conductivity data for (a) La$_{0.33}$Si$_6$O$_{26}$, (b) La$_{0.67}$BaSi$_6$O$_{26}$, (c) La$_9$BaSi$_6$O$_{26.5}$, (d) La$_{3}$Ba$_2$Si$_6$O$_{26}$ and (e) La$_{7.5}$Ba$_{2.5}$Si$_6$O$_{25.75}$.

5.1.4 Conclusions

The initial work on sample preparation revealed that it is possible to prepare a range of alkaline earth doped hexagonal apatite phases (La/M)$_{10-x}$Si$_6$O$_{26+y}$ (M = Ca, Sr, or Ba) by synthesis at 1350 °C.

The results of this study add weight to the importance of non-stoichiometry, in the form of cation vacancies or excess oxygen, in lanthanum silicate based apatite systems. These results also show that systems containing oxygen excess offer the highest conductivities. Unit cell size may also be an important factor for oxide ion conduction, with the barium doped sample that contains oxygen excess, La$_9$BaSi$_6$O$_{26.5}$, showing higher conductivity than the magnesium, calcium and strontium doped analogues. Indeed the sample La$_9$BaSi$_6$O$_{26.5}$ shows the highest conductivity recorded in this work, with a value of $6 \times 10^{-3}$ S cm$^{-1}$ at 500 °C, which is significantly higher than that of YSZ at this temperature, $1 \times 10^{-3}$ S cm$^{-1}$. The results therefore show that this sample represents a highly promising candidate...
material for use as an electrolyte in intermediate temperature SOFCs (500 °C – 700 °C), as well as other technological applications.

As shown in the previous chapter, fully stoichiometric systems and those containing oxygen vacancies are very poor oxide ion conductors, with the latter systems showing the lowest conductivities of all. These particular systems also have high activation energies for oxide ion conduction. The data therefore supports the previous suggestion that interstitial oxide ion defects, rather than oxygen vacancies, are the key to high oxide ion conduction in apatite phases.
5.2 References

Chapter 6.0: The Synthesis and Conductivities of Gallium-Doped Apatite-Type Phases \( \text{La}_{9.33+x}\text{Si}_{6-y}\text{Ga}_y\text{O}_{26+z} \) (0 \( \leq y \leq 2 \)) and Related Systems

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Chapter 6.0: The Synthesis and Conductivities of Gallium-Doped Apatite-Type Phases La$_{9.33+x}$Si$_{6-y}$Ga$_{y}$O$_{26+z}$ ($0 \leq y \leq 2$) and Related Systems

6.1 Introduction

The importance of cation and oxygen non-stoichiometry has been discussed previously in chapters 3 to 5. The importance of the former has also been supported by subsequent studies on the La$_{9.33+x}$Si$_{6-x}$Al$_x$O$_{26}$ system by Abram et al.$^1$ Our own unpublished studies on a similar range of aluminium-doped samples resulted in generally impure samples due to the lower solubility of aluminium at synthesis temperatures below 1500 °C (the limit of achievable temperature for our furnace complement at the time of this work). Abram et al. showed that higher synthesis temperatures were required to achieve pure samples and the conductivity was shown to reach a maximum for $x = 1.5$. We have also tried to dope indium onto the silicon site, although this also led to the formation of significant impurity phases. In contrast, we have established that it is possible to readily dope boron or gallium onto the silicon site. Indeed, it is possible to prepare the full range of samples La$_{9.33+x}$Si$_{6-y}$M$_y$O$_{26+z}$ ($M = B$, Ga) ($0 \leq y \leq 2$), without the formation of significant impurity phases, because the solubility limits of boron and gallium appear to be greater than the solubility limit of aluminium at synthesis temperatures below 1500 °C. The results for the boron doped samples will be discussed in the next chapter; those for the gallium doped samples are discussed in this chapter.

We have prepared a range of new phases based on doping La$_{9.33}$Si$_6$O$_{26}$ with Ga on the Si site, according to the formula La$_{9.33+x}$Si$_{6-x}$Ga$_x$O$_{26}$ ($0 \leq x \leq 2$), in order to observe the effects of varying the cation stoichiometry on the conductivity and activation energy. The doping scheme maintains the oxygen stoichiometry but leads to a reduction in the level of cation vacancies. We have also prepared and tested a range of samples, in which the oxygen content has been increased above stoichiometric O$_{26}$, La$_{9.33+x}$Si$_{6-y}$Ga$_y$O$_{26+z}$ ($0 \leq y \leq 2$ and $z = 0$ to 0.5) to examine the effect of oxygen content on conductivity.
Finally, for comparison reasons a related system has been prepared and tested, La\(_{1-x}\)Sr\(_{2+x}\)GaO\(_5\cdot3x/2\), in which tetrahedral Ga is also present. The structure of LaSr\(_2\)GaO\(_5\) has been determined by Gesing et al.\(^2\) and shown to consist of (La/Sr)\(_2\)O layers separated by isolated GaO\(_4\) tetrahedra, which are themselves coordinated to La/Sr atoms.

### 6.1.1 Synthesis and Experimental

High purity La\(_2\)O\(_3\), Ga\(_2\)O\(_3\) and SiO\(_2\) were used to prepare all samples. The dried starting materials were first ground together in the appropriate ratios. Synthesis details are given below in table 6.1. Samples were reground prior to subsequent heat treatments. Phase purity was examined using powder X-ray diffraction, which indicated the formation of single phase samples in each case.

**Table 6.1. Synthesis conditions for La\(_{9.33+x}\)Si\(_{6-y}\)Ga\(_{y}\)O\(_{26+z}\) (0 ≤ y ≤ 2).**

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>1st Heat Treatment / °C (Duration / hours)</th>
<th>2nd Heat Treatment / °C (Duration / hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(_{9.33})Si(<em>6)O(</em>{26})</td>
<td>1300(16)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>La(_{9.5})Si(_5)Ga(<em>0.5)O(</em>{26})</td>
<td>1350(14)</td>
<td>1350(14)</td>
</tr>
<tr>
<td>La(<em>{9.5})Si(<em>5)Ga(</em>{0.25})O(</em>{26})</td>
<td>1350(14)</td>
<td>1350(14)</td>
</tr>
<tr>
<td>La(_{9.67})Si(_3)Ga(<em>1)O(</em>{26})</td>
<td>1300(16)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>La(_{9.75})Si(_4)Ga(<em>1)O(</em>{26})</td>
<td>1350(14)</td>
<td>1350(14)</td>
</tr>
<tr>
<td>La(_{9.83})Si(_4)Ga(<em>1)O(</em>{26})</td>
<td>1350(14)</td>
<td>1350(14)</td>
</tr>
<tr>
<td>La(_{9.92})Si(_4)Ga(<em>1)O(</em>{26})</td>
<td>1350(14)</td>
<td>1350(14)</td>
</tr>
<tr>
<td>La(_{10})Si(_4)Ga(<em>2)O(</em>{26})</td>
<td>1300(16)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>La(_{10})Si(_4)Ga(<em>1.5)O(</em>{26})</td>
<td>1300(14)</td>
<td>1350(14)</td>
</tr>
<tr>
<td>La(_{10})Si(_3)Ga(<em>2)O(</em>{26})</td>
<td>1350(14)</td>
<td>1350(14)</td>
</tr>
</tbody>
</table>

Conductivities were determined using a.c. impedance measurements. Pellets were prepared for conductivity testing, as described in chapter 2, and then sintered at the appropriate temperature (1500 °C to 1700 °C). The phase purity of each sample pellet used for conductivity testing was also examined using X-ray diffraction.
LaSr$_2$GaO$_5$ was prepared by heating a stoichiometric mixture of La$_2$O$_3$, SrCO$_3$, and Ga$_2$O$_3$ to 1350 °C for 28 hours, with an intermediate regrind. Pellets for conductivity measurements were sintered at the same temperature for 12 hours. Samples with varying La/Sr ratio, La$_{1-x}$Sr$_{2+x}$GaO$_{5-x/2}$ were prepared similarly.

### 6.1.2 Cell Parameters

Details of cell parameter data are given in table 6.2. A general increase in cell size is observed with an increase in gallium content as expected due to the larger size of Ga$^{3+}$ compared to Si$^{4+}$. The X-ray diffraction profiles for La$_{15}$Si$_4$Ga$_2$O$_{26}$ is shown in figure 6.1.

**Table 6.2. Cell parameter data for La$_{9.33+x}$Si$_{6-y}$Ga$_{y}$O$_{26+z} (0 \leq y \leq 2)$.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Unit Cell Parameters (Hexagonal Cell) /Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a = b$</td>
</tr>
<tr>
<td>La$_{9.33}$Si$<em>6$O$</em>{26}$</td>
<td>9.721(3)</td>
</tr>
<tr>
<td>La$<em>{9.5}$Si$</em>{5.5}$Ga$<em>{0.5}$O$</em>{26}$</td>
<td>9.735(2)</td>
</tr>
<tr>
<td>La$<em>{9.58}$Si$</em>{5.25}$Ga$<em>{0.75}$O$</em>{26}$</td>
<td>9.744(4)</td>
</tr>
<tr>
<td>La$<em>{9.67}$Si$<em>5$Ga$</em>{0.25}$O$</em>{26}$</td>
<td>9.745(3)</td>
</tr>
<tr>
<td>La$<em>{9.75}$Si$</em>{4.75}$Ga$<em>{1.25}$O$</em>{26}$</td>
<td>9.749(6)</td>
</tr>
<tr>
<td>La$<em>{9.83}$Si$</em>{4.5}$Ga$<em>{1.5}$O$</em>{26}$</td>
<td>9.759(4)</td>
</tr>
<tr>
<td>La$<em>{9.92}$Si$</em>{4.25}$Ga$<em>{1.75}$O$</em>{26}$</td>
<td>9.772(3)</td>
</tr>
<tr>
<td>La$_{10}$Si$_4$Ga$<em>2$O$</em>{26}$</td>
<td>9.781(3)</td>
</tr>
<tr>
<td>La$<em>{10}$Si$<em>4$Ga$</em>{1.5}$O$</em>{26,25}$</td>
<td>9.766(4)</td>
</tr>
<tr>
<td>La$_{10}$Si$<em>5$Ga$</em>{0.26,25}$</td>
<td>9.758(3)</td>
</tr>
</tbody>
</table>

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6.1.3 Conductivity Measurements

Details of conductivity data for three samples prepared and sintered at 1500 °C are given in table 6.3. Difficulty was encountered in resolving bulk and grain boundary contributions for these samples, as previously observed in related apatite systems, and so the values reported represent total conductivities. The total conductivities are only moderate even for the best samples. This is due to the high porosity of the pellets owing to the low sintering temperature employed, meaning that the conductivity is dominated by the grain boundary component.
Table 6.3. Conductivity data for La$_{9.33+x}$Si$_{6-y}$Ga$_y$O$_{26}$ (Samples sintered at 1500 °C). Conductivity data given are total values (Bulk + grain boundary contributions).

| Sample (Nominal Composition) | Conductivity at 800 °C / S cm$^{-1}$ | Activation energy / eV  
($\approx$300 - $\approx$800 °C)  
(* Sample shows change of $E_a \approx$ 550 °C) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{9.33}$Si$<em>6$O$</em>{26}$</td>
<td>$6.63 \times 10^{-4}$</td>
<td>0.81</td>
</tr>
<tr>
<td>La$<em>{9.67}$Si$<em>5$Ga$</em>{0.33}$O$</em>{26}$</td>
<td>$5.21 \times 10^{-3}$</td>
<td>0.79/0.51*</td>
</tr>
<tr>
<td>La$_{10}$Si$_4$Ga$<em>2$O$</em>{26}$</td>
<td>$3.33 \times 10^{-6}$</td>
<td>0.85</td>
</tr>
</tbody>
</table>

In order to achieve dense pellets (> 90 % of theoretical density) higher sintering temperatures (1600 °C - 1700 °C) were employed. In these cases, it was now possible to resolve bulk and grain boundary contributions for temperatures < 600 °C, and so details of bulk conductivity data for all samples sintered at 1600 °C or 1700 °C are given in table 6.4. An a.c. impedance plot for La$_{9.67}$Si$_5$Ga$_{0.33}$O$_{26}$, recorded at 400 °C, is shown in figure 6.2. The plots of log ($\sigma T$) versus 1000 / $T$ for La$_{9.33}$Si$_6$O$_{26}$, La$_{10}$Si$_4$Ga$_2$O$_{26}$ and La$_{9.83}$Si$_4.5$Ga$_{1.5}$O$_{26}$, are given in figure 6.3.

Figure 6.2. A.C. impedance plot for La$_{9.67}$Si$_5$Ga$_{0.33}$O$_{26}$ (recorded at 400 °C).
The conductivities recorded for the pellets sintered at 1600 °C or 1700 °C are significantly higher than those recorded for the pellets sintered at 1500 °C due to a reduction in grain boundary contribution. This allowed the possibility for the resolution of bulk and grain boundary components from the a.c. impedance data. However, it was only possible to observe the bulk semicircle at low to intermediate temperatures (< 600 °C) for the higher conducting samples (e.g. La$_{0.83}$Si$_{4.5}$Ga$_{1.5}$O$_{26}$) and so the conductivity data at 500 °C is reported in table 6.4. At higher temperatures only a partial grain boundary semicircle or electrode response was observed for these samples, making measurement of the bulk contribution inaccurate.

Table 6.4. Conductivity data (bulk values) for La$_{0.33+x}$Si$_{6-y}$Ga$_{y}$O$_{26+z}$ (0 ≤ y ≤ 2) (Samples sintered at 1700 °C, except for those marked *, which were sintered at 1600 °C).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 500 °C / S cm$^{-1}$ (Unless Stated Otherwise)</th>
<th>Activation energy (∆$300$ - ∆$500$ °C) / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{0.33}$Si$<em>4$O$</em>{26}$</td>
<td>1.13 × 10$^{-4}$</td>
<td>0.78</td>
</tr>
<tr>
<td>La$<em>{0.5}$Si$</em>{4.5}$Ga$<em>{0.5}$O$</em>{26}$</td>
<td>4.56 × 10$^{-4}$</td>
<td>0.67</td>
</tr>
<tr>
<td>La$<em>{0.5}$Si$</em>{5.25}$Ga$<em>{0.75}$O$</em>{26}$</td>
<td>7.64 × 10$^{-4}$</td>
<td>0.62</td>
</tr>
<tr>
<td>*La$<em>{0.5}$Si$</em>{5}$GaO$_{26}$</td>
<td>1.04 × 10$^{-3}$</td>
<td>0.70</td>
</tr>
<tr>
<td>La$<em>{0.75}$Si$</em>{4.75}$Ga$<em>{1.25}$O$</em>{26}$</td>
<td>1.06 × 10$^{-3}$</td>
<td>0.64</td>
</tr>
<tr>
<td>La$<em>{0.83}$Si$</em>{4.5}$Ga$<em>{1.5}$O$</em>{26}$</td>
<td>1.32 × 10$^{-3}$</td>
<td>0.73</td>
</tr>
<tr>
<td>La$<em>{0.9}$Si$</em>{4.25}$Ga$<em>{1.75}$O$</em>{26}$</td>
<td>5.15 × 10$^{-5}$</td>
<td>0.76</td>
</tr>
<tr>
<td>La$<em>{1.1}$Si$<em>4$Ga$</em>{2}$O$</em>{26}$</td>
<td>6.81 × 10$^{-5}$ (800 °C)</td>
<td>0.72</td>
</tr>
<tr>
<td>*La$<em>{1.1}$Si$</em>{4.5}$Ga$<em>{1.5}$O$</em>{26.25}$</td>
<td>2.05 × 10$^{-3}$</td>
<td>0.81</td>
</tr>
<tr>
<td>La$_{1.1}$Si$<em>3$Ga$</em>{26.5}$</td>
<td>2.39 × 10$^{-3}$</td>
<td>0.70</td>
</tr>
</tbody>
</table>
Figure 6.3. Conductivity data for (a) La$_{9.33}$Si$_6$O$_{26}$, (b) La$_{10}$Si$_4$Ga$_2$O$_{26}$ and (c) La$_{9.83}$Si$_{4.5}$Ga$_{1.5}$O$_{26}$.

The results add support to the notion that the presence of cation vacancies enhances conductivity. The conductivity for La$_{9.83}$Si$_{4.5}$Ga$_{1.5}$O$_{26}$ recorded at 500 °C is nearly 2 orders of magnitude greater than the conductivity for La$_{10}$Si$_4$Ga$_2$O$_{26}$ recorded at 800 °C (1.32 x 10$^{-3}$ S cm$^{-1}$ compared to 6.81 x 10$^{-5}$ S cm$^{-1}$). In addition, the level of cation vacancies also appears to be an important factor. Indeed, there appears to be an optimum level of cation vacancies required for maximum conductivity. Figure 6.4 shows a plot of conductivity data (recorded at 500 °C) as a function of lanthanum content for a range of samples that are nominally stoichiometric in oxygen, but vary in cation vacancy content, La$_{9.33+x/3}$Si$_{6-x}$Ga$_x$O$_{26}$ (0 ≤ x ≤ 2).
Figure 6.4. Plot of log conductivity (recorded at 500 °C) as a function of Lanthanum content for the range of samples La\textsubscript{9.33+x/3}Si\textsubscript{6-x}Ga\textsubscript{x}O\textsubscript{26} (0 ≤ x ≤ 2).

The conductivity appears to initially increase with a decrease in the number of cation vacancies, i.e. from La\textsubscript{9.33}Si\textsubscript{6}O\textsubscript{26} towards La\textsubscript{9.83}Si\textsubscript{4.5}Ga\textsubscript{1.5}O\textsubscript{2}, and then decreases significantly on moving towards full stoichiometry, i.e. La\textsubscript{9.92}Si\textsubscript{4.25}Ga\textsubscript{1.75}O\textsubscript{26}. The conductivity data for the fully stoichiometric end member La\textsubscript{10}Si\textsubscript{4}Ga\textsubscript{2}O\textsubscript{26} is not included because it was not possible to measure the conductivity of this system at 500 °C, due to it being too low. These results are similar to the results obtained by Abram et al. for Al doped systems.\textsuperscript{1} These observations indicate that an optimum value in cation vacancy content exists, corresponding to the composition La\textsubscript{9.83}Si\textsubscript{4.5}Ga\textsubscript{1.5}O\textsubscript{26}.

The results for samples containing oxygen excess also add support to the theory that the inclusion of excess interstitial oxygen enhances conductivity because the conductivity increases again with oxygen content, i.e. in moving from La\textsubscript{10}Si\textsubscript{4}Ga\textsubscript{2}O\textsubscript{26} towards La\textsubscript{10}Si\textsubscript{5}GaO\textsubscript{26.5}. Thus, even samples, which are cation stoichiometric, show enhanced conductivity providing the oxygen content is > 26. Indeed, all of the samples with nonstoichiometry are good conductors, with La\textsubscript{10}Si\textsubscript{5}GaO\textsubscript{26.5} showing the highest conductivity (2.39 × 10\textsuperscript{-3} S cm\textsuperscript{-1} at 500 °C). The conductivity for this phase is higher than YSZ at this temperature (1 × 10\textsuperscript{-3} S cm\textsuperscript{-1} at 500 °C). A range of further samples with varying oxygen content has been prepared and will be
characterised in the near future, in order to try and locate an exact maximum for the oxide ion conductivity in these gallium doped systems.

It is also interesting to note that the activation energies for all the samples sintered at 1700 °C are similar in value, $\approx 0.70$ eV, including the nominally cation and oxygen stoichiometric compound La$_{10}$Si$_4$Ga$_2$O$_{26}$. The low conductivity combined with low activation energy for this stoichiometric phase suggests that it does contain some readily mobile oxide ion defects, but they are too few in number and therefore not readily available to facilitate conductivity. Significantly the observed activation energies are lower than for YSZ in this temperature region ($\approx 0.70$ eV compared to $\approx 1$ eV).

Another interesting observation is that a comparison of this data with that of chapter 5 shows that the conductivity is higher for cation deficient systems where gallium is located on the silicon site rather than for related systems where the dopant ion (in this case a alkaline earth cation) is on the lanthanum site, i.e. $\sigma$ La$_{9.67}$Si$_5$MO$_{26} > \sigma$ La$_{8.67}$MSi$_6$O$_{26}$. For example the conductivity for La$_{9.67}$Si$_5$Ga$_{26}$ is significantly greater than the conductivity for La$_{8.67}$SrSi$_6$O$_{26}$ at 500 °C, $1.04 \times 10^{-3}$ S cm$^{-1}$ for the former system compared to $1.00 \times 10^{-4}$ S cm$^{-1}$ for the latter. Also of relevance to this discussion, recent work by Najib et al. has indicated that doping phosphorus onto the silicon site lowers the oxide ion conductivity. This suggests that the conductivity is enhanced by the presence of lower valence ions on the tetrahedral sites, supporting the suggestion that the tetrahedra may play a significant part in the conduction process, as predicted by the modelling studies.

Conductivity data were also recorded for the related phase LaSr$_2$GaO$_5$, which contains tetrahedral gallium. The conductivity of this phase was found to be low with a high activation energy ($7.8 \times 10^{-6}$ S cm$^{-1}$ at 800 °C, $E_a = 1.28$ eV, figure 6.5). Attempts were made to dope this material to introduce either oxygen vacancies or oxygen excess. The latter was unsuccessful with significant impurities being observed, but samples containing oxygen vacancies, La$_{1-x}$Sr$_{2+x}$GaO$_{5-x/2}$ ($x \leq 0.2$) were successfully prepared. As expected the conductivity was significantly increased,
although the values observed are still rather low and the activation energy high (3.4 \times 10^{-4} \text{ S cm}^{-1} \text{ at } 800 \degree \text{C}, E_a = 1.23 \text{ eV}, \text{ for } x = 0.1, \text{ figure 6.5}). More recent work suggests that in this particular system, the ionic conductivity is protonic in nature.\footnote{7}

![Figure 6.5. Conductivity data for (a) LaSr$_2$GaO$_5$ and (b) La$_{0.5}$Sr$_{2.1}$GaO$_{4.05}$. Data is shown for the total conductivity (bulk + grain boundary).}

\section*{6.1.4 Conclusions}

The initial work on sample preparation revealed that it is possible to prepare single phase hexagonal apatite phases in the range La$_{9.33+x}$Si$_{6-y}$Ga$_y$O$_{26}$ ($0 \leq y \leq 2$). These samples were prepared at 1350 \degree \text{C}, indicating a higher solubility of gallium in the La$_{9.33}$Si$_6$O$_{26}$ system compared to aluminium at this temperature.\footnote{1}

Compositions with cation vacancies exhibit high oxide ion conductivity, in contrast to the fully stoichiometric system, La$_{10}$Si$_4$Ga$_2$O$_{26}$, which shows very poor oxide ion conduction. An optimum level of cation vacancies for maximum conductivity was observed for the sample La$_{9.85}$Si$_{4.5}$Ga$_{1.5}$O$_{26}$. Phases without cation vacancies but containing nominal oxygen excess also show high oxide ion conductivity, with La$_{10}$Si$_5$GaO$_{26.5}$ exhibiting the highest conductivity recorded for these gallium doped systems.
It is presumed that, in both the highly conducting cation deficient and oxide ion excess samples, there are interstitial oxide ion defects, which mediate the oxide ion conduction, as observed previously for related systems.\(^4\) This will be confirmed by refinement of neutron diffraction data collected for these samples.

These results reinforce the importance of the presence of cation vacancies, and/or excess oxygen, for fast oxide ion conduction in these apatite-type phases, as discussed previously in chapter 3.

These studies also reveal that the conductivity is higher for cation deficient systems where the dopant ion with a lower valence is located on the silicon site rather than for related systems where the dopant ion is on the lanthanum site, i.e. \(\sigma_{\text{La}_9.67\text{Si}_5\text{MO}_{26}} > \sigma_{\text{La}_8.67\text{MSi}_6\text{O}_{26}}\).

Finally, the conductivity for a related system, \(\text{La}_{1-x}\text{Sr}_x\text{GaO}_{5-3x/2}\), is comparatively low \((3.4 \times 10^{-4} \text{ S cm}^{-1} \text{ at } 800 \text{ °C for } x = 0.1)\) compared to the apatite systems.
6.2 References

5. A. Najib, P.R. Slater; (manuscript in preparation).
7. S. Li, F. Schönberger, P.R. Slater; Chem. Comm., (in press).
Chapter 7.0: The Synthesis and Conductivities of Boron-Doped Apatite-Type Phases La$_{9.33+x}$Si$_{6-y}$ByO$_{26+z}$ ($0 \leq y \leq 2$)

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Chapter 7.0: The Synthesis and Conductivities of Boron-Doped Apatite-Type Phases $\text{La}_{9.33+x}\text{Si}_{6-y}\text{B}_y\text{O}_{26+z}$ ($0 \leq y \leq 2$)

7.1 Introduction

In this chapter we continue our discussion into $\text{La}_{9.33+x}\text{Si}_{6-y}\text{M}_y\text{O}_{26}$ ($0 \leq y \leq 2$) type phases. We have prepared a range of new phases based on doping $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ with boron on the silicon site, according to the formula $\text{La}_{9.33+x/3}\text{Si}_{6-x}\text{B}_x\text{O}_{26}$ ($0 \leq x \leq 2$), in order to observe the effects on conductivity and activation energy. We have collected conductivity data for samples sintered between 1400 °C and 1600 °C. The nature of this study is analogous to the one discussed in the previous chapter, in which gallium was doped onto the silicon site, i.e. maintaining the oxygen stoichiometry, while reducing the level of cation vacancies. A range of samples has also been prepared and tested, $\text{La}_{9.33+x}\text{Si}_{6-y}\text{B}_y\text{O}_{26+z}$ ($0 \leq y \leq 2$ and $z = 0$ to 0.5), in which the oxygen content has been increased above the stoichiometric value, to observe the effect on conductivity and activation energy.

7.1.1 Synthesis and Experimental

High purity $\text{La}_2\text{O}_3$, $\text{H}_3\text{BO}_3$ and $\text{SiO}_2$ were used to prepare the boron doped samples. The mixed starting materials were heated for an initial period of 1 hour at 300 °C, prior to subsequent heat treatments, in order to initiate early reaction of $\text{H}_3\text{BO}_3$ and so limit boron loss before subsequent heat treatments. The samples were then heated to 1100 °C for a further 23 hours, with an intermediate regrind after 11 hours. The samples were then reground and heated for a further 28 hours at 1350 °C, with an intermediate regrind after 14 hours. The Phase purity of each sample was checked after the initial synthesis using powder X-ray diffraction.

Conductivities were determined using a.c. impedance measurements. Pellets (1.6 cm diameter) of each sample were obtained, as described in chapter 2, and sintered at the
appropriate temperature (1400 °C to 1600 °C). The phase purity of each sample pellet used for conductivity testing was also examined using X-ray diffraction.

7.1.2 Cell Parameters

Details of cell parameter data for the single phase samples are given in table 7.1. The solubility of boron in \( \text{La}_{9.33}\text{Si}_6\text{O}_{26} \) at 1350 °C is greater than the solubility of aluminium, as was the case for gallium doping into the same system. The X-ray diffraction profile for \( \text{La}_{10}\text{Si}_3\text{BO}_{26.5} \) is shown in figure 7.1.

A general decrease in cell ‘a’ and ‘b’ parameters is observed with an increase in boron content. The ‘c’ parameter, however, shows a general increase, although overall boron doping leads to a reduction in cell volume, as is expected due to the larger size of Si\(^{4+}\) compared to B\(^{3+}\).

Table 7.1. Cell parameter data for \( \text{La}_{9.33+x}\text{Si}_{6+y}\text{B}_{26+z} \), \((0 \leq y \leq 2)\).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Unit Cell Parameters / Å (Hexagonal Cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a = b)</td>
</tr>
<tr>
<td>(\text{La}_{9.33}\text{Si}<em>6\text{O}</em>{26})</td>
<td>9.721(3)</td>
</tr>
<tr>
<td>(\text{La}<em>{9.67}\text{Si}</em>{5.5}\text{B}<em>{0.5}\text{O}</em>{26})</td>
<td>9.690(5)</td>
</tr>
<tr>
<td>(\text{La}<em>{9.83}\text{Si}</em>{4.5}\text{B}<em>{1.5}\text{O}</em>{26})</td>
<td>9.591(2)</td>
</tr>
<tr>
<td>(\text{La}<em>{10}\text{Si}</em>{4}\text{B}<em>{2}\text{O}</em>{26})</td>
<td>9.552(4)</td>
</tr>
<tr>
<td>(\text{La}<em>{10}\text{Si}</em>{4.5}\text{B}<em>{1.5}\text{O}</em>{26.25})</td>
<td>9.581(5)</td>
</tr>
<tr>
<td>(\text{La}<em>{10}\text{Si}</em>{4}\text{BO}_{26.5})</td>
<td>9.622(4)</td>
</tr>
</tbody>
</table>
7.1.3 Conductivity Measurements

Dense sample pellets (> 80 % theoretical) were obtained by sintering in the temperature range 1400 °C - 1600 °C. However, resolution of bulk and grain boundary contributions was only possible for the impedance data collected at low temperatures. Details of bulk conductivity data for all samples, collected in the ≈ 300 °C to ≈ 500 °C temperature range and quoted at 500 °C, are given in table 7.2. Details of total conductivity data at 800 °C are quoted for selected samples in table 7.3, where determination of the total contribution was possible up to high temperatures. The plots of log (σ T) versus 1000 / T for La$_{9.33}$Si$_6$O$_{26}$, La$_{10}$Si$_4$B$_2$O$_{26}$, La$_{9.5}$Si$_{3.5}$B$_{0.5}$O$_{26}$ and La$_{10}$Si$_3$BO$_{26.5}$ are given in figure 7.2.
Table 7.2. Conductivity data for \( \text{La}_{9.33+x}\text{Si}_{6.3+y}\text{B}_{2.0+z} \) \( (0 \leq y \leq 2) \) at 500 °C. Conductivity data given are bulk values.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 500 °C / S cm(^{-1})</th>
<th>Activation Energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}<em>{9.33}\text{Si}</em>{6}\text{O}_{2.5} )</td>
<td>( 1.14 \times 10^{-4} )</td>
<td>0.79</td>
</tr>
<tr>
<td>( \text{La}<em>{9.33}\text{Si}</em>{5.5}\text{B}<em>{0.5}\text{O}</em>{2.5} )</td>
<td>( 4.13 \times 10^{-4} )</td>
<td>0.69</td>
</tr>
<tr>
<td>( \text{La}<em>{9.67}\text{Si}</em>{5}\text{BO}_{2.5} )</td>
<td>( 2.18 \times 10^{-4} )</td>
<td>0.81</td>
</tr>
<tr>
<td>( \text{La}<em>{9.33}\text{Si}</em>{4.5}\text{B}<em>{1.5}\text{O}</em>{2.5} )</td>
<td>( 2.54 \times 10^{-4} )</td>
<td>0.89</td>
</tr>
<tr>
<td>( \text{La}<em>{10}\text{Si}</em>{4}\text{B}<em>{2}\text{O}</em>{2.5} )</td>
<td>( 5.51 \times 10^{-7} )</td>
<td>0.98</td>
</tr>
<tr>
<td>( \text{La}<em>{10}\text{Si}</em>{4.5}\text{B}<em>{1.5}\text{O}</em>{2.5} )</td>
<td>( 1.74 \times 10^{-4} )</td>
<td>0.90</td>
</tr>
<tr>
<td>( \text{La}<em>{10}\text{Si}</em>{5}\text{BO}_{2.5} )</td>
<td>( 1.14 \times 10^{-3} )</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Figure 7.2. Conductivity data for (a) \( \text{La}_{9.33}\text{Si}_{6}\text{O}_{2.5} \), (b) \( \text{La}_{10}\text{Si}_{4}\text{B}_{2}\text{O}_{2.5} \), (c) \( \text{La}_{9.5}\text{Si}_{5.5}\text{B}_{0.5}\text{O}_{2.5} \) and (d) \( \text{La}_{10}\text{Si}_{5}\text{BO}_{2.5} \).
Table 7.3. Conductivity data for La$_{9.33+x}$Si$_6$B$_x$O$_{26+z}$. Conductivity data given are total values.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 800 °C / S cm$^{-1}$</th>
<th>Activation energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{9.33}$Si$<em>6$O$</em>{26}$</td>
<td>2.30 x 10$^{-3}$</td>
<td>0.79</td>
</tr>
<tr>
<td>La$<em>{9.5}$Si$<em>5$B$</em>{0.5}$O$</em>{26}$</td>
<td>6.64 x 10$^{-3}$</td>
<td>0.74</td>
</tr>
<tr>
<td>La$_{9.67}$Si$<em>5$BO$</em>{26}$</td>
<td>5.94 x 10$^{-3}$</td>
<td>0.97</td>
</tr>
<tr>
<td>La$_{10}$Si$_4$B$<em>2$O$</em>{26}$</td>
<td>3.40 x 10$^{-5}$</td>
<td>1.19</td>
</tr>
<tr>
<td>La$_{10}$Si$<em>5$BO$</em>{25.5}$</td>
<td>0.02</td>
<td>0.89</td>
</tr>
</tbody>
</table>

The results obtained for the boron doped systems add further support to the notion that all samples with either cation vacancies or excess oxygen are good conductors. All samples in the range La$_{9.33+x}$Si$_6$B$_x$O$_{26}$ (0 ≤ x ≤ 1.5) showed similar high values of conductivity at 500 °C. The conductivities of these samples are nearly 3 orders of magnitude greater than the conductivity for the fully stoichiometric system, La$_{10}$Si$_4$B$_2$O$_{26}$, at 500 °C. The activation energies are also significantly lower (table 7.2).

Samples with excess oxygen also showed high oxide ion conductivity. Indeed, La$_{10}$Si$_5$BO$_{26.5}$ shows significantly the highest conductivity out of all the boron doped samples tested. The conductivity for La$_{10}$Si$_5$BO$_{26.5}$ is nearly 4 orders of magnitude greater than for La$_{10}$Si$_4$B$_2$O$_{26}$ at 800 °C, 0.02 S cm$^{-1}$ compared to 3.40 x 10$^{-5}$ S cm$^{-1}$, with a lower activation energy.

These findings are in complete agreement with other systems studied. The conductivity for La$_{10}$Si$_5$BO$_{26.5}$ is similar in value to YSZ at 500 °C, ≈ 1 x 10$^{-3}$ S cm$^{-1}$, however, the activation energy for La$_{10}$Si$_5$BO$_{26.5}$ is lower (0.68 eV compared to 1 eV). Consequently La$_{10}$Si$_5$BO$_{26.5}$ is not as good an oxide ion conductor as YSZ at high temperatures.

The conductivities of the boron doped systems are slightly lower in comparison to their gallium doped analogues. Furthermore, in general their activation energies are higher. The conductivity for La$_{9.85}$Si$_4.5$Ga$_{1.5}$O$_{26}$ is nearly an order of magnitude
higher than the conductivity for La$_{9.83}$Si$_{4.5}$B$_{1.5}$O$_{26}$ when compared at 500 °C (1.32 x 10$^{-3}$ S cm$^{-1}$ compared to 2.54 x 10$^{-4}$ S cm$^{-1}$), and the activation energy is lower for the gallium doped system (0.70 eV compared to 0.81 eV). Similarly the conductivity for La$_{10}$Si$_{5}$GaO$_{26.5}$ is slightly higher than the conductivity for La$_{10}$Si$_{5}$B$_{2.5}$O$_{26.5}$ when compared at 500 °C (2.39 x 10$^{-3}$ S cm$^{-1}$ compared to 1.14 x 10$^{-3}$ S cm$^{-1}$), although in this case the activation energies are similar in value, ≈ 0.7 eV. This may be related to size effects, with boron doping leading to a reduction in cell volume and a consequent contraction of the conducting channels.

### 7.1.4 Conclusions

These studies have shown that it is possible to prepare single phase apatite materials in the range La$_{9.33+x}$Si$_{6-y}$B$_{0.5}$O$_{26+z}$ (0 ≤ y ≤ 2). These samples were prepared at 1350 °C, indicating a higher solubility of boron in the apatite structure, compared to aluminium at this temperature.

Compositions with nominal cation (La) vacancies, e.g. La$_{9.5}$Si$_{5.5}$B$_{0.5}$O$_{26}$, exhibit high oxide ion conductivity, in contrast to La$_{10}$Si$_{4}$B$_{2}$O$_{26}$ which is nominally stoichiometric in both cation and oxygen content, and shows poor oxide ion conduction. Phases without cation vacancies containing nominal oxygen excess, e.g. La$_{10}$Si$_{5}$BO$_{26.5}$, were also shown to exhibit high oxide ion conductivity. Indeed, the oxide ion conduction of these latter systems appears to be greater than that of systems that contain cation vacancies. These results reinforce the importance of the presence of cation vacancies and/or excess oxygen for fast oxide ion conduction in these apatite-type phases. It is presumed that in both the highly conducting cation deficient and oxide ion excess samples there are interstitial oxide ion defects, which mediate the oxide ion conduction, as reported previously for related systems. Structural studies are planned to confirm this.
7.2 References

Chapter 8.0: The Synthesis and Conductivities of the Apatite-Type Phases La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$, (0 $\leq$ x $\leq$ 6)

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Chapter 8.0: The Synthesis and Conductivities of the Apatite-Type Phases La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$, (0 $\leq x \leq 6$)

8.1 Introduction

Germanium loss and high activation energy for oxide ion conductivity represent the main problems associated with germanium based apatite systems, such as La$_{9.33}$Ge$_6$O$_{26}$, as discussed in chapter 4.0. With this in mind a range of novel mixed silicon/germanium containing apatite samples, La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$, (0 $\leq x \leq 6$), were prepared in order to observe how these factors vary with Si to Ge ratio, and to determine if there exists an optimum Si to Ge ratio for these systems, as regards conductivity.

8.1.1 Synthesis and Experimental

All samples were prepared using high purity La$_2$O$_3$, SiO$_2$ and GeO$_2$. The dried starting materials were ground together in stoichiometric proportions. Details of synthesis conditions are shown in table 8.1. Phase purity was checked by X-ray powder diffraction (Siefert 3003TT X-ray diffractometer). The unit cell parameters were also determined from X-ray diffraction data.

Table 8.1. Synthesis conditions for La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ (0 $\leq x \leq 6$).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>$1^{st}$ Heat Treatment / °C (Duration / Hours)</th>
<th>$2^{nd}$ Heat Treatment / °C (Duration / Hours)</th>
<th>$3^{rd}$ Heat Treatment / °C (Duration / Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{9.33}$Si$<em>6$O$</em>{26}$</td>
<td>1250(16)</td>
<td>1350(16)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>La$<em>{9.33}$Si$</em>{6-x}$Ge$<em>x$O$</em>{26}$ (x = 1 - 5)</td>
<td>1100(64)</td>
<td>1250(20)</td>
<td>1250(16)</td>
</tr>
<tr>
<td>La$_{9.33}$Ge$<em>6$O$</em>{26}$</td>
<td>1150(14)</td>
<td>1150(14)</td>
<td></td>
</tr>
</tbody>
</table>
Conductivity values were determined from a.c. impedance measurements. Pellets of each sample were prepared (1.6 cm in diameter), as described in chapter 2, and sintered for 2 hours at 1600 °C. Total conductivities are reported owing to difficulty in resolving individual bulk and grain boundary contributions from the impedance spectra. In addition to checking the phase purity of the samples after their initial synthesis, the phase purity of the pellets used for conductivity measurements was also checked by X-ray powder diffraction.

8.1.1 Cell Parameters

Using the synthesis conditions given in table 8.1, X-ray diffraction showed the successful synthesis of single phase hexagonal apatite materials for \( x = 0 \), and \( x = 4 - 6 \). Refinement of cell parameter data gave the values shown in table 8.2. The other samples in the range, \( x = 1 - 3 \), had shoulders on the apatite peaks indicative of a 2\(^{nd} \) apatite type impurity of different silicon to germanium ratio. Heating these samples to higher temperatures, prior to pellet preparation, was avoided in order to limit possible germanium loss. Data for these systems is therefore excluded from the table. However, the successful synthesis of single phase samples was confirmed for these systems \( (x = 1 - 3) \) by X-ray diffraction, after sintering the pellets used for conductivity measurements for 2 hours at 1600 °C.

Table 8.2. Cell parameter data for \( \text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26} \) \((x = 0, 4 - 6)\) after initial synthesis.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Unit Cell Parameters / Å (Hexagonal Cell)</th>
<th>Unit Cell Volume / Å(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}_{9.33}\text{Si}<em>6\text{O}</em>{26} )</td>
<td>( a = b )</td>
<td>( c )</td>
</tr>
<tr>
<td>( \text{La}_{9.33}\text{Si}_2\text{Ge}<em>4\text{O}</em>{26} )</td>
<td>( 9.721(3) )</td>
<td>( 7.187(3) )</td>
</tr>
<tr>
<td>( \text{La}_{9.33}\text{Si}_4\text{Ge}<em>2\text{O}</em>{26} )</td>
<td>( 9.870(5) )</td>
<td>( 7.257(5) )</td>
</tr>
<tr>
<td>( \text{La}_{9.33}\text{SiGe}<em>2\text{O}</em>{26} )</td>
<td>( 9.902(5) )</td>
<td>( 7.276(5) )</td>
</tr>
<tr>
<td>( \text{La}_{9.33}\text{Ge}<em>6\text{O}</em>{26} )</td>
<td>( 9.912(3) )</td>
<td>( 7.283(3) )</td>
</tr>
</tbody>
</table>
Figure 8.1. Unit cell volume as a function of germanium content, x, for La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ ($x = 0, 4 - 6$) after initial synthesis.

Figure 8.1 shows a plot of unit cell volume as a function of germanium content for La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ ($x = 0, 4 - 6$) after the initial synthesis. A plot of the unit cell 'a' and 'b' parameters is shown as a function of germanium content in figure 8.2, while the corresponding plot for the 'c' cell parameter is shown in figure 8.3. As can be seen, the unit cell volume increases as a function of germanium content. This is as expected because of the larger size of Ge$^{4+}$ compared to Si$^{4+}$, and is consistent with the X-ray data confirming the formation of single phase apatite materials. However, this increase is not linear over the whole range, with particular deviation at the end member, $x = 6$. Possible explanations for the deviation from linearity at high germanium contents might be a structural change, or germanium loss, resulting in a change of composition for the sample.
Figure 8.2. Unit cell ‘a’ and ‘b’ parameters as a function of germanium content, x, for La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ (x = 0, 4 - 6) after initial synthesis.

Figure 8.3. Unit cell ‘c’ parameter as a function of germanium content, x, for La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ (x = 0, 4 - 6) after initial synthesis.
The unit cell parameter data for the pellets used for conductivity measurements are shown in table 8.3. This data includes details for two additional samples ($x = 3.5$ and $4.5$), which were prepared subsequently. The corresponding plot of unit cell volume as a function of germanium content is shown in figure 8.4, with figures 8.5 and 8.6 showing plots of the individual unit cell parameters as a function of germanium content.

Table 8.3. Cell parameter data for $\text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26}$ (pellets used for conductivity measurements).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Unit Cell Parameters / Å (Hexagonal Cell)</th>
<th>Unit Cell Volume / Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}_{9.33}\text{Si}<em>6\text{O}</em>{26}$</td>
<td>$a = b$ 9.721(3) $c$ 7.187(3)</td>
<td>590.7</td>
</tr>
<tr>
<td>$\text{La}_{9.33}\text{Si}_5\text{Ge}<em>1\text{O}</em>{26}$</td>
<td>$a = b$ 9.760(2) $c$ 7.222(2)</td>
<td>595.8</td>
</tr>
<tr>
<td>$\text{La}_{9.33}\text{Si}_4\text{Ge}<em>2\text{O}</em>{26}$</td>
<td>$a = b$ 9.790(4) $c$ 7.247(4)</td>
<td>601.5</td>
</tr>
<tr>
<td>$\text{La}_{9.33}\text{Si}_3\text{Ge}<em>3\text{O}</em>{26}$</td>
<td>$a = b$ 9.811(4) $c$ 7.265(4)</td>
<td>606.0</td>
</tr>
<tr>
<td>$\text{La}_{9.33}\text{Si}_2\text{Ge}<em>4\text{O}</em>{26}$</td>
<td>$a = b$ 9.820(4) $c$ 7.281(4)</td>
<td>608.1</td>
</tr>
<tr>
<td>$\text{La}_{9.33}\text{Si}_1\text{Ge}<em>5\text{O}</em>{26}$</td>
<td>$a = b$ 9.828(4) $c$ 7.289(4)</td>
<td>609.8</td>
</tr>
<tr>
<td>$\text{La}_{9.33}\text{Si}_0\text{Ge}<em>6\text{O}</em>{26}$</td>
<td>$a = b$ 9.825(8) $c$ 7.273(6)</td>
<td>608.0</td>
</tr>
</tbody>
</table>
Figure 8.4. Unit cell volume as a function of germanium content, $x$, $\text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{28}$ ($0 \leq x \leq 6$), of the pellets used for conductivity measurements.

Figure 8.5. Unit cell a parameter as a function of germanium content, $x$, $\text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{28}$ ($0 \leq x \leq 6$), of the pellets used for conductivity measurements.
Figure 8.6. Unit cell c parameter as a function of germanium content, $x$, $\text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26}$ ($0 \leq x \leq 6$), of the pellets used for conductivity measurements.

It can be seen from figures 8.4 to figures 8.6 that the unit cell parameters increase linearly with germanium content until $x \approx 3$, above which deviations from linearity are observed. These deviations are severe for $x \geq 4$, above which the cell parameters show a decrease in value. Distinct broadening of the apatite peaks, and the appearance of extra peaks, was observed in the X-ray diffraction profiles of the sample pellets where $x \geq 4.5$. As a result, the cell parameters could not be determined for these particular samples. It was also noted that these pellets, which are high in germanium content, were very brittle. These effects may be related to germanium loss, which is consistent with the fact that the changes appear to increase with increasing germanium content.
8.1.2 Conductivity Data

Table 8.4 shows conductivity data for the La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ ($0 \leq x \leq 6$) series. The plots of conductivity at 800 °C and activation energy, as a function of germanium content, are shown in figures 8.7 and 8.8 respectively.

Table 8.4. Conductivity data for La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$, recorded at 800 °C.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 800 °C / S cm$^{-1}$</th>
<th>Activation Energy / eV ($\approx 300 - \approx 800$ °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_{9.33}$Si$<em>6$O$</em>{26}$</td>
<td>$2.02 \times 10^{-3}$</td>
<td>0.74</td>
</tr>
<tr>
<td>La$_{9.33}$Si$_5$Ge$<em>1$O$</em>{26}$</td>
<td>0.01</td>
<td>0.87</td>
</tr>
<tr>
<td>La$_{9.33}$Si$_4$Ge$<em>2$O$</em>{26}$</td>
<td>0.03</td>
<td>1.10</td>
</tr>
<tr>
<td>La$_{9.33}$Si$_3$Ge$<em>3$O$</em>{26}$</td>
<td>0.03</td>
<td>1.01</td>
</tr>
<tr>
<td>La$_{9.33}$Si$_2$Ge$<em>4$O$</em>{26}$</td>
<td>0.06</td>
<td>1.16</td>
</tr>
<tr>
<td>La$_{9.33}$Si$_1$Ge$<em>5$O$</em>{26}$</td>
<td>0.06</td>
<td>1.11</td>
</tr>
<tr>
<td>La$_{9.33}$SiGe$<em>6$O$</em>{26}$</td>
<td>0.05</td>
<td>1.13</td>
</tr>
<tr>
<td>La$_{9.33}$Ge$<em>7$O$</em>{26}$</td>
<td>0.05</td>
<td>1.30</td>
</tr>
<tr>
<td>La$_{9.33}$Ge$<em>8$O$</em>{26}$</td>
<td>0.01</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Figure 8.7. Conductivity at 800 °C as a function of germanium content, x, for La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ ($0 \leq x \leq 6$).
Figure 8.8. Activation energy as a function of germanium content, $x$, for La$_{9.33}$Si$_6$-Ge$_x$O$_{26}$ ($0 \leq x \leq 6$).

In general, the conductivity, recorded at 800 °C, increases significantly as a function of germanium content, until a maximum value of 0.06 S cm$^{-1}$ is reached when $x = 4$. The conductivity then appears to decrease with further increase in germanium content, $x \geq 4.5$. The activation energy for oxide ion conductivity also increases as a function of germanium content. However, this increase is not linear, with a plateau in value being reached at $\approx 1.1$ eV, when $x = 2 - 4.5$, before a subsequent increase to a maximum value of 1.3 eV is observed. The conductivity plots for La$_{9.33}$Si$_6$O$_{26}$, La$_{9.33}$Si$_2$Ge$_4$O$_{26}$ and La$_{9.33}$Ge$_6$O$_{26}$ are shown in figure 8.9 for comparison.
Figure 8.9. Conductivity plots for (a) La_{9.33}Ge_{0.6}O_{26}, (b) La_{9.33}Si_{2}Ge_{4}O_{26} and (c) La_{9.33}Si_{6}O_{26}.

8.1.3 Discussion

The results suggest that there appears to be an optimum germanium content (x = 4), corresponding to the nominal starting composition La_{9.33}Si_{2}Ge_{4}O_{26}, where the high temperature conductivity (800 °C) is maximised and activation energy maintained at a moderate value. Interestingly, the cell parameters are at a maximum value for a pellet of this nominal composition. Above this level of germanium content, severe broadening and extra peaks occur in the X-ray diffraction profile. These changes have been attributed to germanium loss (chapter 4.0), and the effect of this germanium volatility on the composition will be to move it towards a lanthanum rich one with oxygen excess, and ultimately towards poorly conducting La_{2}GeO_{3}.

It is possible that the increase in conductivity as a function of germanium content, up to the optimum ratio is due to several factors, including the increase in unit cell size.
and a shift of composition towards oxygen excess due to germanium loss. However, the extent to which this loss is occurring is difficult to quantify. To this end extended sintering studies have been made of the La$_{9.33}$Si$_2$Ge$_4$O$_{26}$ system.

8.1.4 Sintering Studies: La$_{9.33}$Si$_2$Ge$_4$O$_{26}$

In order to examine the long term high temperature stability of the mixed La$_{9.33}$Si$_2$Ge$_4$O$_{26}$ phase, sintering studies were performed. A portion of this material was sintered for 120 hours at 1500 °C. The pellet used for conductivity measurements was also heated for 96 hours at 1500 °C. Both samples were weighed before and after sintering, and the X-ray diffraction profiles obtained. The conductivity of this sample was re-tested after this extended heat treatment.

Synthesis at 1250 °C results in the formation of single phase hexagonal apatite for this system. Refinement of the cell parameters gives the values $a = b = 9.870(5)$ Å and $c = 7.257(5)$ Å after the initial synthesis. The effects on this system on sintering at 1600 °C are interesting. Sintering a pressed pellet of the powder not only results in a mass loss of 2 %, but significant changes in cell parameter values. The ‘a’ and ‘b’ parameters show a 0.4 % reduction in value to 9.828(4) Å, while the ‘c’ parameter shows a 0.4 % increase in value to 7.289(4) Å. Overall, however, the cell volume decreases.

Sintering the pellet for a further 96 hours resulted in a further 1 % mass loss, but the cell parameters remained virtually unchanged, $a = b = 9.827(9)$ and $c = 7.287(9)$. This system still appeared to be single phase, by X-ray diffraction, showing little sign of peak broadening, nor was there any evidence for extra peaks appearing adjacent to the apatite peaks in the profile. The conductivity (Recorded at 800 °C) and the activation energy also remain similar in value, 0.05 S cm$^{-1}$ and 1.12 eV respectively. Sintering a portion of the powder for 120 hours at 1500 °C resulted in a mass loss of > 1 %. The X-ray diffraction profile of the sintered powder showed no broadening of the apatite peaks, but there was evidence for the formation of a La$_2$GeO$_5$ type
impurity phase. Refinement of the cell parameters for the apatite phase give the values $a = b = 9.822(5) \, \text{Å}$, $c = 7.278(5) \, \text{Å}$; these are similar in value to those for the pellet. The conductivity of this system was, however, significantly lower, although the activation energy was of a similar value, $5.09 \times 10^{-4} \, \text{S cm}^{-1}$ and 1.16 eV respectively. The lower conductivity is probably related to the presence of poorly conducting $\text{La}_2\text{GeO}_3$ impurity at the grain boundaries. The results show that germanium loss is still a problem in the mixed silicon/germanium systems but it is not as severe as for $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$ (chapter 6), particularly for sintered pellets.

The change in cell parameters on sintering at high temperature (1600 °C) is interesting and it does not appear as if it can be explained simply by the loss of germanium. Although the decrease in unit cell volume would be consistent with germanium loss resulting in a higher silicon/germanium ratio in the pellet, it should be predicted that all the cell axes should decrease, whereas the ‘c’ axis is observed to increase in size. Structural studies of samples prepared at 1250 °C and 1600 °C are planned to try and rationalise this.

### 8.1.5 Conclusion

The results show that, in terms of conductivity at 800 °C, the optimum nominal starting Si to Ge ratio for $\text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26}$ ($0 \leq x \leq 6$) appears to be 0.5 ($x = 4$). The conductivity of this composition, $\text{La}_{9.33}\text{Si}_4\text{Ge}_2\text{O}_{26}$, is 0.06 S cm$^{-1}$, which is higher than that of YSZ at this temperature. The presence of silicon in the samples appears to inhibit broadening of the apatite peaks in the X-ray diffraction profiles. The obvious deviation of the cell parameters from Vegard’s law for the samples high in germanium content suggests that germanium loss becomes more significant with increasing germanium content. The mixed silicon/germanium systems are therefore still subject to problems related to germanium loss, although this loss appears to be less severe when compared to the end member of the series, $\text{La}_{9.33}\text{Ge}_6\text{O}_{26}$ ($x = 6$), as indicated by extended sintering studies on $\text{La}_{9.33}\text{Si}_2\text{Ge}_4\text{O}_{26}$. 
The high conductivity of \( \text{La}_{9.33}\text{Si}_2\text{Ge}_4\text{O}_{26} \) makes it a possible candidate for an electrolyte material for use in SOFCs, if further optimisation of preparation conditions can be achieved to lower the sintering temperature required. In this respect the investigation of sol gel routes is planned.
Chapter 9.0: The Synthesis and Conductivities of New Apatite-Type Phases $\text{La}_{8.67}\text{BaSi}_{6-x}\text{Ge}_x\text{O}_{26}$ and $\text{La}_9\text{BaSi}_{6-x}\text{Ge}_x\text{O}_{26.5}$ ($0 \leq x \leq 6$)

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Chapter 9.0: The Synthesis and Conductivities of the Apatite-Type Phases La\textsubscript{8.67}BaSi\textsubscript{6-x}Ge\textsubscript{x}O\textsubscript{26} and La\textsubscript{9}BaSi\textsubscript{6-x}Ge\textsubscript{x}O\textsubscript{26.5} (0 ≤ x ≤ 6)

9.1 Introduction

It was shown in the previous chapter that for La\textsubscript{9.33}Si\textsubscript{6-x}Ge\textsubscript{x}O\textsubscript{26} (0 ≤ x ≤ 6), the optimum Ge content in terms of high temperature oxide ion conductivity is x = 4. For comparison, two further novel mixed silicon/germanium apatite series have been examined in which barium has been doped onto the lanthanum site. La\textsubscript{8.67}BaSi\textsubscript{6-x}Ge\textsubscript{x}O\textsubscript{26} (0 ≤ x ≤ 6) was prepared, in order to examine the effect of a reduced number of cation vacancies, and to look at the effect of barium doping on the oxide ion conductivity, activation energy and the problem of germanium loss. In addition the series La\textsubscript{9}BaSi\textsubscript{6-x}Ge\textsubscript{x}O\textsubscript{26.5} (0 ≤ x ≤ 6) was prepared in order to observe how these factors compare in related systems containing nominal excess oxygen.

9.1.1 Synthesis and Experimental

All samples were prepared using high purity La\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, GeO\textsubscript{2}, and BaCO\textsubscript{3}. The dried starting materials were ground together in stoichiometric proportions. Details of synthesis conditions are shown in table 9.1. Phase purity was checked by X-ray powder diffraction (Siefert 3003TT X-ray diffractometer). Cell parameter data were also determined by X-ray diffraction.
Sample pellets were prepared for conductivity testing, as described in chapter 2, and sintered for 2 hours at 1600 °C to obtain dense pellets. Conductivity values were determined from a.c. impedance measurements. Total conductivities are reported owing to difficulty in resolving individual bulk and grain boundary contributions from the impedance spectra. The phase purity for all pellets used for conductivity measurements was checked by X-ray diffraction.

In order to examine the stability of the mixed phases against germanium loss, sintering studies were performed on the mixed silicon/germanium samples showing the highest conductivities. A portion of the powder used to prepare the pellet for conductivity measurements was sintered for 120 hours at 1500 °C. The pellet used for conductivity measurements was also heated for 120 hours at 1500 °C. The stability of La_{8.67}BaGe_6O_{26} and La_9BaGe_6O_{26.5} against germanium loss was also studied. All samples used for extended sintering studies were weighed and X-ray diffraction profiles obtained before and after sintering.

### Table 9.1. Synthesis conditions for La_{9-x}Ba_{6-x}Ge_xO_{26.5} (0 \leq x \leq 6) and La_{8.67}BaSi_{6-x}Ge_xO_{26} (0 \leq x \leq 6).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>1st Heat Treatment / °C (Duration / Hours)</th>
<th>2nd Heat Treatment / °C (Duration / Hours)</th>
<th>3rd Heat Treatment / °C (Duration / Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La_{9}BaSi_{6}O_{26.5}</td>
<td>1350(16)</td>
<td>1350(16)</td>
<td></td>
</tr>
<tr>
<td>La_{9}BaSi_{6-x}Ge_{x}O_{26.5} (x = 1 – 5)</td>
<td>1200(16)</td>
<td>1200(22)</td>
<td></td>
</tr>
<tr>
<td>La_{9}BaGe_{6}O_{26.5}</td>
<td>1250(20)</td>
<td>1250(16)</td>
<td>1250(18)</td>
</tr>
<tr>
<td>La_{8.67}BaSi_{6}O_{26}</td>
<td>1300(16)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>La_{8.67}BaSi_{6-x}Ge_{x}O_{26} (x = 1 – 6)</td>
<td>1200(16)</td>
<td>1200(16)</td>
<td>1200(18)</td>
</tr>
</tbody>
</table>
9.1.2 Cell Parameters: La$_{8.67}$BaSi$_{6-x}$Ge$_x$O$_{26}$ ($0 \leq x \leq 6$)

The successful synthesis of single phase hexagonal apatite materials was confirmed by X-ray powder diffraction for samples in the range La$_{8.67}$BaSi$_{6-x}$Ge$_x$O$_{26}$ ($0 \leq x \leq 6$) where $x = 0, 4 - 6$, using the synthesis conditions given in table 9.1. Details of cell parameter data for these systems are shown in table 9.2, while the plot of unit cell volume as a function of germanium content is shown in figure 9.1. The mixed silicon/germanium systems, which were high in silicon content ($x = 1 - 3$), appeared at first glance to be single phase on synthesis at 1200 °C. However, close inspection of the X-ray diffraction profiles revealed shoulders on the peaks, suggestive of the presence of two apatite phases with different silicon to germanium ratios, indicating that these samples could not be prepared as single phase materials at this synthesis temperature. Heating these samples to temperatures greater than 1200 °C, prior to pellet preparation, was avoided in order to limit possible germanium loss. Data for the impure systems is therefore excluded from the table.

Single phase samples were achieved for the remaining samples, where $x = 1 - 3$, after sintering the pellets for 2 hours at 1600 °C. Table 9.2 also shows the unit cell parameter data for all the sample pellets of La$_{8.67}$BaSi$_{6-x}$Ge$_x$O$_{26}$ ($0 \leq x \leq 6$) used for conductivity measurements. Figure 9.2 shows the corresponding plot of unit cell volume as a function of germanium content.
Table 9.2. Cell parameter data (hexagonal cell) for La_{0.67}Ba_{6-x}Ge_xO_{26} after initial synthesis \((x = 0, 4 - 6)\), and for pellets used for conductivity measurements \((0 \leq x \leq 6)\).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Unit Cell Parameters / Å (After Initial Synthesis)</th>
<th>Unit Cell Volume / Å^3</th>
<th>Unit Cell Parameters / Å (Pellets Used for Conductivity Testing)</th>
<th>Unit Cell Volume / Å^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{La}<em>{0.67}\text{BaSi}</em>{6}\text{O}_{26})</td>
<td>(9.757(3)) (7.275(3)) 599.8</td>
<td>(9.757(3)) (7.275(3)) 599.8</td>
<td>* *</td>
<td>* *</td>
</tr>
<tr>
<td>(\text{La}<em>{0.67}\text{BaSi}</em>{4}\text{Ge}<em>{2}\text{O}</em>{26})</td>
<td>* *</td>
<td>* 9.797(5) 7.303(5) 604.7</td>
<td>* *</td>
<td>* 9.805(4) 7.313(4) 608.9</td>
</tr>
<tr>
<td>(\text{La}<em>{0.67}\text{BaSi}</em>{3}\text{Ge}<em>{3}\text{O}</em>{26})</td>
<td>* *</td>
<td>* 9.842(6) 7.327(5) 614.6</td>
<td>* *</td>
<td>* 9.902(5) 7.361(3) 625.0</td>
</tr>
<tr>
<td>(\text{La}<em>{0.67}\text{BaSi}</em>{2}\text{Ge}<em>{4}\text{O}</em>{26})</td>
<td>9.893(4) 7.329(3) 621.2</td>
<td>9.875(4) 7.341(4) 620.0</td>
<td>9.921(3) 7.340(2) 625.7</td>
<td>9.902(5) 7.361(3) 625.0</td>
</tr>
<tr>
<td>(\text{La}<em>{0.67}\text{BaSi}</em>{1}\text{Ge}<em>{5}\text{O}</em>{26})</td>
<td>9.951(4) 7.355(3) 630.7</td>
<td>9.939(4) 7.377(3) 631.1</td>
<td>9.951(4) 7.355(3) 630.7</td>
<td>9.939(4) 7.377(3) 631.1</td>
</tr>
</tbody>
</table>

* Samples not single phase after initial synthesis

Figure 9.1. Unit cell volume as a function of germanium content, \(x\), for \(\text{La}_{0.67}\text{BaSi}_{6-x}\text{Ge}_x\text{O}_{26}\) \((x = 0, 4 - 6)\) after initial synthesis.
The cell parameters of the samples, both of the initial prepared powders, and of the sintered pellets appear to obey Vegard's law across the full range, unlike for the La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ system. It is noteworthy that the X-ray diffraction data shows that barium doping appears to help stabilise the hexagonal apatite lattice to the high temperatures required for sintering, which is a very positive result. There is, however, slight evidence for broadening of the apatite peaks in the X-ray diffraction profiles taken of the pellets used for conductivity measurements for the end members La$_{8.67}$BaSi$_6$Ge$_x$O$_{26}$ and La$_{8.67}$BaGe$_6$O$_{26}$. Also, it was noted that these pellets were very brittle, as was the case for samples containing a high germanium content in the La$_{9.33}$Si$_{6-x}$Ge$_x$O$_{26}$ series. There also appears to be significant changes in cell parameters on sintering the three germanium rich end members, $x = 4 - 6$, at 1600 °C. These changes are identical in nature to the ones observed previously for the La$_{9.33}$Si$_2$Ge$_4$O$_{26}$ system, indicating a similar effect of high temperature sintering on both systems. The ‘a’ and ‘b’ parameters are observed to decrease in value, while the ‘c’ parameter increases, although these differences are not as great as observed for La$_{9.33}$Si$_2$Ge$_4$O$_{26}$. These changes might be related to germanium loss, and result from a deviation from the starting Si to Ge ratio to higher values, although if this was the
case, a deviation from Vegard’s law might be expected for the end members with a high germanium content. Further work is required in order to fully account for these changes observed in cell parameters on sintering at high temperature.

9.1.3 Conductivity Data: \( \text{La}_{8.67}\text{BaSi}_{6-x}\text{Ge}_x\text{O}_{26} \) \( (0 \leq x \leq 6) \)

Table 9.3 shows conductivity data for these samples. Plots of conductivity and activation energy as a function of germanium content are shown in figures 9.3 and 9.4 respectively, while plots of log \( (\sigma \ T / \text{S cm}^{-1} \text{ K}) \) against \( 1000 \text{ K} / \text{T} \) for \( \text{La}_{8.67}\text{BaSi}_6\text{O}_{26} \), \( \text{La}_{8.67}\text{BaSi}_3\text{Ge}_3\text{O}_{26} \) and \( \text{La}_{8.67}\text{BaGe}_6\text{O}_{26} \) are shown in figure 9.5.

Table 9.3. Conductivity data for \( \text{La}_{8.67}\text{BaSi}_{6-x}\text{Ge}_x\text{O}_{26} \), recorded at 800 °C.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 800 °C / S cm(^{-1})</th>
<th>Activation Energy / eV (≈300 - ≈800 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}_{8.67}\text{BaSi}<em>6\text{O}</em>{26} )</td>
<td>( 1.68 \times 10^{-3} )</td>
<td>0.67</td>
</tr>
<tr>
<td>( \text{La}_{8.67}\text{BaSi}_4\text{Ge}<em>2\text{O}</em>{26} )</td>
<td>( 8.04 \times 10^{-3} )</td>
<td>0.81</td>
</tr>
<tr>
<td>( \text{La}_{8.67}\text{BaSi}_3\text{Ge}<em>3\text{O}</em>{26} )</td>
<td>( 0.02 )</td>
<td>1.02</td>
</tr>
<tr>
<td>( \text{La}_{8.67}\text{BaSi}_2\text{Ge}<em>4\text{O}</em>{26} )</td>
<td>( 5.31 \times 10^{-3} )</td>
<td>1.28</td>
</tr>
<tr>
<td>( \text{La}_{8.67}\text{BaSiGe}<em>5\text{O}</em>{26} )</td>
<td>( 4.93 \times 10^{-3} )</td>
<td>1.17</td>
</tr>
<tr>
<td>( \text{La}_{8.67}\text{BaGe}<em>6\text{O}</em>{26} )</td>
<td>( 7.70 \times 10^{-3} )</td>
<td>0.97</td>
</tr>
</tbody>
</table>
Figure 9.3. Conductivity at 800 °C as a function of germanium content, $x$, for La$_{8.87}$Ba$_{6-x}$Ge$_x$O$_{26}$ ($0 \leq x \leq 6$).

Figure 9.4. Activation energy as a function of germanium content, $x$, for La$_{8.87}$Ba$_{6-x}$Ge$_x$O$_{26}$ ($0 \leq x \leq 6$).
Figure 9.5. Conductivity data for (a) La$_{8.67}$BaSi$_6$O$_{26}$, (b) La$_{8.67}$BaSi$_3$Ge$_3$O$_{26}$ and (c) La$_{8.67}$BaGe$_6$O$_{26}$.

The systems containing germanium appear to have higher conductivities and activation energies than the pure silicate system, La$_{8.67}$BaSi$_6$O$_{26}$, when compared at 800 °C. There would also appear to be an optimum starting Si to Ge ratio of ≈ 1.4 (x = 2 – 3), where conductivity is maximised and activation energy maintained at a moderate level. Initially, the high temperature conductivities appear to increase as a function of germanium content, from 1.68 x 10$^{-3}$ S cm$^{-1}$ for La$_{8.67}$BaSi$_6$O$_{26}$, until a maximum value of 0.02 S cm$^{-1}$ is reached for the compositions where x = 2 and 3. For systems containing higher germanium contents, the conductivities are significantly lower, with the value for the end member, La$_{8.67}$BaGe$_6$O$_{26}$, being 7.70 x 10$^{-3}$ S cm$^{-1}$. Activation energies initially appear to increase in value, as a function of germanium content, from 0.67 eV for La$_{8.67}$BaSi$_6$O$_{26}$ to the moderate value of ≈ 1 eV for the compositions where x = 2 and 3. A maximum value in activation of 1.28 eV is reached for the composition where x = 4. Further increase in germanium content corresponds to a decrease in activation energy, with the end member, La$_{8.67}$BaGe$_6$O$_{26}$, showing a value of 0.97 eV. It is possible that some of the changes
observed in the total conductivity values reported are due to variations in grain boundary contributions. In this respect, it is important to note that the samples high in germanium content were very brittle. It is therefore likely that the grain boundary contribution towards the conductivity for these samples may be high, thus leading to a decrease in the total conductivity.

9.1.4 Stability Studies: La$_{8.67}$BaSi$_4$Ge$_2$O$_{26}$

Synthesis at 1200 °C did not result in the formation of single phase apatite for La$_{8.67}$BaSi$_4$Ge$_2$O$_{26}$. Phase purity was only confirmed after sintering a prepared pellet at 1600 °C for 2 hours. Refinement of the cell parameters give the values $a = b = 9.805(4)$ Å and $c = 7.313(4)$ Å. Sintering the pellet used for conductivity testing at 1500 °C for a further 120 hours results in a mass loss of 1 %. However, no significant change in the unit cell parameters was observed and there was no obvious sign of peak broadening in the X-ray diffraction profile for this system on extended sintering (figure 9.6). Values for conductivity and activation energy were similar to those recorded prior to extended sintering, 0.03 S cm$^{-1}$ (800 °C) and 1.06 eV respectively. Similarly, a 1 % mass loss was observed for a portion of the powder sintered at 1500 °C for 120 hours, and there was no significant change in the cell parameters.
9.1.5 Stability Studies: La\textsubscript{8.67}Ba\textsubscript{4.26}Ge\textsubscript{2}O\textsubscript{26}

Synthesis at 1200 °C resulted in the formation of pure hexagonal apatite for this system. Refinement of the unit cell parameters gave a = b = 9.951(4) Å and c = 7.355(4) Å. Sintering a portion of this powder for 120 hours at 1500 °C resulted in a > 1 % mass loss. Examination of the X-ray diffraction profile subsequent to this extended sintering revealed the appearance of extra peaks in the spectrum that could be attributed to a La\textsubscript{2}GeO\textsubscript{5} type impurity (figure 9.7). Interestingly, there was no evidence of increased broadening of the apatite peaks.
Figure 9.7. X-ray diffraction profile for La$_{8.67}$BaGe$_{6}$O$_{26}$ after heating for 120 hours at 1500 °C.

9.1.6 Cell Parameters: La$_{9}$BaSi$_{6-x}$Ge$_{x}$O$_{26.5}$ ($0 \leq x \leq 6$)

The successful synthesis of single phase hexagonal materials was confirmed by X-ray powder diffraction for compositions La$_{9}$BaSi$_{6-x}$Ge$_{x}$O$_{26.5}$, where $x = 0, 4 - 6$, for the synthesis conditions shown in table 9.1. Table 9.4 shows details of cell parameters for these samples after initial synthesis, while figure 9.8 shows a plot of unit cell volume as a function of germanium content. Silicon rich systems, where $x = 1 - 3$, could not be prepared as single phase materials by synthesis at 1200 °C. The X-ray diffraction profiles for these systems revealed the presence of two apatite phases with different silicon to germanium ratios, as observed previously for the La$_{8.67}$BaSi$_{6-x}$Ge$_{x}$O$_{26}$ samples. Data for these systems is therefore excluded from the table.
Phase purity was confirmed for the remaining samples, where $x = 1 - 3$, after sintering the pellets for 2 hours at 1600 °C. Table 9.4 also shows unit cell parameter data for the complete range of the sample pellets used for conductivity measurements. Figure 9.9 shows the related plot of unit cell volume as a function of germanium content.

**Table 9.4.** Cell parameter data (hexagonal cell) for $\text{La}_9\text{BaSi}_{6-x}\text{Ge}_x\text{O}_{26.5}$, after initial synthesis ($x = 0, 4 - 6$), and for pellets used for conductivity measurements ($0 \leq x \leq 6$).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Unit Cell Parameters / Å (After Initial Synthesis)</th>
<th>Unit Cell Volume / Å³</th>
<th>Unit Cell Parameters / Å (Pellets Used for Conductivity Testing)</th>
<th>Unit Cell Volume / Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}_9\text{BaSi}<em>6\text{O}</em>{26.5}$</td>
<td>$a=b$ 9.743(4) $c$ 7.268(4)</td>
<td>597.5</td>
<td>$a=b$ 9.743(4) $c$ 7.268(4)</td>
<td>597.5</td>
</tr>
</tbody>
</table>
| $\text{La}_9\text{BaSi}_{4.5}\text{Ge}_{2.5}\text{O}_{26.5}$ | * | * | * | *
| $\text{La}_9\text{BaSi}_3\text{Ge}_3\text{O}_{26.5}$ | * | * | * | *
| $\text{La}_9\text{BaSi}_{2.5}\text{Ge}_4\text{O}_{26.5}$ | * | * | * | *
| $\text{La}_9\text{BaSi}_{2}\text{Ge}_5\text{O}_{26.5}$ | 9.898(6) | 7.344(5) | 623.1 | 9.874(3) | 7.349(3) | 620.5 |
| $\text{La}_9\text{BaSi}_1\text{Ge}_6\text{O}_{26.5}$ | 9.914(3) | 7.345(2) | 625.2 | 9.907(5) | 7.359(5) | 625.5 |
| $\text{La}_9\text{BaGe}_6\text{O}_{26.5}$ | 9.940(3) | 7.363(3) | 630.0 | 9.927(9) | 7.364(9) | 628.5 |

* Samples not single phase after initial synthesis

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**Figure 9.8.** Plot of unit cell volume as a function of germanium content, $x$, for $\text{La}_9\text{BaSi}_{6-x}\text{Ge}_x\text{O}_{26.5}$ ($x = 0, 4 - 6$) after initial synthesis.
Figure 9.9. Plot of unit cell volume as a function of germanium content, $x$, for pellets used for conductivity measurements, $\text{La}_9\text{BaSi}_{6-x}\text{Ge}_x\text{O}_{26.5}$ ($0 \leq x \leq 6$).

The cell parameters appear to increase proportionally as a function of germanium content across the range from $x = 1$ to 5. This trend is consistent with the X-ray data confirming the formation of single-phase apatite materials. However, there appears to be a significantly larger increase in cell parameters on moving from $x = 0$ to $x = 1$, which might be related to different structural arrangements between the silicate and the mixed silicon/germanium systems containing oxygen excess. Conversely there appears to be only a relatively small increase in cell parameters on moving from $x = 5$ to $x = 6$; this might be related to germanium loss.

There appears to be a change in cell parameter values on sintering the germanium rich end members, $(x = 4$ to 6) at 1600 °C, although the changes are not quite so significant as observed previously for the $\text{La}_{9.33}\text{Si}_2\text{Ge}_4\text{O}_{26}$. The ‘a’ and ‘b’ parameters either remain approximately the same $(x = 5)$ or shift to lower values $(x = 4$ and 6), while the ‘c’ parameters either remain approximately the same $(x = 4$ and 6) or shift to higher values $(x = 5)$. These changes require further investigation. There was, however, no apparent evidence of peak broadening or the appearance of extra peaks adjacent to the apatite peaks in the X-ray diffraction profiles for these systems,
and so barium doping seems to help stabilise the hexagonal apatite phase to high temperatures.

### 9.1.7 Conductivity Data: $\text{La}_9\text{BaSi}_{5-x}\text{Ge}_x\text{O}_{26.5}$ ($0 \leq x \leq 6$)

Table 9.5 shows conductivity data for samples in the range $\text{La}_9\text{BaSi}_{5-x}\text{Ge}_x\text{O}_{26.5}$ ($0 \leq x \leq 6$). Plots of conductivity at 800 °C and activation energy, as a function of germanium content, are shown in figures 9.10 and 9.11 respectively, while plots of log $\sigma$ / T vs. 1000 K / T for $\text{La}_9\text{BaSi}_{5}\text{O}_{26.5}$, $\text{La}_9\text{BaSi}_5\text{Ge}_2\text{O}_{26.5}$ and $\text{La}_9\text{BaGe}_6\text{O}_{26.5}$ are shown in figure 9.12.

#### Table 9.5. Conductivity data for $\text{La}_9\text{BaSi}_{5-x}\text{Ge}_x\text{O}_{26.5}$ ($0 \leq x \leq 6$).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 800 °C / S cm$^{-1}$</th>
<th>Activation Energy / eV * Sample shows change in $E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}<em>9\text{BaSi}</em>{5}\text{O}_{26.5}$</td>
<td>0.05</td>
<td>*0.59/0.51</td>
</tr>
<tr>
<td>$\text{La}_9\text{BaSi}_3\text{Ge}<em>2\text{O}</em>{26.5}$</td>
<td>0.03</td>
<td>0.85</td>
</tr>
<tr>
<td>$\text{La}_9\text{BaSi}_4\text{Ge}<em>2\text{O}</em>{26.5}$</td>
<td>0.02</td>
<td>*1.01/0.88</td>
</tr>
<tr>
<td>$\text{La}_9\text{BaSi}_3\text{Ge}<em>3\text{O}</em>{26.5}$</td>
<td>0.02</td>
<td>1.02</td>
</tr>
<tr>
<td>$\text{La}_9\text{BaSi}_3\text{Ge}<em>4\text{O}</em>{26.5}$</td>
<td>0.03</td>
<td>1.06</td>
</tr>
<tr>
<td>$\text{La}_9\text{BaSi}_4\text{Ge}<em>5\text{O}</em>{26.5}$</td>
<td>0.02</td>
<td>*1.15/0.97</td>
</tr>
<tr>
<td>$\text{La}_9\text{BaGe}<em>6\text{O}</em>{26.5}$</td>
<td>0.03</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Figure 9.10. Plot of conductivity, recorded at 800 °C, as a function of germanium content, $x$, for $\text{La}_9\text{BaSi}_{5-x}\text{Ge}_x\text{O}_{26.5}$ ($0 \leq x \leq 6$).
Figure 9.11. Activation energy as a function of germanium content for La₇BaSi₆₋ₓGeₓO₂₆.₅ (0 ≤ x ≤ 6).

Figure 9.12. Conductivity data for (a) La₇BaSi₆O₂₆.₅, (b) La₇BaSi₆Ge₃O₂₆.₅ and (c) La₇BaGe₆O₂₆.₅.
The conductivities recorded at 800 °C for La₉BaSi₆₋ₓGeₓO₂₆·₅ (0 ≤ x ≤ 6) are high for all samples, ranging between 0.02 and 0.05 S cm⁻¹. In this case the silicate end member La₉BaSi₆O₂₆·₅ appears to be the optimum composition. This system shows the highest conductivity, 0.05 S cm⁻¹, and the lowest activation energy, 0.59/0.51 eV. The activation energies for all the systems containing germanium are higher in value, compared to La₉BaSi₆O₂₆·₅, ranging between 0.85 eV and 1.06 eV. The low activation energy for La₉BaSi₆O₂₆·₅ means that at lower temperatures this material shows even higher conductivity than any of the germanium containing phases, as can be seen clearly from figure 9.12. In this particular series, the conductivity of the sample without germanium appears to be the best by far. In addition, this sample shows better conductivity than YSZ, particularly at low temperatures, and is therefore a promising electrolyte material for use in SOFCs, as mentioned previously in chapter 5.

9.1.8 Stability studies: La₉BaGe₆O₂₆·₅

Synthesis at 1250 °C resulted in the formation of single phase apatite for La₉BaGe₆O₂₆·₅. Refinement of the cell parameters gave the values a = b = 9.940(3) Å and c = 7.363(3) Å. Sintering a portion of this powder for 120 hours at 1500 °C resulted in a 2 % mass loss. Examination of the X-ray diffraction profile after this extended sintering revealed the appearance of extra peaks in the spectrum that could be attributed to a La₂GeO₅ type impurity (figure 9.13). Other impurity peaks were also observed, but these could not be assigned. Interestingly, there was no evidence of broadening of the apatite peaks. This suggests that germanium loss is still a problem in the doped samples, although the hexagonal apatite lattice is stabilised by barium doping.
The X-ray diffraction profile of the pellet used for conductivity measurements also showed significant $\text{La}_2\text{GeO}_5$ impurity peaks after sintering for 120 hours at 1500 °C. This is an interesting observation because the preparation of a dense sample pellet should help inhibit germanium loss to some extent. The conductivity for this system was found to be very poor indeed, $8.21 \times 10^{-6}$ S cm$^{-1}$ (Recorded at 800 °C). This value has decreased several orders of magnitude on extended sintering, from 0.03 S cm$^{-1}$ at 800 °C (for the sample sintered for 2 hours at 1600 °C). However, the activation energy remained similar in value, 1.06 eV. This decrease in conductivity could be related to an increase in the grain boundary contribution due to the presence of $\text{La}_2\text{GeO}_5$. These results show the general problems caused by germanium volatility in these systems.
9.1.9 Conclusions

Structural studies suggest that the inclusion of barium into mixed germanium/silicon apatite systems limits broadening of the apatite peaks, as observed by X-ray diffraction, but does not ultimately prevent germanium loss as determined from extended high temperature sintering studies performed on selected samples. Samples of La₈.₆₇Ba₅₆₆ₓGeₓO₂₆ (x = 4 - 6) and La₉Ba₅₆₆ₓGeₓO₂₆.₅ (x = 4 - 6) as prepared initially at 1200 °C show changes in cell parameters on sintering at 1600 °C for two hours, which could be related to germanium loss and/or structural changes, the exact origin of which requires further investigation.

Conductivity studies indicate that La₈.₆₇Ba₅₆₆₂GeₓO₂₆ and La₈.₆₇Ba₅₆₆₃GeₓO₂₆, where x = 2 and 3, are the optimum compositions in terms of conductivity at high temperature (800 °C) for the La₈.₆₇Ba₅₆₆ₓGeₓO₂₆ (0 ≤ x ≤ 6) range of samples. As with previous studies, systems containing excess oxygen appear to offer the best properties in terms of oxide ion conductivity, with the La₉Ba₅₆₆₂.₅ composition appearing to be the optimum phase in terms of both oxide ion conductivity and activation energy for the La₉Ba₅₆₆ₓGeₓO₂₆.₅ series. The conductivity at 500 °C is ≈ 6 × 10⁻³ S cm⁻¹. This is better than YSZ at this temperature, making La₉Ba₅₆₆₂.₅ a good candidate as a replacement material for YSZ in intermediate temperature SOFCs. Another great advantage of this system is that it does not contain germanium, so the problems associated with germanium volatility are eliminated. Further work is planned to develop suitable anode and cathode materials to use with this electrolyte, so that an apatite based SOFC can be tested.

If the synthesis temperatures could be lowered for the phases which are high in germanium content, then it is possible that these too could become promising electrolyte materials. Synthesis at low temperatures is likely to reduce germanium loss and hence grain boundary contributions to the conductivities. It is planned to investigate the possibility of using sol gel synthesis to prepare these phases, in order to reduce particle size, and hence the synthesis and sintering temperatures employed.
Chapter 10.0: The Synthesis and Conductivities of the Doped Germanium Based Apatite-Type Phases $\text{La}_{10-x}\text{Ge}_{6-y}\text{M}_y\text{O}_{26}\pm z$
($\text{M} = \text{B or Ga}$) and $(\text{La/M})_{10-x}\text{Ge}_6\text{O}_{26}\pm y$ ($\text{M} = \text{Mg, Ca, Sr or Ba}$)

10.1 Introduction

10.1.1 Synthesis and Experimental

10.1.2 Cell Parameters and Conductivity: $\text{La}_{10-x}\text{Ge}_{6-y}\text{M}_y\text{O}_{26}\pm z$
($\text{M} = \text{B or Ga}$)

10.1.3 Cell Parameters and Conductivity: $(\text{La/M})_{10-x}\text{Ge}_6\text{O}_{26}\pm y$
($\text{M} = \text{Mg, Ca, Sr or Ba}$)

10.1.4 Extended Sintering Studies: $\text{La}_8\text{Mg}_2\text{Ge}_6\text{O}_{26}$

10.1.5 Conclusions

10.2 References
Chapter 10.0: The Synthesis and Conductivities of the Doped Germanium Based Apatite-Type Phases \( \text{La}_{10-x}\text{Ge}_6\text{M}_y\text{O}_{26+z} \) \((M = \text{B or Ga})\) and \( \text{(La/M)}_{10-x}\text{Ge}_6\text{O}_{26+y} \) \((M = \text{Mg, Ca, Sr or Ba})\)

10.1 Introduction

Studies into the effects of doping barium onto the lanthanum site in germanium based apatite systems were discussed in the previous chapter. In this chapter we extend this discussion to include additional barium doped samples, as well as a further selection of samples in which magnesium, calcium or strontium have been doped onto the lanthanum site, or in which boron or gallium have been doped onto the germanium site.

10.1.1 Synthesis and Experimental

High purity starting materials, \( \text{La}_2\text{O}_3, \text{GeO}_2, \text{MgO, CaCO}_3, \text{SrCO}_3, \text{BaCO}_3, \text{H}_3\text{BO}_3 \) and \( \text{Ga}_2\text{O}_3 \), were used for sample preparation. Samples were prepared by intimate mixing of the appropriate starting materials in the correct ratio prior to heat treatment. The mixed starting materials for the boron doped systems were calcined for an initial period of 1 hour at 300 °C, prior to subsequent heat treatments, in order to initiate early reaction of \( \text{H}_3\text{BO}_3 \) and so limit boron loss. Details of heat treatments are given in tables 10.1 and 10.2. Phase purity was checked using X-ray diffraction.
Table 10.1. Synthesis conditions for $\text{La}_{10-x}\text{Ge}_6\text{M}_y\text{O}_{26+y}$ ($\text{M} = \text{B, Ga}$).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>1st Heat Treatment / °C (Duration / hours)</th>
<th>2nd and 3rd Heat Treatments / °C (Duration / hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}<em>{9.83}\text{Ge}</em>{5.5}\text{B}<em>{0.5}\text{O}</em>{26.5}$</td>
<td>1350(14)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>$\text{La}<em>{9.67}\text{Ge}</em>{5}\text{BO}_{26}$</td>
<td>1350(12)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>$\text{La}<em>{9.83}\text{Ge}</em>{4.5}\text{B}<em>{1.5}\text{O}</em>{26}$</td>
<td>1350(12)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>$\text{La}<em>{9.5}\text{Ge}</em>{5.5}\text{Ga}<em>{0.5}\text{O}</em>{26.5}$</td>
<td>1300(14)</td>
<td>1300(14)</td>
</tr>
<tr>
<td>$\text{La}<em>{9.67}\text{Ge}</em>{5.5}\text{Ga}<em>{0.5}\text{O}</em>{26.25}$</td>
<td>1300(14)</td>
<td>1300(14)</td>
</tr>
<tr>
<td>$\text{La}<em>{9.83}\text{Ge}</em>{4.5}\text{Ga}<em>{0.5}\text{O}</em>{26.5}$</td>
<td>1300(14)</td>
<td>1300(14)</td>
</tr>
<tr>
<td>$\text{La}<em>{10}\text{Ge}</em>{4}\text{Ga}<em>{2}\text{O}</em>{26}$</td>
<td>1300(14)</td>
<td>1300(14)</td>
</tr>
</tbody>
</table>

Table 10.2. Synthesis conditions for $(\text{La/M})_{10-x}\text{Ge}_6\text{O}_{26+y}$ ($\text{M} = \text{Ba, Ca, Mg and Sr}$).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>1st Heat Treatment / °C (Duration / hours)</th>
<th>2nd and 3rd Heat Treatments / °C (Duration / hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}_8\text{Ba}_2\text{Ge}<em>6\text{O}</em>{26}$</td>
<td>1150(14)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>$\text{La}_8\text{Ca}_2\text{Ge}<em>6\text{O}</em>{26}$</td>
<td>1000(7)</td>
<td>1150(15) 1150(14)</td>
</tr>
<tr>
<td>$\text{La}_8\text{Mg}_2\text{Ge}<em>6\text{O}</em>{26}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>$\text{La}_{8.67}\text{MgGe}<em>6\text{O}</em>{26}$</td>
<td>1350(16)</td>
<td>1350(16)</td>
</tr>
<tr>
<td>$\text{La}_{7.5}\text{Sr}_2.5\text{Ge}<em>6\text{O}</em>{25.75}$</td>
<td>1200(16)</td>
<td>1250(20)</td>
</tr>
<tr>
<td>$\text{La}_{8.67}\text{SrGe}<em>6\text{O}</em>{26}$</td>
<td>1200(16)</td>
<td>1250(20)</td>
</tr>
<tr>
<td>$\text{La}_8\text{Sr}_2\text{Ge}<em>6\text{O}</em>{26}$</td>
<td>1350(14)</td>
<td>1350(14)</td>
</tr>
<tr>
<td>$\text{La}_9\text{SrGe}<em>6\text{O}</em>{26.5}$</td>
<td>1200(16)</td>
<td>1250(20)</td>
</tr>
</tbody>
</table>

Conductivities were determined using a.c. impedance spectroscopy. Total conductivities are reported owing to difficulty in resolving individual bulk and grain boundary contributions from the impedance spectra.

Pellets of each sample (1.6 cm diameter) were prepared for conductivity testing, as described in chapter 2, and then sintered at high temperatures to obtain dense samples. The sample pellets for the boron doped systems were sintered between 1400 °C and 1450 °C and were all found to be dense, with values greater than 80 % of their theoretical density. Boron therefore appears to lower the sintering temperature.
required to achieve dense pellets. The sample pellets for the gallium doped systems were sintered at 1500 °C and found to be more porous, with density values within the region of 65 % to 80 %. We were unable to resinter these samples to obtain more dense pellets owing to lack of time at the end of the project.

Sintering temperatures between 1500 °C and 1650 °C were employed for pellets pressed of the magnesium, calcium, strontium and barium doped systems. The sample pellets for these systems were found to be well sintered, with densities greater than 85 % of their theoretical.

10.1.2 Cell Parameters and Conductivity: La$_{10-x}$Ge$_{6-y}$M$_x$O$_{26+y}$z ($M = B$, Ga)

Details of conductivity values, quoted at 500 °C and 800 °C, and cell parameters for the boron and gallium doped samples are shown in table 10.3. Data for La$_{9.33}$Ge$_6$O$_{26}$ has also been included in this table for comparison. The cell parameters for the boron doped samples are smaller than those for La$_{9.33}$Ge$_6$O$_{26}$, with the values decreasing with increasing boron content. This is consistent with the X-ray diffraction data indicating that boron was successfully doped into the apatite system. Interestingly, there was no evidence of broadening of the apatite peaks in the X-ray diffraction profiles recorded after the initial synthesis at 1350 °C, unlike for the undoped sample as discussed in chapter 4. We also attempted to prepare a sample of La$_{10}$Ge$_4$B$_2$O$_{26}$ for conductivity testing. However, the X-ray diffraction profile showed significant signs of impurity after synthesis, suggesting that we had exceeded the solubility limit for boron. Thus the solubility limit of boron in La$_{9.33}$Ge$_6$O$_{26}$ appears to be lower than that for the silicon based analogue.

For the gallium doped samples, the X-ray diffraction profiles showed significant peak broadening/extra peaks in all cases. Therefore cell parameter data could not be obtained for these samples. As a result of this peak broadening/extra peaks it was therefore not possible to determine the extent to which gallium is present in these
systems. However, the absence of impurities, such as LaGaO$_3$, suggested that gallium may have substituted into the structure.

Table 10.3. Unit cell parameter and conductivity data for La$_{10-x}$Ge$_{6-y}$M$_{y+2}$O$_{28+2x}$ (M = B or Ga), (Conductivity data given represent total values).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 500 °C / S cm$^{-1}$</th>
<th>$E_a$ / eV</th>
<th>Conductivity at 800 °C / S cm$^{-1}$</th>
<th>$E_a$ / eV</th>
<th>Cell Parameters / Å (Hexagonal Cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$a = b$</td>
</tr>
<tr>
<td>La$<em>{0.85}$Ge$</em>{5.3}$B$<em>{0.5}$O$</em>{26.5}$</td>
<td>1.46 x 10$^{-4}$</td>
<td>1.27</td>
<td>0.02</td>
<td>1.27</td>
<td>9.865(1) 7.29(1)</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ge$</em>{4}$BO$_{26}$</td>
<td>2.75 x 10$^{-4}$</td>
<td>1.07</td>
<td>0.01</td>
<td>0.91</td>
<td>9.829(4) 7.294(4)</td>
</tr>
<tr>
<td>La$<em>{0.85}$Ge$</em>{4.3}$B$<em>{1.5}$O$</em>{26}$</td>
<td>2.10 x 10$^{-4}$</td>
<td>0.93</td>
<td>8.30 x 10$^{-3}$</td>
<td>0.93</td>
<td>9.762(4) 7.289(4)</td>
</tr>
<tr>
<td>La$<em>{0.33}$Ge$</em>{4}$O$_{26}$</td>
<td>8.67 x 10$^{-5}$</td>
<td>1.28</td>
<td>0.01</td>
<td>1.28</td>
<td>9.912(1) 7.283(1)</td>
</tr>
<tr>
<td>La$<em>{0.33}$Ge$</em>{5.3}$Ga$<em>{0.5}$O$</em>{26}$</td>
<td>7.18 x 10$^{-6}$</td>
<td>1.46</td>
<td>2.35 x 10$^{-3}$</td>
<td>1.46</td>
<td>* *</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ge$</em>{5.3}$Ga$<em>{0.5}$O$</em>{26.23}$</td>
<td>1.32 x 10$^{-5}$</td>
<td>1.46</td>
<td>4.32 x 10$^{-3}$</td>
<td>1.46</td>
<td>* *</td>
</tr>
<tr>
<td>La$<em>{0.85}$Ge$</em>{4.5}$Ga$<em>{0.5}$O$</em>{26.5}$</td>
<td>4.98 x 10$^{-6}$</td>
<td>1.55</td>
<td>2.40 x 10$^{-3}$</td>
<td>1.55</td>
<td>* *</td>
</tr>
</tbody>
</table>

* It was not possible to accurately determine cell parameter values for these samples due to broadening of the peaks in the X-ray diffraction profile.

Boron doped samples showed good oxide ion conductivity, achieving values between 8.30 x 10$^{-3}$ S cm$^{-1}$ and 0.02 S cm$^{-1}$ at 800 °C. The La$_{0.85}$Ge$_{5.3}$B$_{0.5}$O$_{26.5}$ sample showed the highest conductivity of 0.02 S cm$^{-1}$, and the plot of the data is included in figure 10.2. These observations for the boron doped samples are in agreement with those for previous apatite systems, where conductivity can be seen to be high in systems containing either cation vacancies or excess oxygen. It should be noted that although the X-ray diffraction profiles of the as prepared samples showed a single phase hexagonal apatite, the X-ray diffraction profile of the La$_{0.85}$Ge$_{5.3}$B$_{0.5}$O$_{26.5}$ pellet showed significant evidence of broadening of the apatite peaks after it was sintered at 1350 °C. This may explain the high activation energy recorded for this system, 1.27 eV. Furthermore, there was also evidence of slight broadening of the apatite peaks in the X-ray diffraction profile for La$_{0.67}$Ge$_{4}$BO$_{26}$ after sintering the sample pellet at 1400 °C. It would therefore appear that although the inclusion of boron into these systems initially stabilises the hexagonal apatite lattice to high temperatures, they are
still vulnerable to changes on extended sintering at high temperatures. The X-ray diffraction profile for La$_{9.83}$Ge$_{5.5}$B$_{0.3}$O$_{28.5}$, after sintering the pellet at 1350 °C is shown in figure 10.1.

In terms of activation energy for oxide ion conduction, there appears to be a reduction on doping with boron, consistent with the presence of a hexagonal apatite lattice. In addition La$_{9.67}$Ge$_5$BO$_{26}$ showed a change in activation energy to lower values, 0.91 eV, with increase in temperature.

![X-ray diffraction profile](image)

**Figure 10.1.** X-ray diffraction profile for La$_{9.83}$Ge$_{5.5}$B$_{0.3}$O$_{28.5}$ after sintering the pellet used for conductivity measurements at 1350 °C.
Figure 10.2. Conductivity plots for (a) \( \text{La}_{9.83}\text{Ge}_{5.5}\text{B}_{0.5}\text{O}_{26.5} \) and (b) \( \text{La}_{9.83}\text{Ge}_{5.5}\text{Ga}_{0.5}\text{O}_{26.5} \).

In comparison to the boron doped samples, the gallium doped systems showed reduced oxide ion conductivities, although this may be at least partly related to the fact that the pellets were more porous. These systems would require sintering at higher temperatures in order to confirm this. However, since it appears as if gallium doping destabilises the hexagonal apatite lattice, and it was hence not clear whether or not these samples were prepared as single phase, they became low priority for testing. It is planned to reinvestigate these samples in the future.

10.1.3 Cell Parameters and Conductivity: \( \text{(La/M)}_{10-x}\text{Ge}_x\text{O}_{26+y} \) (M = Ba, Ca, Mg, Sr)

Details of conductivities and cell parameters for the barium, calcium, magnesium and strontium doped samples are shown in table 10.4. Data for \( \text{La}_{9.33}\text{Ge}_6\text{O}_{26} \) is also included in the table for comparison. The variation in cell parameters are consistent
with both the relative size and level of the dopant species employed, with barium increasing the unit cell size significantly, while a corresponding reduction in unit cell size was observed for the magnesium and calcium doped systems. The X-ray diffraction profiles for La$_8$Mg$_2$Ge$_6$O$_{26}$ and La$_8$Ba$_2$Ge$_6$O$_{26}$, taken after their initial synthesis, are shown in figure 10.3. They show the characteristic profiles for a hexagonal apatite phase, indicating that the inclusion of divalent dopant species onto the lanthanum site appears to aid the stability of the hexagonal lattice at high temperature.

Table 10.4. Unit cell parameter and conductivity data for (La/M)$_{10-x}$Ge$_6$O$_{26+y}$ (M = Ba, Ca, Mg or Sr), (Conductivity data given represent total values).

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 500 °C / S cm$^{-1}$</th>
<th>$E_a$ / eV</th>
<th>Conductivity at 800 °C / S cm$^{-1}$</th>
<th>$E_a$ / eV</th>
<th>Cell Parameters / Å (Hexagonal Cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$a = b$</td>
</tr>
<tr>
<td>La$_9$Ba$_2$Ge$<em>6$O$</em>{26}$</td>
<td>$3.65 \times 10^{-5}$</td>
<td>1.05</td>
<td>$5.52 \times 10^{-5}$</td>
<td>0.62</td>
<td>10.002(4)</td>
</tr>
<tr>
<td>La$_8$Ca$_2$Ge$<em>6$O$</em>{26}$</td>
<td>$7.48 \times 10^{-6}$</td>
<td>1.11</td>
<td>$5.90 \times 10^{-5}$</td>
<td>0.49</td>
<td>9.874(3)</td>
</tr>
<tr>
<td>La$_9$Mg$_2$Ge$<em>6$O$</em>{26}$</td>
<td>$3.94 \times 10^{-4}$</td>
<td>0.89</td>
<td>0.01</td>
<td>0.89</td>
<td>9.853(2)</td>
</tr>
<tr>
<td>La$_8$Sr$_2$Ge$<em>6$O$</em>{26}$</td>
<td>$4.04 \times 10^{-4}$</td>
<td>0.91</td>
<td>0.01</td>
<td>0.91</td>
<td>9.879(3)</td>
</tr>
<tr>
<td>La$_7$Sr$_2$Ge$<em>6$O$</em>{25.75}$</td>
<td>*</td>
<td>*</td>
<td>$5.13 \times 10^{-7}$</td>
<td>1.78</td>
<td>9.921(4)</td>
</tr>
<tr>
<td>La$_8$Sr$_2$Ge$<em>6$O$</em>{26}$</td>
<td>$3.84 \times 10^{-4}$</td>
<td>1.37</td>
<td>0.04</td>
<td>0.96</td>
<td>9.915(3)</td>
</tr>
<tr>
<td>La$_9$Sr$_2$Ge$<em>6$O$</em>{26.5}$</td>
<td>$8.6 \times 10^{-8}$</td>
<td>0.98</td>
<td>$5.0 \times 10^{-6}$</td>
<td>0.98</td>
<td>9.911(2)</td>
</tr>
<tr>
<td>La$_9$Sr$_2$Ge$<em>6$O$</em>{26.5}$</td>
<td>$2.93 \times 10^{-4}$</td>
<td>1.51</td>
<td>0.03</td>
<td>1.06</td>
<td>9.900(6)</td>
</tr>
</tbody>
</table>

* Conductivity too low to be measured

We also attempted to prepare samples of La$_{7.5}$Ba$_{2.5}$Ge$_6$O$_{25.75}$, La$_{7.5}$Mg$_{2.5}$Ge$_6$O$_{25.75}$, La$_8$Mg$_1.5$Ge$_6$O$_{26.25}$ and La$_9$MgGe$_6$O$_{26.5}$ for conductivity testing. However, although the X-ray diffraction profiles for La$_{7.5}$Ba$_{2.5}$Ge$_6$O$_{25.75}$, La$_{7.5}$Mg$_{2.5}$Ge$_6$O$_{25.75}$ and La$_8$Mg$_1.5$Ge$_6$O$_{26.25}$ did not reveal any significant impurity phases, the cell parameter values were not consistent with the formation of single phase materials, e.g. the cell parameters for La$_{7.5}$Ba$_{2.5}$Ge$_6$O$_{25.75}$ were identical to those for La$_8$Ba$_2$Ge$_6$O$_{26}$. In the
case of La₈Mg₆Ge₂O₂₆.5 the X-ray diffraction profiles showed the presence of significant impurities after synthesis, indicating a problem with incorporating excess oxygen for the magnesium doped samples.

![X-ray diffraction profiles](image.png)

**Figure 10.3.** X-ray diffraction profiles for (a) La₈Mg₂Ge₆O₂₆ and (b) La₈Ba₂Ge₆O₂₆ after initial synthesis.

The most interesting observation from the table is the fact that the fully stoichiometric system La₈Mg₂Ge₆O₂₆ shows high oxide ion conductivity, 0.01 S cm⁻¹ at 800 °C, with a moderate value of activation energy, ≈ 0.9 eV. In contrast, the conductivities of related stoichiometric systems, where the dopant is a larger alkaline earth cation (Ca, Sr or Ba), are low. For example, the conductivity of La₈Sr₂Ge₆O₂₆ is over three orders of magnitude lower than that of La₈Mg₂Ge₆O₂₆ at 800 °C. These differences in conductivity are shown clearly in figure 10.4. It was initially thought that the high conductivity observed for La₈Mg₂Ge₆O₂₆ was related to structural effects owing to the inclusion of a relatively small dopant ion on the large lanthanum site, causing similar effects to that of cation vacancies. In support of this, further work showed that the conductivity of the stoichiometric system La₈LiGe₆O₂₆ was also high (0.01 S cm⁻¹ at 800 °C). Because of the interesting results, samples of
LasMg₂Ge₆O₂₆ were recently prepared for neutron diffraction studies in order to identify why the conductivity of this apparently fully stoichiometric phase was so high. The results showed the presence of Mg₂GeO₄ impurity, indicating that the main phase was in fact slightly non-stoichiometric. This impurity was barely visible by X-ray diffraction due to the low scattering factors of magnesium and germanium, compared to lanthanum. It is not clear yet whether the sample La₉LiGe₆O₂₆ is also non-stoichiometric. In this case lithium loss could lead to non-stoichiometry and this requires further study.

It is also interesting to note that, despite the low conductivities observed for LasM₂Ge₆O₂₆ (M = Ca, Sr and Ba), the activation energies are comparatively low, unlike the case for the stoichiometric silicon based systems. In addition the activation energies for LasBa₂Ge₆O₂₆ and LasCa₂Ge₆O₂₆ change to even lower values at elevated temperatures. This suggests that in these stoichiometric germanium based systems, the oxide ion charge carriers are free to move but are few in number, hence the low conductivities observed.

Figure 10.4. Conductivity plots for (a) La₉Ba₂Ge₆O₂₆, (b) La₉Mg₂Ge₆O₂₆ and (c) La₉Ca₂Ge₆O₂₆.
It should also be noted that the X-ray diffraction profiles of the sintered pellets used for conductivity measurements for the barium, magnesium and calcium doped systems, did not show any apparent signs of peak broadening, or the appearance of extra peaks adjacent to the apatite peaks. This indicates that divalent cation doping onto the lanthanum site stabilises the hexagonal apatite lattice to high temperatures.

In the case of the strontium doped samples, although there were no signs of peak broadening in the samples as prepared, the X-ray diffraction profiles for the pellets sintered at 1600 °C did reveal some broadening, and the appearance of extra peaks adjacent to the apatite peaks. This can be seen clearly for the La$_{8.67}$SrGe$_6$O$_{26}$ system in figure 10.5.

The data in table 10.4 confirms the conclusions from the previous chapter, that as for the silicon based systems, samples containing excess oxygen or cation vacancies, i.e. La$_{8.67}$SrGe$_6$O$_{26}$ and La$_8$SrGe$_6$O$_{26.5}$, are very good oxide ion conductors. Their conductivities were found to be nearly four orders of magnitude higher than for the stoichiometric La$_8$Sr$_2$Ge$_6$O$_{26}$ system. In addition the nominally oxygen deficient La$_{7.5}$Sr$_{2.5}$Ge$_6$O$_{25.75}$ system was a very poor oxide ion conductor indeed, $5.13 \times 10^{-7}$ S cm$^{-1}$ at 800 °C, with a very high activation energy, 1.78 eV. The conductivity for La$_{7.5}$Sr$_{2.5}$Ge$_6$O$_{25.75}$ was found to be so poor that it was not possible to collect impedance data for this system at temperatures below 600 °C. This again supports previous conclusions that the key defect for conductivity in these systems is interstitial oxide ions rather than vacancies.
Figure 10.5. X-ray diffraction profiles for La$_{0.67}$SrGe$_6$O$_{26}$ (a) after initial synthesis and (b) after sintering at 1600 °C.

10.1.4 Extended Sintering Studies: La$_6$Mg$_2$Ge$_6$O$_{26}$

Extended sintering studies were performed on the La$_8$Mg$_2$Ge$_6$O$_{26}$ system owing to both its high oxide ion conductivity and its apparent stability as a hexagonal apatite phase. In order to examine the effect of long term heating at high temperature on conductivity and structure, a sample was sintered for a period of 120 hours at 1500 °C. The sample was weighed before and after heat treatment, and X-ray diffraction profiles obtained.

As for other germanium based systems, both a mass loss and change in X-ray profile were observed. The X-ray profile showed the presence of the perovskite phase La$_2$MgGeO$_6$, previously reported by Swaffer et al.$^2$ The mass loss and formation of this phase are both consistent with germanium loss. Thus, germanium loss still appears to be a problem at high temperatures for the magnesium doped samples, as for the undoped and barium doped systems.
Figure 10.6. X-ray diffraction profiles for (a) La$_6$Mg$_2$Ge$_6$O$_{26}$ after sintering for 120 hours at 1500 °C. The main peaks due to La$_2$MgGeO$_6$ are marked *.

10.1.5 Conclusions

Doping La-Ge-O apatite systems with a range of ions (Mg, Ca, Sr, Ba on the La site, and B on the Ge site) appears to help stabilise the hexagonal apatite lattice to high temperatures. Magnesium, calcium and barium doping appeared to be the most successful in this respect, providing that the sintering time was kept short. In contrast to boron doping, gallium doping on the germanium site does not appear to stabilise the hexagonal phase. Preliminary work on related systems, where comparatively sized ions to gallium (iron and cobalt) have been doped onto the germanium site, gave similar results, suggesting that the size of the dopant on the germanium site is important to the stability of these systems.

Systems that contain cation vacancies or oxygen excess appear to be very good oxide ion conductors, whereas stoichiometric systems appear to be poor oxide ion
conductors, as observed for the silicon based systems. The apparent high oxide ion conductivity observed for the nominally stoichiometric La₈Mg₂Ge₆O₂₆ appears to be due to this phase not being pure, and thus the apatite phase probably contains a small degree of non-stoichiometry.

Extended sintering studies at high temperature studies of the La₈Mg₂Ge₆O₂₆ system show that although these dopant ions do help to stabilise the hexagonal phase, the problem of germanium loss is still not eliminated.
10.2 References

1 P.R. Slater; unpublished work, (2003).

2 M. Swaffer, P.R. Slater, R.K.B. Gover, T. Matsumura, R. Kanno, T. Kamiyama; 

3 S. Barth; Undergraduate Project Report, University of Surrey, (2002).
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Chapter 11.0: Cathode Materials: An Investigation into Cuprate-Based Perovskite-Type Phases for use as Cathode Materials in SOFCs

11.1 Introduction

The perovskite type phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) is a superconductor below 93 K and has been reported to show high oxide ion conductivity and high electronic conductivity at temperatures in excess of 300 °C, raising the prospect of using this material as a cathode in SOFCs. There are, however, a number of problems associated with using YBCO as a cathode material. YBCO degrades, decomposes and reacts with YSZ substrate at temperatures above 900 °C. Furthermore, there is reported electrochemical decomposition at low current densities ($20 \text{ mA cm}^{-2}$). These are all serious problems in the potential use of this material as an SOFC cathode.

The main problem is likely to be to the instability of the Cu (1) site (figure 11.1). This problem can potentially be decreased or eliminated by the substitution of other cations, e.g. Fe, Co, Ga, onto the Cu (1) site. Thermal stability can also be improved by substituting Sr for Ba to give the range of phases with the general formula $\text{YSr}_2\text{Cu}_3_x\text{M}_x\text{O}_{7-y}$ ($\text{M} = \text{Ga, Co, Fe}$). We have therefore prepared a range of such phases in order to investigate their potential as cathode materials for SOFCs, and have examined the conductivities of these cuprate systems as a function of both temperature and $\rho(\text{O}_2)$. In addition, we have tested the stability of these systems against reaction with a range of potential SOFC electrolyte materials.
11.1.1 Experimental

The following samples were prepared following the same general procedure: YSr$_2$Cu$_2$CoO$_{7+x}$, YSr$_2$Cu$_2$FeO$_{7+x}$, YSr$_2$Cu$_2$GaO$_7$, YSr$_2$Cu$_2$Co$_{0.8}$Fe$_{0.2}$O$_{7+x}$, YSr$_2$Cu$_2$Co$_{0.2}$Fe$_{0.8}$O$_{7+x}$ and Y$_{0.8}$Ca$_{0.2}$Sr$_2$Cu$_2$CoO$_{7-x}$. High purity Y$_2$O$_3$, SrCO$_3$, CuO, Ga$_2$O$_3$, Co$_3$O$_4$, Fe$_2$O$_3$ and CaCO$_3$ were used for sample preparation. The starting materials were ground together in the appropriate ratios, heated between 915 °C and 1000 °C for 16 hours in air, reground, and reheated at 1000 °C for a further 16 hours.

Conductivity measurements were made using the standard four-probe d.c. technique. Pellets were prepared (1.6 cm diameter) by pressing at 6000 kg cm$^{-2}$ and sintering at 950 °C to 1000 °C for 16 hours. This gave pellets with densities 60 % to 90 % of
their theoretical value. Four strips of platinum foil were then attached across the diameter of the pellet using platinum paste, before firing at 850 °C for 30 minutes to ensure bonding of the platinum to the sample. Conductivity measurements were then taken in air as a function of temperature (25 °C to 900 °C). Measurements of conductivity vs. oxygen partial pressure were made at a temperature of 900 °C for the samples YSr2Cu2CoO7, YSr2Cu2FeO7+x, YSr2Cu2GaO7, YSr2Cu2Co0.8Fe0.2O7-x, YSr2Cu2Co0.2Fe0.8O7+x and Y0.8Ca0.2Sr2Cu2CoO7-x, with additional measurements taken at a temperature of 800 °C for YSr2Cu2FeO7+x. For the measurements with varying ρ(O2), conductivities were measured initially in going from oxidising to reducing conditions, where nitrogen gas was allowed to pass slowly into the system. In this case the change in ρ(O2) proceeds quite rapidly (0.2 – 10^{-5} atmospheres in 1 hour). The sample was then held under a N2 atmosphere for at least 15 hours, in order for the system under test to equilibrate fully, prior to any measurements being taken in the reverse direction (from reducing to oxidising). The N2 flow was then turned off and oxygen was allowed naturally to leak back into the system over a period of approximately 24 hours, with the conductivity followed with changing oxygen partial pressure (measured with a YSZ sensor). X-ray diffraction was used to check phase purity after conductivity measurements were completed, to confirm that the sample had not decomposed under the experimental conditions.

The compatibility of the samples with potential SOFC electrolytes, YSZ, La9.33Si6O26, La9.33Ge6O26, CeO2 and LaGaO3 was studied by grinding together the sample and electrolyte in a 1:1 by mass ratio and heating at 900 °C for up to 1 week. In the case of La9.33Si6O26, CeO2 and LaGaO3 the samples were reheated for a further 2 weeks at a temperature of 1000 °C. X-ray diffraction was used to check for evidence of any reaction after each heat treatment.

The reaction of CeO2 with YSr2Cu2CoO7 or YSr2Cu2FeO7+x was shown to result in the formation of phases of the type (Y/Ce)2Sr2Cu2MO9+x (M = Co, Fe). These phases (Y1.5Ce0.5Sr2Cu2CoO9+x and Y1.5Ce0.5Sr2Cu2FeO9+x) were therefore also synthesised. High purity Y2O3, CeO2, SrCO3, CuO, Co3O4 and Fe2O3 were used, and the reaction
conditions were similar to those reported earlier for the YSr2Cu2MO7+x samples. Their electrical conductivities were then determined as described above.

11.1.2 Synthesis

The cell parameters for YSr2Cu2CoO7, YSr2Cu2FeO7+x, YSr2Cu2Co0.8Fe0.2O7+x, YSr2Cu2Co0.8Fe0.2O7+x, YSr2Cu2GaO7, Y0.8Ca0.2Sr2Cu2CoO7+x, Y1.5Ce0.5Sr2Cu2CoO9+x and Y1.5Ce0.5Sr2Cu2FeO9+x are shown in Table 11.1. All these samples were shown to be single phase by X-ray diffraction.

Table 11.1. Cell Parameters for the cuprate samples.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Unit Cell Volume / Å³</th>
<th>Cell</th>
<th>Unit Cell Parameters / Å</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSr2Cu2CoO7</td>
<td>673.45</td>
<td>Ortho</td>
<td>22.820(3) 5.454(1) 5.415(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSr2Cu2FeO7+x</td>
<td>168.18</td>
<td>Tetra</td>
<td>3.830(3) 3.830(3) 11.465(9)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSr2Cu2Co0.8Fe0.2O7+x</td>
<td>168.04</td>
<td>Tetra</td>
<td>3.836(5) 3.836(5) 11.42(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSr2Cu2Co0.2Fe0.8O7+x</td>
<td>167.72</td>
<td>Tetra</td>
<td>3.834(6) 3.834(6) 11.41(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YSr2Cu2GaO7</td>
<td>676.70</td>
<td>Ortho</td>
<td>22.847(4) 5.485(2) 5.400(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y0.8Ca0.2Sr2Cu2CoO7+x</td>
<td>168.32</td>
<td>Tetra</td>
<td>3.837(3) 3.837(3) 11.433(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y1.5Ce0.5Sr2Cu2CoO9+x</td>
<td>414.20</td>
<td>Tetra</td>
<td>3.823(2) 3.823(2) 28.34(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y1.5Ce0.5Sr2Cu2FeO9+x</td>
<td>412.91</td>
<td>Tetra</td>
<td>3.813(5) 3.813(5) 28.40(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

11.1.3 Variation of Conductivity with $\rho(O_2)$: YSr2Cu2CoO7, YSr2Cu2FeO7+x, YSr2Cu2Co0.8Fe0.2O7+x, YSr2Cu2Co0.2Fe0.8O7+x, YSr2Cu2GaO7 and Y0.8Ca0.2Sr2Cu2CoO7+x

Plots of log ($\sigma$ / S cm⁻¹) vs. log ($\rho(O_2)$ / atm) for samples YSr2Cu2CoO7, YSr2Cu2FeO7+x, YSr2Cu2Co0.8Fe0.2O7+x, YSr2Cu2Co0.2Fe0.8O7+x, YSr2Cu2GaO7 and Y0.8Ca0.2Sr2Cu2CoO7+x are shown in figures 11.2 to 11.8. The phase purity of the samples was confirmed by X-ray diffraction after conductivity measurements were completed. It should be noted that for data obtained at low $\rho(O_2)$ (log ($\rho(O_2)$ / atm) = 10^5 to 10^3) the values are unlikely to be at equilibrium, since for this $\rho(O_2)$ range leakage of the measurement cell was too fast. This is supported by the hysteresis observed in oxidation/reduction curves.
Figure 11.2. Plot of log conductivity vs. log $\rho(\text{O}_2)$ for YSr$_2$Cu$_2$CoO$_7$ at 900 °C.

Figure 11.3. Plot of log conductivity vs. log $\rho(\text{O}_2)$ for YSr$_2$Cu$_2$FeO$_{7+x}$ at 900 °C.
Figure 11.4. Plot of log conductivity vs. log ρ(O₂) for YSr₂Cu₂FeO₇₋ₓ at 800 °C.

Figure 11.5. Plot of log conductivity vs. log ρ(O₂) for YSr₂Cu₂GaO₇ at 900 °C.
Figure 11.6. Plot of log conductivity vs. log $\rho(O_2)$ for YSr$_2$Cu$_2$Co$_{0.8}$Fe$_{0.2}$O$_{7+x}$ at 900 °C.

Figure 11.7. Plot of log conductivity vs. log $\rho(O_2)$ for YSr$_2$Cu$_2$Co$_{0.2}$Fe$_{0.8}$O$_{7+x}$ at 900 °C.
Figure 11.8. Plot of log conductivity vs. log $\rho(\text{O}_2)$ for Y$_{0.8}$Ca$_{0.2}$Sr$_2$Cu$_2$CoO$_{7-x}$ at 900 °C.

The hysteresis behaviour observed in these plots for all samples indicates poor equilibration between the sample and the atmosphere. This is normally indicative of poor oxide ion transport, poor oxygen surface exchange kinetics, or a combination of both these factors. Interestingly the data at 800 °C for YSr$_2$Cu$_2$FeO$_{7+x}$ showed reduced hysteresis suggesting better equilibration at lower temperatures. This might be related to a reduction in the extent of the variation in the oxygen content in the $\rho(\text{O}_2)$ range studied at this temperature, or it could suggest that another feature, maybe structural in origin, is affecting the $\rho(\text{O}_2)$ dependence. The poor equilibration observed means that it is not possible to calculate accurate gradients for the log $\sigma$ vs. $\rho(\text{O}_2)$ graphs to relate to the defect nature. In the initial discussion we have therefore taken the two end points (which correspond to equilibrated values) and determined the average gradient from them (Table 11.2.).
Table 11.2. Conductivities and gradient of the plot of log $\sigma$ vs. log $\rho(\text{O}_2)$ for selected cuprate samples.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Temp. / °C</th>
<th>Gradient</th>
<th>$\sigma$/S cm$^{-1}$ (Initial Reading in Air)</th>
<th>$\sigma$/S cm$^{-1}$ (Final Reading in Air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSr$_2$Cu$_2$CoO$_7$</td>
<td>900</td>
<td>0.08</td>
<td>13.71</td>
<td>14.23</td>
</tr>
<tr>
<td>Y$<em>{0.5}$Ca$</em>{0.5}$Sr$_2$Cu$<em>2$CoO$</em>{7+x}$</td>
<td>900</td>
<td>0.13</td>
<td>10.31</td>
<td>15.85</td>
</tr>
<tr>
<td>YSr$<em>2$Cu$<em>2$Co$</em>{0.8}$Fe$</em>{0.2}$O$_{7+x}$</td>
<td>900</td>
<td>0.13</td>
<td>11.07</td>
<td>9.18</td>
</tr>
<tr>
<td>YSr$<em>2$Cu$<em>2$Co$</em>{0.2}$Fe$</em>{0.8}$O$_{7+x}$</td>
<td>900</td>
<td>0.24</td>
<td>6.84</td>
<td>5.80</td>
</tr>
<tr>
<td>YSr$_2$Cu$<em>2$FeO$</em>{7+x}$</td>
<td>900</td>
<td>0.37</td>
<td>6.87</td>
<td>6.65</td>
</tr>
<tr>
<td>YSr$_2$Cu$<em>2$FeO$</em>{7+x}$</td>
<td>800</td>
<td>0.28</td>
<td>10.58</td>
<td>10.81</td>
</tr>
<tr>
<td>YSr$_2$Cu$_2$GaO$_7$</td>
<td>900</td>
<td>0.83</td>
<td>12.66</td>
<td>3.12</td>
</tr>
</tbody>
</table>

It is interesting to compare the sequence of samples YSr$_2$Cu$_2$CoO$_7$, YSr$_2$Cu$_2$Co$_{0.8}$Fe$_{0.2}$O$_{7+x}$, YSr$_2$Cu$_2$Co$_{0.2}$Fe$_{0.8}$O$_{7+x}$ and YSr$_2$Cu$_2$FeO$_{7+x}$. The data shows that the $\rho(\text{O}_2)$ dependence of the conductivity increases significantly with increasing iron content. In the case of the end members YSr$_2$Cu$_2$CoO$_7$ and YSr$_2$Cu$_2$FeO$_{7+x}$, the initial and final conductivities after the experiment are comparable, whereas for YSr$_2$Cu$_2$Co$_{0.8}$Fe$_{0.2}$O$_{7+x}$, YSr$_2$Cu$_2$Co$_{0.2}$Fe$_{0.8}$O$_{7+x}$ and Y$_{0.8}$Ca$_{0.2}$Sr$_2$Cu$_2$CoO$_{7-x}$ there does appear to be a small difference, suggesting that partial decomposition or structural change may have occurred. In terms of the former possibility, the X-ray diffraction profiles for these systems after heating in N$_2$ did not show any sign of decomposition. The difference observed in conductivities between the initial and final values recorded in air might be due to a small redistribution of dopant over the Cu (1) and Cu (2) sites. Recent results on YSr$_2$Cu$_2$FeO$_{7+x}$ have indicated that this occurs on heating at high temperature under N$_2$, although it is interesting to note that this particular sample shows no significant difference in conductivity values before and after this experiment. The redistribution of Fe over the two Cu sites, however, might also be partly responsible for the large hysteresis between oxidising and reducing conditions.

All of the samples show an increase in conductivity with increasing $\rho(\text{O}_2)$ indicating p-type conductivity. If it is assumed that the conductivity is due to "Cu$^{3+}$" hole
movement then we can predict the expected \( \rho(O_2) \) dependence, via defect equations. 

The defect equation for the generation of holes is as follows:

\[
2Cu^{\bullet\bullet}_{Cu} + V_0^{\bullet\bullet} + \frac{1}{2} O_2 \leftrightarrow 2Cu_{Cu}^{\bullet\bullet} + O_2^\circ,
\]

this then gives

\[
k_1 = \frac{[Cu_{Cu}^{\bullet\bullet}][O_2^\circ]}{[Cu_{Cu}^{\bullet\bullet}][V_0^{\bullet\bullet}][O_2]^2},
\]

where \([Cu_{Cu}^{\bullet\bullet}] = n^2 = \frac{k_1[V_0^{\bullet\bullet}][O_2]^2}{[O_2^\circ]} \).

If \([V_0^{\bullet\bullet}] \) is effectively constant due to the presence of a large number of inherent oxygen vacancies, then a \( [\rho(O_2)]^n \) dependence would be predicted. If \([V_0^{\bullet\bullet}] \) is not effectively constant then a more complicated dependence would be observed.

Interestingly, the apparent average \( \rho(O_2) \) dependence for YSr\(_2\)Cu\(_2\)GaO\(_7\) and YSr\(_2\)Cu\(_2\)FeO\(_{7+x}\) are both very high at 900 °C, at 0.83 and 0.37 respectively. This might suggest either some sort of decomposition (which stability studies under N\(_2\) seem to contradict) or a major structural change in varying the \( \rho(O_2) \), e.g. the redistribution of dopants over the two Cu sites. In the case of YSr\(_2\)Cu\(_2\)FeO\(_{7+x}\) the \( \rho(O_2) \) dependence could be influenced by charge transfer between the Cu and Fe sites. In addition conduction via the Fe sites is possible in this system, which further complicates matters. Perhaps the most surprising result, however, was the extremely high \( \rho(O_2) \) dependence observed for YSr\(_2\)Cu\(_2\)GaO\(_7\). In this case charge transfer between the Cu and Ga sites is not likely to occur, and so the possibility of a redistribution of dopant over the two Cu sites needs to be investigated.

In contrast to the samples above, a much lower \( \rho(O_2) \) dependence was observed for YSr\(_2\)Cu\(_2\)CoO\(_7\), which needs further study. Again, this could be related to charge transfer between Co and Cu, which helps to maintain the charge carrier
concentration. As for the Fe containing sample, conduction via the Co sites is also possible.

### 11.1.4 Variation of Conductivity with Temperature: $\text{Y}_2\text{Sr}_2\text{Cu}_2\text{CoO}_7$, $\text{Y}_2\text{Sr}_2\text{Cu}_2\text{FeO}_{7+x}$, $\text{Y}_2\text{Sr}_2\text{Cu}_{0.2}\text{Fe}_{0.2}\text{O}_{7+x}$, $\text{Y}_2\text{Sr}_2\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{7+x}$, $\text{Y}_2\text{Sr}_2\text{Cu}_2\text{GaO}_7$ and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cu}_2\text{CoO}_{7-x}$

Plots of log ($\sigma / \text{S cm}^{-1}$) vs. $1 / T$ (K) for $\text{Y}_2\text{Sr}_2\text{Cu}_2\text{CoO}_7$, $\text{Y}_2\text{Sr}_2\text{Cu}_2\text{FeO}_{7+x}$, $\text{Y}_2\text{Sr}_2\text{Cu}_{0.2}\text{Fe}_{0.2}\text{O}_{7+x}$, $\text{Y}_2\text{Sr}_2\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{7+x}$, $\text{Y}_2\text{Sr}_2\text{Cu}_2\text{GaO}_7$ and $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Cu}_2\text{CoO}_{7-x}$ are shown below in figures 11.9 to 11.14. Their conductivities are summarised in table 11.3. Conductivity data for $\text{Y}_{1.5}\text{Ce}_{0.5}\text{Sr}_2\text{Cu}_2\text{O}_{9+x}$ and $\text{Y}_{1.5}\text{Ce}_{0.5}\text{Sr}_2\text{Cu}_2\text{FeO}_{9+x}$ are also included in this table, which forms part of the discussion in a later section.

#### Table 11.3. Conductivity data for selected cuprate samples.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Conductivity at 900 °C / S cm⁻¹</th>
<th>Maximum Conductivity / S cm⁻¹ (Temp. / °C)</th>
<th>Low Temperature Conductivity / S cm⁻¹ (Temp. / °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Y}_2\text{Sr}_2\text{Cu}_2\text{CoO}_7$</td>
<td>13.98</td>
<td>13.98 (900)</td>
<td>2.30 (364)</td>
</tr>
<tr>
<td>$\text{Y}<em>2\text{Sr}<em>2\text{Cu}</em>{0.2}\text{Fe}</em>{0.2}\text{O}_{7+x}$</td>
<td>9.18</td>
<td>9.18 (900)</td>
<td>0.13 (38)</td>
</tr>
<tr>
<td>$\text{Y}<em>2\text{Sr}<em>2\text{Cu}</em>{0.2}\text{Fe}</em>{0.8}\text{O}_{7+x}$</td>
<td>6.03</td>
<td>8.48 (709)</td>
<td>0.42 (38)</td>
</tr>
<tr>
<td>$\text{Y}_2\text{Sr}_2\text{Cu}<em>2\text{FeO}</em>{7+x}$</td>
<td>6.38</td>
<td>35.00 (402)</td>
<td>17.63 (30)</td>
</tr>
<tr>
<td>$\text{Y}<em>{0.8}\text{Ca}</em>{0.2}\text{Sr}_2\text{Cu}<em>2\text{CoO}</em>{7-x}$</td>
<td>13.81</td>
<td>16.20 (478)</td>
<td>11.12 (96)</td>
</tr>
<tr>
<td>$\text{Y}_2\text{Sr}_2\text{Cu}_2\text{GaO}_7$</td>
<td>3.12</td>
<td>4.05 ($\approx$ 535)</td>
<td>3.37 (55)</td>
</tr>
<tr>
<td>$\text{Y}<em>{1.5}\text{Ce}</em>{0.5}\text{Sr}_2\text{Cu}<em>2\text{O}</em>{9+x}$</td>
<td>13.42</td>
<td>$\approx$ 42.45 (192 – 460)</td>
<td></td>
</tr>
<tr>
<td>$\text{Y}<em>{1.5}\text{Ce}</em>{0.5}\text{Sr}_2\text{Cu}<em>2\text{FeO}</em>{9+x}$</td>
<td>7.41</td>
<td>7.41 (900)</td>
<td>70.56 (172)</td>
</tr>
</tbody>
</table>
Figure 11.9. Plot of log conductivity vs. $1/T$ for YSr$_2$Cu$_2$CoO$_7$.

Figure 11.10. Plot of log conductivity vs. $1/T$ for YSr$_2$Cu$_2$FeO$_{1+x}$.
Figure 11.11. Plot of log conductivity vs. 1/T for YSr$_2$Cu$_2$GaO$_7$.

Figure 11.12. Plot of log conductivity vs. 1/T for YSr$_2$Cu$_2$Co$_{0.8}$Fe$_{0.2}$O$_{7+x}$.
Figure 11.13. Plot of log conductivity vs. 1/T for $\text{YSr}_2\text{Cu}_2\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{7+x}$.

Figure 11.14. Plot of log conductivity vs. 1/T for $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Sr}_2\text{Cu}_2\text{CoO}_{7+x}$. 

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All samples exhibit semiconducting type behaviour up to intermediate temperatures. 
YSr$_2$Cu$_2$CoO$_7$ and YSr$_2$Cu$_2$Co$_{0.8}$Fe$_{0.2}$O$_{7+x}$ show semiconducting behaviour over the entire temperature range observed, although there is evidence for a small but significant jump in conductivity above 800 °C for these samples, most notably for YSr$_2$Cu$_2$CoO$_7$. This could possibly indicate some sort of structural transition, maybe an order-disorder transition on the oxygen sites which then influences charge transfer processes between the Cu (2) sites and CoO$_4$ tetrahedra. Data obtained recently from high temperature X-ray diffraction studies show that an orthorhombic-tetragonal transition occurs in this temperature range, corresponding to the jump in conductivity.$^8$

In contrast to YSr$_2$Cu$_2$CoO$_7$, both YSr$_2$Cu$_2$FeO$_{7+x}$ and YSr$_2$Cu$_2$GaO$_7$ exhibit apparent metallic type conductivity at elevated temperatures (above 402 °C for the former sample and above 535 °C for the latter), with the conductivity decreasing with increasing temperature, although, the decrease in conductivity is much smaller for YSr$_2$Cu$_2$GaO$_7$ compared to YSr$_2$Cu$_2$FeO$_{7+x}$. Consequently, the maximum conductivity occurs at intermediate temperatures for these two samples. Similarly YSr$_2$Cu$_2$Co$_{0.2}$Fe$_{0.8}$O$_{7+x}$ shows a maximum in conductivity at 708 °C. In this case however, the drop in conductivity with increase in temperature is even less pronounced. It is possible that the decrease in conductivity observed for YSr$_2$Cu$_2$FeO$_{7+x}$, YSr$_2$Cu$_2$Co$_{0.2}$Fe$_{0.8}$O$_{7+x}$ and YSr$_2$Cu$_2$GaO$_7$ may be a result of oxygen loss, resulting in a decrease in the number of available charge carriers within these systems. Thermogravimetric studies for the iron containing systems support this conclusion.

One unusual feature is that the conductivity observed for YSr$_2$Cu$_2$GaO$_7$ appears too high (the conductivity at room temperature is significantly higher than that of the comparable phase YSr$_2$Cu$_2$CoO$_7$), considering that it is a nominally “pure” Cu$^{2+}$ system. One possible explanation is that the sample prepared contains a small degree of non stoichiometry, and this requires further investigation, with a re-synthesis of this sample.
The conductivities for $Y_{0.8}Ca_{0.2}Sr_2Cu_2CoO_{7-x}$ and $YSr_2Cu_2CoO_7$ are similar in value at 900 °C. The conductivity for $Y_{0.8}Ca_{0.2}Sr_2Cu_2CoO_{7-x}$ is however much greater in value than for $YSr_2Cu_2CoO_7$ at low temperatures, indicating that doping with calcium helps improve conductivity at low temperatures, presumably due to the oxidation of the CuO$_2$ layers.

11.1.5 Chemical Compatibility with Electrolyte Materials: $YSr_2Cu_2CoO_7$, $YSr_2Cu_2FeO_{7+x}$ and $YSr_2Cu_2GaO_7$

The compatibility of samples $YSr_2Cu_2CoO_7$, $YSr_2Cu_2FeO_{7+x}$ and $YSr_2Cu_2GaO_7$ with current SOFC electrolyte materials YSZ, CeO$_2$ and LaGaO$_3$ was examined, alongside comparable studies with new potential electrolytes $La_{9.33}Si_6O_{26}$ and $La_{9.33}Ge_6O_{26}$. The studies were carried out initially at 900 °C, and repeated again at 1000 °C with $La_{9.33}Si_6O_{26}$, CeO$_2$ and LaGaO$_3$. The X-ray diffraction profiles for all three cuprate systems showed the formation of SrZrO$_3$ impurity phase after heating with YSZ for a period of one week at 900 °C. SrZrO$_3$ is an electrically insulating phase and therefore formation of this phase at the interface between the electrolyte and the cathode would present a major problem. It therefore seems as if these materials are not suitable for very high temperature SOFC operation (900 - 1000 °C) with YSZ electrolytes. It may be possible to use these materials at lower temperatures, although heating for a short time at elevated temperatures (900-1000 °C) is likely to be required to ensure bonding to the electrolyte.

Impurity phases were also formed on heating all three cuprate systems with $La_{9.33}Si_6O_{26}$ and $La_{9.33}Ge_6O_{26}$ over a period of one week at 900 °C. The peaks in the profiles were too poorly defined to identify the impurity phases after heating at this temperature. However, the impurity peaks became more resolved after sintering for a period of two weeks at 1000 °C. Some of the peaks could be assigned to $La_{1-x}Sr_xCu_1-yM_yO_3$ ($M =$ Co, Fe and Ga) perovskite-type phases. The nature of the other impurity phase(s) formed with the silicon and germanium based apatite materials was unclear owing to the complicated nature of the X-ray diffraction profiles, although it appears
to involve cross substitution between the apatite and cuprate. It is possible that yttrium and strontium will migrate onto the lanthanum site in the apatite systems and cobalt, iron and gallium will migrate onto the silicon or germanium site. These phases are likely to be mixed conductors. Therefore, although there is also reaction between the electrolyte and the cathode in the case of the apatite electrolytes, all the phases appear to be conducting, and so this is likely to be less of a problem than is the case for YSZ.

In the case of CeO₂ there was no obvious reaction with the cuprate samples at 900 °C. A reaction was observed on re-heating at 1000 °C for 80 hours, and became more significant on heating for a period of two weeks. In this case \( Y_{2-x}Ce_xSr_{2}Cu_{3-x}M_yO_{9+x} \) type impurity phases are formed (\( M = \text{Co}, \text{Fe}, \text{or Ga} \)). These impurity phases are likely to be mixed conductors, the presence of which would be much less likely to cause a problem, compared to \( \text{SrZrO}_3 \). Due to the formation of these phases it was decided to prepare and examine the conductivity of these phases, the details of which will be discussed later in this chapter.

In the case of \( \text{LaGaO}_3 \) there was no obvious reaction with the cuprate materials after heating for 1 week at 900 °C. They did not show any significant reaction until they were heated with \( \text{LaGaO}_3 \) for two weeks at 1000 °C. In all three cases the X-ray diffraction data suggested the formation of a mixed perovskite phase, \( \text{La}_{1-x}\text{Sr}_x\text{Cu}_1.y \text{M}_y \text{O}_3 \) (\( M = \text{Co}, \text{Fe} \) and \( \text{Ga} \)). However, the exact nature of the compositions in each case is unclear, although they are likely to be good mixed conductors. The formation of \( \text{Y}_2\text{Cu}_2\text{O}_5 \) was also observed for the reaction of \( \text{YSr}_2\text{Cu}_2\text{CoO}_7 \) and \( \text{YSr}_2\text{Cu}_2\text{GaO}_7 \) with \( \text{LaGaO}_3 \). \( \text{Y}_2\text{Cu}_2\text{O}_5 \) is likely to be a poor mixed conductor. It therefore seems as if \( \text{YSr}_2\text{Cu}_2\text{CoO}_7 \) and \( \text{YSr}_2\text{Cu}_2\text{GaO}_7 \) are not suitable for very high temperature SOFC operation (900 - 1000 °C) with \( \text{LaGaO}_3 \) based electrolytes.
11.1.6 Conductivity Data for Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}CoO_{9+x} and Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}FeO_{9+x}

Since the reaction with CeO_2 gave impurity phases presumed to be Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}CoO_{9+x} and Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}FeO_{9+x}, it was decided to prepare these phases and examine their conductivities as a function of $\rho$(O_2) and temperature. Table 11.4 shows data on the $\rho$(O_2) dependence and conductivities taken at 900 °C for these samples. Data for YSr_{2}Cu_{2}CoO_{7} and YSr_{2}Cu_{2}FeO_{7+x} is also included in this table for comparison. Figures showing plots of log ($\sigma$/ S cm$^{-1}$) vs. log ($\rho$(O_2) / atm) for samples Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}CoO_{9+x} and Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}FeO_{9+x} are shown below in figures 11.15 and 11.16. As previously mentioned, conductivity values obtained at low $\rho$(O_2) (log ($\rho$(O_2) / atm) = 10$^{-5}$ to 10$^{-3}$) are not equilibrium values, since for this $\rho$(O_2) range leakage of the measurement cell was too fast, as indicated by the hysteresis in oxidation/reduction curves. This hysteresis response indicates poor equilibration, normally attributed to either poor oxide ion conduction or oxygen surface exchange, or a combination of these two factors. The phase purity of both samples was confirmed by X-ray diffraction after the conductivity measurements were completed.

Table 11.4. Conductivities and average gradient of the plot of log $\sigma$ vs. $\rho$(O_2) for selected cuprate samples.

<table>
<thead>
<tr>
<th>Sample (Nominal Composition)</th>
<th>Temp. / °C</th>
<th>Gradient</th>
<th>$\sigma$/S cm$^{-1}$ (Air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}CoO_{9+x}</td>
<td>900</td>
<td>0.33</td>
<td>13.95</td>
</tr>
<tr>
<td>YSr_{2}Cu_{2}CoO_{7}</td>
<td>900</td>
<td>0.08</td>
<td>13.71</td>
</tr>
<tr>
<td>Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}FeO_{9+x}</td>
<td>900</td>
<td>0.44</td>
<td>8.94</td>
</tr>
<tr>
<td>YSr_{2}Cu_{2}FeO_{7+x}</td>
<td>900</td>
<td>0.37</td>
<td>6.38</td>
</tr>
</tbody>
</table>

The conductivities of Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}CoO_{9+x} and Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}FeO_{9+x} show high $\rho$(O_2) dependence at 900 °C as can be seen from table 11.4. The $\rho$(O_2) dependence of these phases containing fluorite blocks is greater than for the respective simple perovskite phases, although the conductivities recorded in air are similar in value. This, again, may suggest a redistribution of dopant over the two Cu sites in reducing conditions.
Figure 11.15. Plot of log conductivity vs. log $\rho(O_2)$ for Y$_{1.8}$Ce$_{0.2}$Sr$_2$Cu$_2$CoO$_{9+x}$ at 900 °C.

Figure 11.16. Plot of log conductivity vs. log $\rho(O_2)$ for Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$FeO$_{9+x}$ at 900 °C.

Plots of log ($\sigma$ / S cm$^{-1}$) vs. 1 / T (K) for the samples Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$CoO$_{9+x}$ and Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$FeO$_{9+x}$ are shown below in figures 11.17 and 11.18.
The conductivity of $Y_{1.5}Ce_{0.5}Sr_2Cu_2CoO_{9+x}$ remains approximately constant ($\approx 40 \text{ S cm}^{-1}$) over the temperature range 190 to 460 °C. The decrease in conductivity could again be related to oxygen loss causing a decrease in the number of charge carriers,
although further work is needed to confirm this. Alternatively the changes could be due to the effect of changes in the charge transfer between Cu and Co sites. This sample then shows apparent metallic type conductivity with further increase in temperature up to 900 °C. In contrast $Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}FeO_{9+x}$ shows apparent metallic conductivity across the temperature range studied. The fact that the conductivity decreases continuously from room temperature suggests that this sample may indeed be metallic. The increase in the gradient of the change in conductivity at $\approx 480 °C$ may be related to oxygen loss, or changes in the charge transfer between Cu and Fe sites. The increase in room temperature conductivity for both samples compared to $YSr_{2}Cu_{2}MO_{7+x}$ ($M = Co$, Fe) can be attributed to oxidation of the CuO$_2$ layers: we are replacing $Y^{3+}$ by $(Y_{1.5}Ce_{0.5}O_{2})^{2.5+}$ giving rise to an oxidation of the CuO$_2$ layers to charge balance.

11.1.7 Summary

Six cuprate systems $YSr_{2}Cu_{2}CoO_{7}$, $YSr_{2}Cu_{2}Co_{0.8}Fe_{0.2}O_{7+x}$, $YSr_{2}Cu_{2}Co_{0.2}Fe_{0.8}O_{7+x}$, $YSr_{2}Cu_{2}FeO_{7+x}$, $YSr_{2}Cu_{2}GaO_{7}$ and $Y_{0.8}Ca_{0.2}Cu_{2}CoO_{7-x}$ have been studied in detail. Moderately high total conductivities in the range 4 - 14 S cm$^{-1}$ at 900°C have been observed, as well as interesting variations of conductivity with both temperature and $\rho$(O$_2$). All six cuprate samples tested showed a significant hysteresis for the conductivity in moving from oxidising to reducing conditions. This indicates poor equilibration between sample and atmosphere, normally attributed to low oxide ion conductivity, poor oxygen surface exchange, or a combination of these two factors. Another explanation, however, could be the redistribution of dopant over the two Cu sites in reducing conditions. The explanations behind the $\rho$(O$_2$) and temperature dependence of the samples require further investigation. Although, again, the redistribution of dopant over the two Cu sites could be playing a major role in some cases.

The presence of calcium appears to enhance conductivity at low temperature, as does the incorporation of cerium as part of a fluorite type layer between the CuO$_2$ sheets.
This is consistent with such doping strategies leading to oxidation of the CuO$_2$ layers, as expected.

In terms of chemical compatibility with potential electrolyte materials for use in SOFCs, YSr$_2$Cu$_2$CoO$_7$, YSr$_2$Cu$_2$FeO$_{7+x}$, and YSr$_2$Cu$_2$GaO$_7$ were all shown to react with YSZ to form the insulating impurity phase SrZrO$_3$. The reaction of these systems with La$_{9.33}$Si$_6$O$_{26}$, La$_{9.33}$Ge$_6$O$_{26}$ and CeO$_2$ formed phases that are likely to be mixed conductors. Therefore it may be possible to use these cuprates as cathodes with such electrolytes. The cuprates were also shown to react with LaGaO$_3$ to form La$_{1-x}$Sr$_x$Cu$_{1-y}$M$_y$O$_3$ type impurity phases that are also likely to be good mixed conductors. The reaction with LaGaO$_3$ however, also resulted in the formation of Y$_2$Cu$_2$O$_5$, which is likely to be insulating in nature, and so again could cause problems.

**11.1.8 Conclusion**

The results suggest that the cuprate samples tested are not promising candidates as replacement cathode materials for use in high temperature solid oxide fuel cells. The main reasons being that they all show only moderately high conductivity, and exhibit large hysteresis between conductivities on changing from reducing to oxidising conditions, suggesting either poor oxide ion conduction/surface exchange characteristics or major structural change. Furthermore, significant impurity phases are produced between all these cuprate phases and currently favoured electrolyte materials. It may be possible that some of these cuprate materials are of potential use as cathode materials in moderate temperature fuel cells, and this would need to be examined.
11.2 References


8 H.A. Rudge-Pickard; *unpublished work*, University of Surrey, (2003).
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Chapter 12.0: Update of Latest Research and Future Work

12.1 Latest Research

12.1.1 Results from Modelling Studies

Recent studies based on atomistic simulations performed at the University of Surrey have shown that the high conductivity and low activation energy observed for La\textsubscript{9.33}Si\textsubscript{6}O\textsubscript{26} is related to a conduction mechanism, which occurs via the migration of interstitial oxide ions. The oxide ions appear to follow a non-linear sinusoidal type mechanism along the direction of the z-axis of the unit cell. Conversely, the low conductivity and high activation energy observed for La\textsubscript{8}Sr\textsubscript{2}Si\textsubscript{6}O\textsubscript{26} is accounted for by a conduction mechanism, which occurs primarily via vacancy migration of oxide ions. In this case the oxide ions appear to follow a linear pathway along the direction of the z-axis of the unit cell.\textsuperscript{1,2}

12.1.2 La-Ge-O Based Systems

Work by Leon-Reina et al. has confirmed the conclusions from our studies on the La-Ge-O system that the conducting phase is apatite-type. This group has succeeded in fitting the high temperature sintered phase to a complex pseudohexagonal triclinic apatite structure. The cell parameters for La\textsubscript{9.75}Ge\textsubscript{6}O\textsubscript{26.62} are $a = 9.9368(4)$ Å, $b = 9.9220(3)$ Å, $c = 7.2925(2)$ Å, $\alpha = 90.566(3)\degree$, $\beta = 88.992(4)\degree$, $\gamma = 120.3340\degree$ and the unit cell volume $= 620.460$ Å\textsuperscript{3}.\textsuperscript{3}
12.2 Future Work

12.2.1 Accounting for Changes in Activation Energy

Conductivity studies have revealed that many of the apatite samples tested in this work show a change in activation energy at elevated temperatures, e.g. $\text{La}_{9.67}\text{Ge}_{5}\text{BO}_{26}$ (chapter 10). High temperature structural investigations are required to help explain the origin of such changes. Neutron diffraction data has been collected recently in this respect.

12.2.2 Optimisation of Conductivities and Pellet Production

In an attempt to limit germanium loss from germanium based apatite systems the mechanism behind the volatility of germanium loss needs to be investigated. The benefit of limiting this loss would be to enhance conductivity and minimise the activation energy, by reducing contributions from insulating phases such as $\text{La}_2\text{GeO}_5$ at the grain boundary.

In an attempt to improve the conductivity and reduce the activation energy of both germanium and silicon based apatite systems, lower temperature synthesis techniques such as sol-gel will be investigated for the phases already displaying high conductivities. If successful this should both minimise the co-formation of impurity phases, e.g. $\text{La}_2\text{GeO}_5$ in the case of germanium based systems, and aid pellet sintering by reducing the particle size.

Further work is also required on the mixed silicon/germanium systems $\text{La}_{9.33}\text{Si}_{6-x}\text{Ge}_x\text{O}_{26}$, $\text{La}_{8.67}\text{BaSi}_{6-x}\text{Ge}_x\text{O}_{26}$ and $\text{La}_9\text{BaSi}_{6-x}\text{Ge}_x\text{O}_{26.5}$ in order to fully account for the unusual changes observed in cell parameters on sintering.

Gallium doping into $\text{La}_{9.33}\text{Ge}_5\text{O}_{26}$ showed a reduction in oxide ion conductivities. This in part might be related to the fact that the pellets used for conductivity testing were porous. Since gallium doping appears to destabilise the hexagonal apatite
phase, these pellets were not sintered at high temperatures. With the identification of the triclinic cell by Leon-Reina et al., further work could be performed on these phases to determine if they are in fact single phase, and to obtain more accurate conductivity data on samples which have been sintered at high temperatures.

12.2.3 Utilisation of La$_9$BaSi$_6$O$_{26.5}$ as an Electrolyte Material for use in SOFCs

Before La$_9$BaSi$_6$O$_{26.5}$ can be utilised as an electrolyte material in SOFCs it needs to be matched to suitable cathode and anode materials. To this end the thermal expansion coefficient of La$_9$BaSi$_6$O$_{26.5}$ needs to be determined and compared with that of electrode materials currently available. If such a match is forthcoming then compatibility studies followed by cell testing can be performed. In addition to the simple electrode material, composite electrodes with La$_9$BaSi$_6$O$_{26}$ will be tested.

Another approach is to develop electrode materials, based on La$_9$BaSi$_6$O$_{26.5}$. Any promising compositions will therefore inherently be chemically compatible and hopefully have similar expansion coefficients. This will be attempted by doping transition metals into La$_9$BaSi$_6$O$_{26.5}$ in order to enhance their electronic and catalytic properties. Catalytic testing will then be performed on promising compositions. Upon successful identification of a chemically and mechanically compatible set of fuel cell components, single cell tests can then be performed.

Finally it is also necessary to demonstrate the commercial viability of such cells. Part of this study should include experimenting with various cost effective production techniques, such as tape casting of the electrolyte material in planar electrolyte supported cells, followed by plasma spraying and/or screen printing of the electrodes. In view of an increased interest in anode supported cells, owing to their potential for lower temperature operation, these could be prepared using wet slip-casting techniques for the anode, followed by screen printing and co-firing of the electrolyte, and screen printing and sintering of the cathode.\textsuperscript{4}
12.2.4 Cuprate Work

The relatively high conductivity observed for YSr$_2$Cu$_2$GaO$_7$ requires further investigation, to determine if this is due to a slight degree of non-stoichiometry.

The conductivity of Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$CoO$_9$+x remains approximately constant ($\approx 40$ S cm$^{-1}$) over the temperature range 190 to 460 °C. However, the conductivity of this system shows a decrease in value above 460 °C. Further work is therefore needed to confirm whether this decrease in conductivity is related to oxygen loss causing a decrease in the number of charge carriers, or alternatively, due to the possible effect of changes in the charge transfer between Cu and Co sites.
12.3 References

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Chapter 13.0: Summary of Conclusions: Apatite Systems

13.1 Preliminary Results: Silicate Systems

Neutron diffraction studies reveal that apatite systems are complex in their structure, particularly within the channel oxygen sites. It appears as if the lower conductivity and higher activation energy in $\text{La}_9\text{Sr}_2\text{Si}_6\text{O}_{26}$ compared to $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ is due to the fact that the channel oxygen atoms are essentially ordered close to the ideal $(0,0,0.25)$ sites in the former, while the latter contains significant oxygen displacements. It is possible that the reason for this difference is the presence of significant cation vacancies in $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$.

13.1.1 Doping Studies: Silicate Systems

It is possible to prepare alkaline earth doped hexagonal apatite phases $(\text{La/M})_{10-x}\text{Si}_6\text{O}_{26+y}$ ($M = \text{Ca}, \text{Sr}, \text{or Ba}$) by synthesis at $1350^\circ\text{C}$. The importance of non-stoichiometry, in the form of cation vacancies or excess oxygen, in lanthanum silicate based apatite systems was reinforced by the results from conductivity studies. They help to confirm that systems containing oxygen excess offer the highest conductivities. In addition, they suggest that unit cell size may also be an important factor for oxide ion conduction, with the barium doped sample that contains oxygen excess, $\text{La}_9\text{BaSi}_6\text{O}_{26.5}$, showing higher conductivity than the magnesium, calcium and strontium doped analogues. Conversely, systems containing oxygen vacancies appear to be very poor oxide ion conductors. Indeed, they show the lowest conductivities and highest activation energies of all, suggesting that interstitial oxide ion defects, rather than oxygen vacancies, are the key to high oxide ion conduction in apatite phases.

It is also possible to prepare trivalent doped single-phase hexagonal apatite phases in the range $\text{La}_{9.33}x\text{Si}_6y(\text{Ga/B})_z\text{O}_{26}$ ($0 \leq y \leq 2$). These samples were prepared at $1350^\circ\text{C}$. Results from conductivity studies add further support to the importance of the presence of cation vacancies, and/or excess oxygen, for fast oxide ion conduction in these apatite-type phases. In the case of gallium doping, there appears to be an optimum level of cation vacancies for maximum conductivity ($\text{La}_{9.83}\text{Si}_{4.5}\text{Ga}_{1.5}\text{O}_{26}$).
However, phases containing nominal oxygen excess show the highest oxide ion conductivity, with La$_{10}$Si$_5$GaO$_{26.5}$ exhibiting the highest conductivity recorded for these gallium doped systems. It is presumed that, in both the highly conducting cation deficient and oxide ion excess samples, there are interstitial oxide ion defects, which mediate the oxide ion conduction, which will be confirmed by refinement of neutron diffraction data collected for these samples.

Interestingly, higher conductivities are observed in cation deficient systems where the dopant ion with a lower valence is located on the silicon site rather than for related systems where the dopant ion is on the lanthanum site, i.e. $\sigma$ La$_{9.67}$Si$_3$MO$_{26}$ > $\sigma$ La$_{8.67}$MSi$_6$O$_{26}$.

### 13.2 Germanium Systems

The hexagonal apatite-type La$_{9.33}$Ge$_6$O$_{26}$ can be prepared at moderate temperatures, 1150 °C, and shows high oxide ion conductivity. Heating to high temperatures, however, results in peak broadening, which increases with sintering temperature and time, such that it resolves into clear extra peaks. Prolonged heat treatment at high temperatures leads to a large change in X-ray diffraction profile and the formation of a La$_2$GeO$_5$ type system. These changes have been attributed to loss of Ge at high temperatures, which is a significant problem for the potential use of these materials in SOFCs.

### 13.2.1 Doping Studies: Germanium Systems

Doping La-Ge-O apatite systems with a range of ions (Mg, Ca, Sr, and Ba on the La site, and B on the Ge site) appears to help stabilise the hexagonal apatite lattice to high temperatures. Magnesium, calcium and barium doping appear to be the most successful in this respect, providing that the sintering time is kept short. However, extended sintering studies at high temperature studies show that although these dopant ions do help to stabilise the hexagonal phase, the problem of germanium loss is still not eliminated.
In contrast to boron doping, gallium doping on the germanium site does not appear to stabilise the hexagonal phase. Preliminary work on related systems, where comparatively sized ions to gallium (iron and cobalt) have been doped onto the germanium site, gave similar results, suggesting that the size of the dopant on the germanium site is important to the stability of these systems.

As with the silicate apatite phases, systems that contain cation vacancies or oxygen excess appear to be very good oxide ion conductors, whereas stoichiometric systems appear to be poor oxide ion conductors. The apparent high oxide ion conductivity observed for the nominally stoichiometric La$_8$Mg$_2$Ge$_6$O$_{26}$ appears to be due to this phase containing a small degree of non-stoichiometry, due to the solubility limit being exceeded, as shown by the presence of Mg$_2$GeO$_4$ impurity in the neutron diffraction data.

### 13.3 Mixed Silicon/Germanium Systems

The results show that, in terms of conductivity at 800 °C, the optimum nominal starting Si to Ge ratio for La$_{9.33}$Si$_6$Ge$_x$O$_{26}$ (0 ≤ x ≤ 6) appears to be 0.5 (x = 4). The conductivity of this composition, La$_{9.33}$Si$_2$Ge$_4$O$_{26}$, is 0.06 S cm$^{-1}$, which is higher than that of YSZ at this temperature making it a possible candidate as an electrolyte material for use in SOFCs. The presence of silicon in the samples appears to inhibit broadening of the apatite peaks in the X-ray diffraction profiles. The obvious deviation of the cell parameters from Vegard’s law for the samples high in germanium content suggests that germanium loss becomes more significant with increasing germanium content. The mixed silicon/germanium systems are therefore still subject to problems related to germanium loss, although this loss appears to be less severe when compared to the end member of the series, La$_{9.33}$Ge$_6$O$_{26}$ (x = 6), as indicated by extended sintering studies on La$_{9.33}$Si$_2$Ge$_4$O$_{26}$.
13.3.1 Doping Studies: Mixed Silicon/Germanium Systems

X-ray diffraction studies suggest that the inclusion of barium into mixed germanium/silicon apatite systems limits broadening of the apatite peaks, but does not ultimately prevent germanium loss. Conductivity studies indicate that La$_{8.67}$BaSi$_4$Ge$_2$O$_{26}$ and La$_{8.67}$BaSi$_3$Ge$_3$O$_{26}$, where $x = 2$ and 3, are the optimum compositions in terms of conductivity at high temperature (800 °C) for the La$_{8.67}$BaSi$_{6-x}$Ge$_x$O$_{26}$ ($0 \leq x \leq 6$) range of samples. As with previous findings, systems containing excess oxygen appear to offer the best properties in terms of oxide ion conductivity. In the case of the La$_9$BaSi$_{6-x}$Ge$_x$O$_{26.5}$ series, the La$_9$BaSi$_6$O$_{26.5}$ composition appears to be the optimum phase in terms of both oxide ion conductivity and activation energy. This phase shows significantly higher conductivity than YSZ at 500 °C making it a potential replacement material to YSZ, for use as an electrolyte in intermediate temperature fuel cell applications.
13.4 List of Publications Resulting from this Work


3. Synthesis and conductivities of the apatite-type systems, $\text{La}_{9.33+x}\text{Si}_{6-y}\text{M}_y\text{O}_{26+z}$ (M=Co, Fe, Mn) and $\text{La}_9\text{Mn}_2\text{Si}_{6}\text{O}_{26}$; J. McFarlane, S. Barth, M. Swaffer, J.E.H. Sansom, P.R. Slater; Ionics 8, 149-154, 2002.

4. The synthesis and conductivities of the new apatite-type phases $\text{La}_{10-x}\text{Si}_{6-y}\text{Ga}_y\text{O}_{26+z}$ and related systems; J.E.H. Sansom and P.R. Slater; Proc. 5th Euro SOFC forum 2, 627-634, 2002.


11. Synthesis and structural characterisation of apatite-type oxide ion conductors La$_{10-x}$Si$_6$O$_{26+y}$ doped with Ga; J.R. Tolchard, J.E.H. Sansom, P.R. Slater and M.S. Islam; submitted to Solid State Ionics.


13. Oxide ion conductivity in mixed Si/Ge based apatite-type systems; J.E.H. Sansom, A. Najib, P. R. Slater; submitted to Solid State Ionics.