A Thesis Submitted for the Degree of PhD at the University of Warwick

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Microscopic Mechanisms in Multiferroic Materials

by

Gabriel Richard Michael Clarke

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry

University of Warwick, Department of Chemistry

March 2022
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Acknowledgements

I don’t think I knew exactly how much of a challenge I was signing up for when I started my PhD, and I owe thanks to many people for their support. To begin with, I would like to extend huge thanks to Mark Senn for permitting me to take on this project and for taking the time to teach me. Though my work occasionally took a bit longer than I’d expected (this thesis included!), his patience, enthusiasm and encouragement were invaluable. No part of this thesis would exist without him.

The knowledge and experience of all of the academic staff at Warwick were enormously helpful. In particular, I am grateful to Professor Richard Walton for helpful discussions on all of my projects, and Dr Martin Lees for his assistance with magnetometry. Thanks are also due to Dr David Walker and Dr Steve Huband for their assistance and chats in the X-ray suite. During these projects, I’ve had the pleasure of working with collaborators from all over the world. Their expertise and assistance have all enhanced this thesis, and I would like to thank all of the beamline staff at I11, PEARL, GEM and D2B for their help with the work presented in Chapters 2 and 3, the staff at I15 for Chapter 4, and Dr John Daniels, Scarlet Kong, and all of the staff at ID15A for their help with the experimental work in Chapter 5. I’d like to acknowledge the expertise offered by Dr Wei-Tin Chen and Dr Clemens Ritter, as well as thank everyone I was lucky enough to get to know during the long weekends on BAG time at I11, especially Dr Simon Cassidy and the Oxford contingent.

Moving on to the Senn group: I’m thankful to have had the chance to work with you all. I love you all. Tobie, I couldn’t have asked for a better friend when I started at Warwick. You might not be the most talkative PhD student I’ve ever met (not before a few pints, anyway), but you’re definitely the most knowledgeable and reliable. Thank you for patiently wading through so many of my terrible Python scripts to find a very obvious bug that I’d missed and for mostly targeting your sarcasm at Jere. I owe you more beer and tea than I can remember.

To Fernando: I miss you and your calm presence in the office! Thank you for all of your talks on crystallography, magnetism, and the benefits of rice cakes and dulce de leche. I hope your adventure into the world of cheesemaking is lucrative and enjoyable. Chris, I didn’t get to spend as much time with you as I would have liked, but I enjoyed what time we had. Without you, I still wouldn’t be able to code! Jere, I’m grateful for many things. Your scientific and professional advice are always sound, especially where lab safety is concerned. Thank you for putting up with all of my complaining and for being so generous with coffee and snacks. Thank you for expanding my music library, and I’m sorry for not yet joining the cult of HiFi! I’ll send you the contents of the HR Jar after my viva. Anna, you’re going to be fine. I’ve never
met anyone as bright and level-headed, and I’m fairly certain I’ve never taught you anything you didn’t already know. I wish you all the best in your new postdoc and beyond. You’re going to smash it. Dash, your enthusiasm and energy are infectious, but you’re never going to trick me into playing a MOBA. I hope you continue to enjoy the small victories when they happen and make sure everyone takes a break every once in a while. Ben and Evie: I would’ve loved to spend some more time in the group to get to know you guys better. Keep Jere on his toes.

I’m grateful to have friends with whom I get to talk about things other than crystallography. Special mentions go out to Scott, Gerald and all the FoDs, as well as the Chaplins for taking a chance and inviting me along to so many things.

I would like to say an extra thank-you to every single member of staff at the University Hospital Coventry & Warwickshire, especially Mr Sumit Sood and the colorectal nurses. Receiving a bowel cancer diagnosis at 26 was unfortunate, but having it happen during a pandemic, midway through writing up my PhD thesis and several weeks before plans to move house was just ridiculous! I’m happier than I can express to be cancer-free going into 2022 and the future. On a related note, I’m extremely grateful to Dr Ruth Webster, who was kind enough to offer me a desk in her group’s office at the University of Bath to finish this thesis while I recovered. Every single member of her group welcomed me with open arms, and I cannot thank them enough, but I’ll keep sending baked goods and hope for the best!

My family have been there for me for my entire life, and I definitely can’t sum everything up in a paragraph, but here goes: Mum and Dad, thank you for emotional and financial support and for encouraging my curiosity and education from day zero. Francis, Joe and Dan: thank you for keeping me sane, driving me around, and just generally making me laugh. Laughter is the best medicine, except when you’ve just had major surgery on your abdomen. Gemma and the sprogs: thank you for helping me forget the PhD stress by being Uncle Gabe every now and then. To friends and family who haven’t been mentioned by name, don’t worry. I didn’t forget you, I just ran out of space.

Last, but not least: Tom. You’re my best friend, and a better partner than I would dare to ask for. Thank you for sharing the ups and the downs from the last four and a half years, for proofreading, cooking and cleaning when I couldn’t, and energising me when I needed it. Your support and encouragement means the world, and I couldn’t have done this without you.
Declaration of Collaborative and Published Work

This thesis is submitted to the University of Warwick in support of my application for the degree of Doctor of Philosophy. It has been composed by myself and has not been submitted in any previous application for any degree.

The work presented (including data generated and data analysis) was carried out by the author except in the cases outlined below:

- The high-pressure time-of-flight powder neutron diffraction experiments on Sr$_2$Ca$_3$Mn$_4$O$_{15}$ (described in Chapter 2) were performed at PEARL by Dr Nick Funnell, ISIS.
- An unsuccessful attempt at synthesising Ba$_7$Mn$_4$O$_{15}$ under high-pressure conditions (described in Chapter 2) was performed by Dr Wei-Tin Chen, Center for Condensed Matter Sciences, National Taiwan University.
- Data collection for the low-temperature powder neutron diffraction experiment on Ba$_7$Mn$_4$O$_{15}$ were performed at GEM by Dr Ivan da Silva, ISIS.
- Data collection for the magnetisation versus field experiment on Ba$_7$Mn$_4$O$_{15}$ were performed by Dr Martin Lees, University of Warwick.
- Data collection for the high-pressure experiment on Ca$_3$Ti$_2$O$_7$ and Ca$_3$Mn$_2$O$_7$ (Chapter 4) was performed by Dr Mark Senn, University of Warwick and Dr Dominik Daisenberger, I15, Diamond Light Source, with assistance from Dr Claire Murray, Diamond Light Source and Ms Sarah Craddock.
- *Ab initio* calculations were performed on the Ca$_3$Ti$_2$O$_7$ n = 2 Ruddlesden-Popper phase (described in Chapter 4) by Dr Nicholas Bristowe, Department of Physics, Durham University.

Parts of this thesis have been published by the author:

Abstract

Ferroic materials are of fundamental importance in the modern world with applications ranging from sensors to computational memory and beyond, and multiferroic materials displaying several ferroic properties simultaneously have a great deal of potential for future devices. The antiferromagnetic Sr$_7$Mn$_4$O$_{15}$ phase was recently identified as a potential multiferroic material. Chapters 2 and 3 explore the synthetic conditions necessary to expand the solid solution Sr$_7$A$_x$Mn$_4$O$_{15}$ for A: Ca$^{2+}$ and Ba$^{2+}$. The structure is investigated using X-ray and neutron diffraction methods under variation of chemical substitution, temperature and hydrostatic pressure. Magnetic analysis is also performed using direct current magnetic susceptibility measurements, and long-range spin orderings are identified using low-temperature neutron diffraction experiments. Several novel compositions are synthesised and characterised; in particular, the Ba$_7$Mn$_4$O$_{15}$ composition described in Chapter 3 exhibits a magnetoelectric ground state below 50 K.

The second half of this thesis is concerned with the responses of hybrid improper ferroelectric n = 2 Ruddlesden-Popper phases to hydrostatic pressure and electric fields. Chapter 4 describes a high-pressure experiment on Ca$_3$Mn$_2$O$_7$ and Ca$_3$Ti$_2$O$_7$, with accompanying computational analysis showing that both phases undergo a ferroelectric phase transition to a non-polar phase above 1 GPa and 30 GPa, respectively. Despite this, the relative energies of the polar and non-polar phases unexpectedly show that the polar phase is actually stabilised by increased pressure, meaning that the polarisation itself may increase with pressure up to a limit, contrary to the trend normally observed in proper ferroelectrics.

Chapter 5 reports an in situ synchrotron X-ray diffraction experiment on the substituted phase Ca$_{2.15}$Sr$_{0.85}$Ti$_2$O$_7$ in which compressed powder samples were subjected to an applied electric field while diffraction patterns were measured. The output time-resolved data are analysed to attempt to identify how ferroelectric switching may proceed in this and related phases, with octahedral rotations being identified as a plausible pathway. Throughout all chapters, the symmetries and phase transitions of the various materials are analysed through representation analysis.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Antiferromagnetic</td>
</tr>
<tr>
<td>BVS</td>
<td>Bond Valence Sum</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin Zone</td>
</tr>
<tr>
<td>cgs</td>
<td>centimetre-gram-second</td>
</tr>
<tr>
<td>.cif</td>
<td>Crystallographic Information File</td>
</tr>
<tr>
<td>DAC</td>
<td>Diamond Anvil Cell</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DM</td>
<td>Dzyaloshinskii-Moriya</td>
</tr>
<tr>
<td>ESRF</td>
<td>European Synchrotron Radiation Facility</td>
</tr>
<tr>
<td>FC</td>
<td>Field-Cooled</td>
</tr>
<tr>
<td>FE</td>
<td>Ferroelectric</td>
</tr>
<tr>
<td>FM</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>HIF</td>
<td>Hybrid Improper Ferroelectric</td>
</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
</tr>
<tr>
<td>ILL</td>
<td>Institut Laue-Langevin</td>
</tr>
<tr>
<td>IUCr</td>
<td>International Union of Crystallography</td>
</tr>
<tr>
<td>irrep</td>
<td>Irreducible Representation</td>
</tr>
<tr>
<td>MAC</td>
<td>Multi-Analyser Crystal</td>
</tr>
<tr>
<td>OP</td>
<td>Order Parameter</td>
</tr>
<tr>
<td>OPD</td>
<td>Order Parameter Direction</td>
</tr>
<tr>
<td>PASCAl</td>
<td>Principal Axis Strain Calculator</td>
</tr>
<tr>
<td>PE</td>
<td>Paraelectric</td>
</tr>
<tr>
<td>PND</td>
<td>Powder Neutron Diffraction</td>
</tr>
<tr>
<td>PSD</td>
<td>Position-Sensitive Detector</td>
</tr>
<tr>
<td>RP</td>
<td>Ruddlesden-Popper</td>
</tr>
<tr>
<td>SI</td>
<td>Système International</td>
</tr>
<tr>
<td>SOJT</td>
<td>Second-Order Jahn-Teller</td>
</tr>
<tr>
<td>SQuID</td>
<td>Superconductive Quantum Interference Device</td>
</tr>
<tr>
<td>TOF</td>
<td>Time-Of-Flight</td>
</tr>
<tr>
<td>VT</td>
<td>Variable-Temperature</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-Ray Diffraction</td>
</tr>
<tr>
<td>ZFC</td>
<td>Zero Field-Cooled</td>
</tr>
</tbody>
</table>
Chapter 1. Introduction

1.1 Overview
One of the fundamental aims of all solid-state chemistry is the targeted generation and control of functionality. The vast array of functional materials which are ubiquitous in daily life are the result of years of research spent working towards the understanding and tuning of properties, from relatively straightforward characteristics such as hardness and colour to the more arcane aspects intrinsic to modern technologies such as ferroelectricity and magnetism. The unifying factor in all of these is that to control the behaviour of a material, one must understand the structure-property relationships associated with it. In this introductory chapter, the essential concepts underpinning solid-state chemistry will be described, followed by overviews of the methods used in this thesis such as diffraction experiments and representation analysis, followed by an introduction to ferroic materials illustrated with relevant examples from the literature. For additional details, the interested reader is referred to the works of Cotton1, Molloy2 and Clegg et al.3

1.2 Fundamentals of Crystallography

1.2.1 Crystal Structure
The current definition of a crystal endorsed by the International Union of Crystallography (IUCr) is split into two (theoretically equivalent) parts: the direct-space definition states that a solid compound is a crystal if its constituent particles (atoms, ions, or molecules) form, on average, a long-range ordered arrangement. The reciprocal-space definition states that a material is a crystal if it has an essentially sharp diffraction pattern notwithstanding diffuse scattering. Mathematically, a crystal can be described as a convolution of a lattice with a motif, and its diffraction pattern is related to the Fourier transform of this construction. A simple 2-dimensional representation of convolution is shown in Figure 1.1.

![Figure 1.1 A convolution of a 2-dimensional lattice of points (marked with black dots) with a smiley face motif.](image-url)
In three dimensions the relative positions of the lattice points are described by the basis vectors \( \mathbf{a}, \mathbf{b} \) and \( \mathbf{c} \). The location of electron density within a motif may be found according to:

\[
\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}
\]

For real crystals, the motif which is convoluted with the lattice is a repeating array of atoms or ions which are contained within a unit cell: the smallest repeating unit which contains the full symmetry of the crystal structure. The choices of origin and orientation for the unit cell are not unique; instead, different choices may be made depending on which aspects of the structure the crystallographer wishes to emphasise, such as specific symmetry elements. A symmetry element is a geometrical entity (such as a point or plane) within an assemblage (such as a unit cell) upon which a symmetry operation may be applied to convert the assemblage to a state which is indistinguishable from the initial state. For example, the square shown in Figure 1.2 appears identical after a fourfold rotation about point P, but each of its corners has been shifted by one position anticlockwise.

![Figure 1.2 Example of a fourfold rotation operation about point P.](image)

The choice of origin in unit cells commonly place symmetric operators at special positions such as corners and edge centres. The size and shape of the unit cell is described by the lattice parameters: three edge lengths \( a, b \) and \( c \) and three angles: \( \alpha \) is the angle between the \( b \) and \( c \) directions, \( \beta \) is the angle between the \( a \) and \( c \) directions and \( \gamma \) is the angle between the \( a \) and \( b \) directions.

### 1.2.2 Crystal Systems

In addition to the translational symmetry between unit cells, various symmetry elements may be present in a unit cell, and it is these which truly determine how the cell is described. For example, a unit cell which possesses four intersecting threefold axes of rotation must be cubic. This does not necessarily apply in reverse, as a cell with all three sides of equal length and three right angles may have atoms arranged in such a way as to prohibit all of the required threefold rotations. Unit cells which geometrically approximate a given crystal system but which lack the essential symmetry are described as pseudo-symmetric. The
essential symmetry is what truly defines the seven crystal systems, which are summarised in Table 1.1.

Table 1.1 The lattice parameters, essential symmetry, permitted centring and primary axes for each of the seven crystal systems using standard settings. Note that ≠ in this table means ‘not necessarily equal’. It is possible for two lattice parameters to be serendipitously equal, but where ≠ is indicated, it is not required for the given crystal system.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Lattice parameters</th>
<th>Essential symmetry</th>
<th>Permitted centrings</th>
<th>Primary axis</th>
</tr>
</thead>
</table>
| Cubic              | \( a = b = c \)  
                   | \( a = \beta = \gamma = 90^\circ \) | Four threefold axes | P, F, I       | \( a \) |
| Tetragonal         | \( a = b \neq c \)  
                   | \( a = \beta = \gamma = 90^\circ \) | One fourfold axis  | P, I          | \( c \) |
| Orthorhombic       | \( a \neq b = c \)  
                   | \( a = \beta = \gamma = 90^\circ \) | Three twofold axes or mirror planes | P, F, I, A   | \( c \) |
| Hexagonal          | \( a = b \neq c \)  
                   | \( a = \beta = \gamma = 90^\circ \) | One sixfold axis   | P             | \( c \) |
| Trigonal (hexagonal setting) | \( a = b \neq c \)  
                   | \( a = \beta = 90^\circ, \gamma = 120^\circ \) | One threefold axis | P             | \( a \) |
| Trigonal (rhombohedral setting) | \( a = b = c \)  
                   | \( a = \beta = \gamma \neq 90^\circ \) | One threefold axis | R             | \( a \) |
| Monoclinic         | \( a \neq b = c \)  
                   | \( a = \gamma = 90^\circ, \beta \neq 90^\circ \) | One twofold axis or mirror plane | P, C         | \( b \) |
| Triclinic          | \( a \neq b = c \)  
                   | \( a \neq \beta \neq \gamma \neq 90^\circ \) | None               | P             | N/A |

The centring (or ‘lattice type’) of a unit cell describes the positioning of lattice points in the unit cell. The simplest lattice type is described as primitive (P) and contains lattice points only at the corners of the cell. A face-centred lattice (F) is constructed by adding lattice points at the centre of each face of the cell; this is distinct from lattice points being added to only one pair of faces, which is labelled based on which faces possess the additional points. For example, an A-centred lattice has additional lattice points on the \( bc \) faces of the unit cell.

*The hexagonal crystal family consists of the hexagonal and trigonal systems, the latter of which may be separated into two settings: hexagonal and rhombohedral. These are indicated in Table 1.1.*
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A body-centred lattice (I, from *innenzentriert*) contains only one additional lattice point at the centre of the cell. The combination of a crystal system with one of its permitted centring yields one of the fourteen Bravais lattices.

Finally, the setting of a space group describes the labelling of the positive $x$, $y$ and $z$ directions and the choice of the origin. Different space group settings are produced by permutating the lattice vectors or changing the origin. There are a variety of standard settings according to IUCr conventions, but occasionally non-standard settings may be chosen in order to highlight particular structural features, such as the choice of an $A2_{1}am$ cell instead of $Cmc2_{1}$ in the case of $n = 2$ Ruddlesden-Popper phases. The $A2_{1}am$ cell has short $a$ and $b$ axes and a long $c$ axis, making comparisons between it and the related $I4/mmm$ structure of these phases more convenient. Unit cells with centring and a larger volume are also selected if they have higher symmetry than a smaller cell, such as a C-centred orthorhombic unit cell being chosen over a primitive monoclinic.

### 1.2.3 Space Groups

As was briefly mentioned above, various symmetry elements may appear in a given unit cell. Those symmetry operations which leave at least one lattice point unchanged are elements of point symmetry; they include proper and improper rotation axes, mirror planes and inversion centres. There are 32 point group symmetries which are compatible with the crystal systems described above. Two additional types of symmetry elements also occur, which include a translation component in addition to a point symmetry operation. These are the screw axis (which combines an initial translation with a rotation about an axis parallel to the translation) and the glide plane (which combines an initial translation with a reflection in a plane parallel to the translation). The allowed combinations of crystal systems with point symmetry elements and translational symmetry elements produce the 230 crystallographic space groups.

In this thesis, Hermann-Mauguin notation is used to denote space groups, following international conventions for crystallography. In this notation, space groups comprise a lattice type (centring) as noted in Table 1.1, followed by a point group. The meaning of each symmetry operation listed in the point group part of the symbol is listed in Table 1.2. The position of a symmetry operation in the point group label defines its direction and depends on the number of higher-order axes in the group. For triclinic, monoclinic and orthorhombic crystal systems, symmetry operations appear in the order of the [100], [010] and [001] directions, respectively, where the bracketed numbers refer to Miller indices. For trigonal and tetragonal systems, the order is [001], [100] and [110], while for cubic systems the order is [100] (which is equivalent to [010] and [001]), then [111], then [110] (which is
equivalent to [101] and [011]). In cases where both a rotation axis and mirror plane share a direction, they are denoted similarly to a fraction with the rotation axis as the numerator and the mirror plane as the denominator. If two or more axes share a direction, the axis with the higher symmetry (generating more points) is shown. For example, a 3 rotation axis generates a 3-point pattern, while a 3 axis generates a 6-point pattern, so the 3 is shown. When both a rotation and rotoinversion axis generate the same number of points, the rotation axis is shown.

Table 1.2 Point group symmetry operation definitions in Hermann-Mauguin notation.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m$</td>
<td>Reflection plane perpendicular to axis</td>
</tr>
<tr>
<td>$a$ (or $b$ or $c$)</td>
<td>Glide plane perpendicular to axis with translation in $a$ (or $b$ or $c$)*</td>
</tr>
<tr>
<td>$x$ (e.g. 1, 2, 3, etc.)</td>
<td>Rotation axis of angle $\frac{360}{x}$ degrees</td>
</tr>
<tr>
<td>$R_n$ (e.g. 2₁)</td>
<td>Screw axis of angle $\frac{360}{R}$ and translation $\frac{n}{R}$ along axis</td>
</tr>
<tr>
<td>$\bar{x}$ (e.g. $\bar{1}$, $\bar{2}$, $\bar{3}$, etc.)</td>
<td>Rotoinversion axis (combined rotation operation and inversion through a point on the axis)</td>
</tr>
</tbody>
</table>

1.2.4 Diffraction Theory

1.2.4.1 Bragg’s Law

At the unit cell scale, structure determination in the solid state is founded on the principle that crystalline materials are capable of diffracting incident radiation in coherent patterns, (‘coherent’ here meaning that the scattered radiation has a non-random distribution of phases). Diffraction occurs when the incident radiation is of similar wavelength to the interatomic separation of the particles being studied; for many unit cells this is typically around 2-20 Å so X-ray, neutron and electron radiation sources are the most appropriate. The key differences between these radiation sources will be summarised in Section 1.3.1. Other types of crystallography, such as the study of proteins, may result in much larger unit cells, though X-rays and neutrons are still appropriate probes to characterise these structures.

In order to make use of diffraction for structural analysis, Bragg’s law must be fulfilled for experimentally-achievable 2θ values. In the Bragg construction, crystals are considered to be constructed from layers of atoms such that each layer behaves as a semi-transparent

---

*Translations may also be along diagonal directions and labelled with $n$ or $d$, depending on the direction with which they are aligned, but these will not be considered in detail here.
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mirror, diffracting some of the incident radiation while transmitting the rest to reach the following planes. In three dimensions, planes are usually referred to by their Miller indices: a set of values \((h, k, l)\) which indicate where a plane intersects the unit cell axes; the general form of the notation being \((a/h, b/k, c/l)\).

Figure 1.3 Illustration of Bragg’s law using a pair of parallel waves (1 and 2) incident on a pair of parallel planes (A and B).

Constructive interference between beams diffracted by a crystal is a requirement for observable diffraction. For a pair of parallel X-ray beams (1 and 2) with wavelength \(\lambda\) being reflected by two adjacent planes (A and B), Beam 2 must travel an additional distance \(\overline{xy} + \overline{yz}\) compared to Beam 1. This is illustrated in Figure 1.3. In order to remain in-phase and hence produce constructive interference, this additional distance must equal an integer number of wavelengths. The distance between the adjacent planes, referred to as d-spacing, \(d\), and the angle of incidence (or Bragg angle), \(\theta\), are related to the distance \(\overline{xy}\) by:

\[
\overline{xy} = \overline{yz} = d \sin \theta
\]  

1.2

For constructive interference to occur, the distance \(\overline{xy}z = n\lambda\), so Equation 1.2 may be rearranged to give Bragg’s law:

\[
n\lambda = 2d \sin \theta
\]  

1.3

The resolution of a crystal structure (the quality of the determined electron density) will depend on the minimum d-spacing which may be measured in an experiment.

1.2.4.2 The Reciprocal Lattice

In order to describe when a set of Miller planes are in a diffracting position, the orientation of the planes must be defined in addition to the interplanar spacing. This is achieved using the scattering vector, the direction of which bisects the incident and diffracted X-rays on a given plane and the magnitude of which, \((1/d_{hk})\), is proportional to the interplanar spacing. For the 3-dimensional array of lattice points used to define a crystal, there is therefore a corresponding 3-dimensional array of vectors which form the reciprocal lattice.
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In the same manner as the direct lattice is described by the basis vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, the reciprocal lattice is described by the vectors $\mathbf{a}^\ast$, $\mathbf{b}^\ast$ and $\mathbf{c}^\ast$, which are related to the direct vectors according to:

\[
\mathbf{a}^\ast = \frac{(\mathbf{b} \times \mathbf{c})}{V} \tag{1.4}
\]
\[
\mathbf{b}^\ast = \frac{(\mathbf{c} \times \mathbf{a})}{V} \tag{1.5}
\]
\[
\mathbf{c}^\ast = \frac{(\mathbf{a} \times \mathbf{b})}{V} \tag{1.6}
\]
\[
V^\ast = \mathbf{a}^\ast \cdot \mathbf{b}^\ast \times \mathbf{c}^\ast = \frac{1}{V} \tag{1.7}
\]

Where $V$ and $V^\ast$ are the volume of the unit cell in direct space and reciprocal space, respectively. The scattering vector, $\mathbf{s}$, for a given reflection is therefore related to the reciprocal lattice vectors:

\[
\mathbf{s} = h\mathbf{a}^\ast + k\mathbf{b}^\ast + l\mathbf{c}^\ast \tag{1.8}
\]

1.2.4.3 Wigner-Seitz Cells and the Brillouin Zone

In real space, the Wigner-Seitz\textsuperscript{4} cell is a primitive unit cell which is sometimes used to help describe the symmetry of a structure. It is constructed in two dimensions by choosing a lattice point and drawing a line to all of the lattice points which form its nearest neighbours. By drawing a set of additional perpendicular lines, bisecting each of the nearest-neighbour lines, a Wigner-Seitz cell is formed; this process is known as Voronoi decomposition\textsuperscript{5,6}. A three-dimensional Wigner-Seitz cell is constructed in exactly the same way but uses planes to bisect the lines to the nearest-neighbour lattice points. In practice, unit cells are used more often than Wigner-Seitz cells to describe crystals in real space. However, performing Voronoi decomposition in reciprocal space generates a useful construction: the Brillouin zone (BZ)\textsuperscript{7}. The BZ has uses in band theory and can be thought of as the set of points that can be reached from the origin of reciprocal space without crossing any Bragg planes. Since crystals have translational symmetry, further BZs can be constructed by using the next-nearest sets of points. High-symmetry points in the BZ are referred to as critical points and depend on the type of lattice; the critical points and propagation vectors for the first BZ of the $I4/mmm$ space group are summarised in Table 1.3.
Table 1.3 High-symmetry points of the first Brillouin zone of the I4/mmm space group.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>k-vector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ</td>
<td>Centre of the BZ</td>
<td>[0, 0, 0]</td>
</tr>
<tr>
<td>M</td>
<td>Centre of an edge</td>
<td>[0, 0, 1]</td>
</tr>
<tr>
<td>X</td>
<td>Centre of a face (ab plane)</td>
<td>(\frac{1}{2}, \frac{1}{2}, 0)</td>
</tr>
<tr>
<td>N</td>
<td>Centre of a face (ac plane)</td>
<td>(\frac{1}{2}, 0, \frac{1}{2})</td>
</tr>
<tr>
<td>P</td>
<td>Corner point joining three edges</td>
<td>(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})</td>
</tr>
</tbody>
</table>

1.2.4.4 The Ewald Construction

The Ewald construction relates the incident and diffracted radiation, the diffraction angle for a given reflection and the reciprocal lattice. A 2-dimensional representation of the Ewald construction (known as the Ewald circle) is shown in Figure 1.4. The construction begins with a crystal oriented such that diffraction from the hkl planes is observed. The reciprocal lattice vector is perpendicular to these planes with a magnitude \(\frac{1}{d_{hkl}}\). A sphere with radius \(\frac{1}{\lambda}\) is drawn; this is the reflecting sphere. The crystal may sometimes be represented in the centre of the sphere to aid visualisation. Bragg’s law will always be satisfied when the vector from the point where the direct beam exits the reflecting sphere (point Q) to the point where the diffracted beam exits the sphere (point P) is equal to the reciprocal lattice vector. Thus, if the origin of the reciprocal lattice is considered to be at point O, then Bragg’s law is satisfied whenever a reciprocal lattice point with Miller indices \((h k l)\) lies on the reflecting sphere. To reach the diffraction condition, the reciprocal lattice is rotated about point O until a reciprocal lattice point intersects the sphere; the direction of diffraction is found if a line is then drawn from the crystal to that point.
For a single-crystal experiment, the crystal is rotated about several axes to bring a variety of reciprocal lattice points on to the surface of the reflecting sphere. Those reciprocal lattice points which lie outside the reflecting sphere and which can never be made to intersect the surface of the sphere via rotation of the lattice about point O are not observable using the given wavelength of radiation. They are outside the so-called limiting sphere that is centred on the origin of reciprocal space (point O) and has radius $2/\lambda$.

1.3 Methods

1.3.1 Diffraction Experiments

In a diffraction experiment, a crystal is exposed to an appropriate source of radiation and reflection intensities, $I_{hkl}$, are recorded. These intensities are proportional to the amplitudes, $F_{oBS}$, and phases of the reflections. It is not possible to resolve the relative phases of the X-rays in a diffraction experiment and they must be estimated in some way; this is known as the ‘phase problem’. Without a reasonable starting estimate of the phases, it is not possible to convert the measured intensities to electron densities and hence atomic positions. Several approaches to circumventing the phase problem are summarised in Section 1.3.2.

The description of diffraction provided above is based on the concept of a single-crystal diffraction experiment. As this thesis is concerned with powder diffraction experiments and the information which may be extracted from them, the following section will provide an overview of the key differences between single-crystal and powder methods.
1.3.1.1 Powder Diffraction Experiments

There are a variety of reasons why a powder diffraction experiment may be preferred. While many techniques exist to grow single crystals of a material, it is not always achievable. Crystals may be unsuitable for single-crystal diffraction experiments due to their size or quality, or as a result of phenomena such as twinning. Powder experiments have historically been used mainly as launching points for further investigations due to their relative simplicity and speed, but with the increasing resolution achievable by modern diffractometers and central facilities, entire families of phases which are inaccessible by single-crystal methods may be explored.

The most obvious difference between single-crystal and powder diffraction is the configuration of the resulting pattern. A powder sample may be imagined as a collection of many microscopic crystals. Provided that the powder has been sufficiently finely-ground and has no tendency towards preferred orientation, these crystals are randomly-oriented in all directions. The lattice planes associated with each crystal are therefore also present in every possible orientation. For each set of planes, some crystals are oriented at the Bragg angle with respect to the incident radiation and diffraction is therefore possible. This results in the distinct diffraction spots which appear for single-crystal diffraction experiments being converted into rings of diffracted intensity, as illustrated in Figure 1.5. The way in which the diffracted intensity is measured depends on the experimental apparatus.

![Figure 1.5 Expansion from single-crystal diffraction patterns to powder diffraction rings. The rings and lines drawn for the single-crystal and two-crystal diffraction patterns are intended as a guide to the eye.](image)

1.3.1.2 Laboratory Powder X-ray Diffraction

One of the most common configurations of laboratory-scale diffractometers is a type of reflection geometry known as Bragg-Brentano geometry. This type of geometry focusses X-rays (which is not possible using lenses in the traditional sense due to the small wavelengths involved) by exploiting the properties of a circle, which are illustrated in Figure 1.6: the arc XY forms part of a circle and all of the angles subtended on the
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circumference of the circle by XY are equal (XPY = XP’Y = α). Point X is considered to be a source of X-rays and the points XP and XP’ represent the extremities of an X-ray beam emitted from X. If a sample is considered to cover the arc between points P and P’ such that its diffracting planes are tangential to the circle, the diffracted beam (represented by PY and P’Y) will focus at point Y. Ensuring that the X-ray source, sample and detector all lie on the circumference of an appropriate circle results in convergent X-rays, improving the intensity of the beam. In practice, sample holders ensure that powder samples have flat, even surfaces rather than curved surfaces; however, since the X-ray beam is considerably smaller than the radius of the focusing circle, the effect is minimal and convergent X-rays are still observed. Typically, either the X-ray source is held motionless and the sample and detector are rotated through angles θ and 2θ, respectively, or the sample is fixed horizontally and the X-ray source and detector are moved by −θ and θ, giving access to a range of d-spacings (and hence various hkl reflections).

![Diagram](image)

Figure 1.6 (Left) The reflection properties of a circle and (right) a representation of Bragg-Brentano geometry. The sample is situated such that it, the X-ray source and the detector are all located on the circumference of the circle shown on the left. Ideally the sample would be curved to focus the diffracted X-rays, but a flat-plate approximation is usually sufficient to describe the diffraction.
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X-rays are generated when high-energy charged particles such as electrons collide with matter. Two types of radiation are generated in these collisions: white radiation and characteristic radiation. White radiation is the result of inelastic collisions wherein the kinetic energy lost by the electron is converted to electromagnetic radiation; typically, multiple collisions occur for a given electron. This produces a continuous spectrum of X-rays, the minimum wavelength, $\lambda$, of which is dependent on the voltage of the X-ray generator:

$$E = eV = \frac{hc}{\lambda}$$

Where $e$ is the charge on the electron, $V$ is the voltage, $h$ is the Planck constant and $c$ is the speed of light. The higher the voltage, the greater the acceleration of the electrons and the shorter the minimum wavelength. Since every other component of this equation is a constant, it may be simplified to:

$$\lambda = \frac{12.398}{V}$$

Where $\lambda$ is in ångströms and $V$ is in kilovolts. Characteristic radiation is more useful than white radiation for the purposes of diffraction. When X-rays of appropriate energy collide with a metal target, electrons are ionised from the 1s orbital. An electron from a higher-energy orbital immediately drops to fill the vacant 1s orbital and X-ray radiation is emitted. The wavelength of the X-rays depends on the metal used as the target, the initial spin state of the electron which transitions to the 1s orbital and from which orbital the electron transition occurs. The characteristic X-ray wavelengths of common target metals are listed in Table 1.4.

Table 1.4 Characteristic X-ray wavelengths of common target metals. $\bar{\alpha}$ is the intensity-weighted average of $\alpha_1$ and $\alpha_2$.

<table>
<thead>
<tr>
<th>Target</th>
<th>$K\alpha_1$ (Å)</th>
<th>$K\alpha_2$ (Å)</th>
<th>$K\bar{\alpha}$ (Å)</th>
<th>$K\beta$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>2.2896</td>
<td>2.2935</td>
<td>2.2909</td>
<td>2.0849</td>
</tr>
<tr>
<td>Fe</td>
<td>1.9360</td>
<td>1.9399</td>
<td>1.9373</td>
<td>1.7566</td>
</tr>
<tr>
<td>Co</td>
<td>1.7903</td>
<td>1.7890</td>
<td>1.7929</td>
<td>1.6208</td>
</tr>
<tr>
<td>Cu</td>
<td>1.5405</td>
<td>1.5443</td>
<td>1.5418</td>
<td>1.3870</td>
</tr>
<tr>
<td>Mo</td>
<td>0.7093</td>
<td>0.7135</td>
<td>0.7107</td>
<td>0.6323</td>
</tr>
<tr>
<td>Ag</td>
<td>0.5594</td>
<td>0.5638</td>
<td>0.5608</td>
<td>0.4971</td>
</tr>
</tbody>
</table>
Labelling of the various characteristic wavelengths conventionally follows Siegbahn notation*: the letters K, L, M and onwards refer to the electron energy level to which the transition occurs, with K corresponding to the level with principal quantum number 1 and so on. The Greek letter refers to the separation of the energy involved in the transition: a transition between adjacent levels (such as from level 2 to level 1) is labelled α, while a transition between levels with one intermediate level (such as from level 3 to level 1, bypassing level 2) is labelled β and so on. Finally, the number refers to the initial spin state of the transiting electron: a 2p electron may have a total angular momentum value, \( J \), of either \( \frac{1}{2} \) or \( \frac{3}{2} \), with the \( J = \frac{1}{2} \) state being slightly higher in energy. The energy difference between these states results in two X-ray wavelengths for the transition.

Selecting an X-ray source which produces a shorter wavelength may allow for better resolution in a diffraction pattern, while selecting a longer wavelength can improve the separation between Bragg peaks. However, if a material contains certain transition metal elements, the use of particular X-ray wavelengths will result in fluorescence produced by electron excitations. This fluorescence can be in the X-ray range of electromagnetic radiation, resulting in ‘noise’ in a diffraction pattern; in extreme cases the diffraction pattern may be entirely unusable for structure solution. More commonly, the use of unfiltered characteristic wavelengths results in the multiplication of Bragg peaks in a diffraction pattern: for every reflection arising from the K\( \alpha_1 \) radiation, an additional peak will appear for K\( \alpha_2 \) and Kβ if they are not removed, either before the X-rays are incident upon the sample or before detection.

The selection of optics for a diffraction experiment can mitigate issues arising from undesirable interactions between X-rays and a sample and improve the overall quality of acquired diffraction patterns. For example, if copper is used as an X-ray source, a nickel foil filter may be used to selectively absorb Kβ X-rays as its absorption edge lies at 1.488 Å, between the wavelengths of Cu K\( \alpha_1 \) (\( \lambda = 1.5418 \) Å) and Kβ (\( \lambda = 1.387 \) Å) radiation. The removal of K\( \alpha_2 \) radiation cannot be achieved with a filter as the difference in wavelength between K\( \alpha_1 \) and K\( \alpha_2 \) radiation is too small. This function is instead performed by a monochromator, which is typically a single crystal of a material such as silicon, germanium, pyrolytic graphite or lithium chloride. Monochromators work by diffracting only those X-rays which fulfil the Bragg equation at a fixed angle; the mosaic spread (the degree to which the Bragg planes are misaligned within a single crystal) of the monochromator material determines how wide the band of permitted X-rays will be. For example, a single-

---

*Strictly, the International Union of Pure and Applied Chemistry (IUPAC) prefers a more recent form of X-ray notation, but this has yet to be universally adopted by crystallographers.
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crystal silicon monochromator has a cubic unit cell with lattice parameter \( a = 5.4309 \, \text{Å} \) and a maximum d-spacing \( d_{111} = 3.136 \, \text{Å} \). Using the Bragg equation, the diffraction condition will be satisfied for Cu K\( \alpha_1 \) radiation at \( 2\theta = 28.442^\circ \), while for Cu K\( \alpha_2 \) it is satisfied at \( 2\theta = 28.514^\circ \). With careful alignment, a silicon monochromator can therefore be used to filter Cu K\( \alpha_2 \). Different monochromator materials and configurations also exist for other wavelengths of radiation.

Other common optics apparatus include slits and collimators; both are apertures which are used to control the divergence of the X-ray beam and therefore the size of the footprint of the beam upon a sample or a detector. The final key component of a diffractometer is the detector, which may be a point detector or an area detector. These are differentiated in the size of the surface over which X-rays may be detected, with point detectors being smaller and more common in laboratory powder diffractometers.

1.3.1.3 Synchrotron Powder X-ray Diffraction

While laboratory-scale diffractometers offer a convenient route to phase identification and structural analysis, they are limited in their applications for high-resolution analysis by the characteristic wavelengths available using metal targets, with silver anodes providing the shortest-wavelength X-rays which are commonly accessible in the laboratory. Synchrotron X-rays may reach much smaller wavelengths with much greater intensity (number of photons per second incident on a sample), providing vastly superior resolution and much shorter experiment times, though these benefits require the construction and maintenance of a large and expensive dedicated facility. In spite of this, several dozen synchrotron facilities are active around the world, such as the UK’s Diamond Light Source, the European Synchrotron Radiation Facility (ESRF) in France, SPring-8 in Japan and the Advanced Photon Source in the USA.

A synchrotron is composed of three main components (which are highlighted in Figure 1.7): an electron gun to produce a beam of low-energy electrons with a linear accelerator to increase the kinetic energy of the beam, a booster synchrotron to further accelerate the beam and a storage ring to maintain and confine the beam, as well as to produce usable radiation. Strictly, the ‘rings’ are not true rings, but rather a large number of straight sections separated by dipole magnets which produce a vertical magnetic field between the poles. The electron beam experiences a force (the Lorentz force) perpendicular to its velocity and the field, and its path is bent. It is this bending action which produces X-rays. This is known as bremsstrahlung radiation (from German: ‘braking radiation’), referring to the fact that photons are emitted due to the change in acceleration of the electrons as their path is bent. The change in acceleration results in a loss of kinetic energy, which is converted
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to electromagnetic radiation. At Diamond Light Source, for example, electrons are accelerated to an energy of 3 GeV (< 99% of the speed of light) so the corresponding electromagnetic radiation is in the X-ray range; the Diamond storage ring consists of 25 straight sections and 50 dipole magnets.

![Figure 1.7 Schematic of the key components of a synchrotron. The blue line indicates the path of the electron beam and the red lines indicate X-ray beamlines.](image)

X-rays may also be produced in the straight sections through the use of insertion devices. There are two main types of insertion devices: wigglers and undulators. In their simplest form, wigglers comprise three dipole magnets which are arranged such that the outer two oppose the inner magnet. As the electron beam enters the wiggler, the first magnet causes the beam to bend in the opposite direction to its curvature around the storage ring. The second magnet (which is much more intense, typically a superconducting magnet) then over-compensates for this, causing the beam to change direction abruptly and emit high-energy X-rays. The final magnet then returns the electron beam to its original course. In an undulator, a large number of relatively weak dipole magnets (typically 20-30) cause the electron beam to undulate more slowly than a wiggler. The constructive interference resulting from the undulation of the beam can produce X-rays several orders of magnitude more intense than the (already extremely intense) standard radiation of the bending magnets. By designing the magnets used in undulators appropriately, the emitted X-rays may be tuned to a specific region of wavelengths, making them similar to monochromators. The emitted X-rays are directed to beamlines using optics which are essentially similar to those found in laboratory diffractometers, though larger in scale and engineered to greater precision. Depending on the experiment to be performed, white radiation can also be used as the X-rays emitted in a synchrotron are a continuous spectrum of energies.
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Two of the main differences between synchrotrons and laboratory X-ray sources are that higher energies (shorter wavelengths) and higher intensity X-rays are achievable at synchrotron sources. The shorter wavelengths produced in a synchrotron allow for greater d-spacing resolution (i.e. a smaller d-spacing minimum), improving the probability that a robust refinement may be performed. Another reason for the high resolution achievable using synchrotron radiation is that the bremsstrahlung X-rays are highly collimated (parallel to one another). The greater intensities allow more monochromatic X-rays to be produced without sacrificing the number of photons which strike a sample, improving the signal-to-noise ratio.

The greater the number of photons which are incident upon a sample over a given time period, the faster a complete diffraction pattern can be measured. This permits time-resolved experiments, allowing crystallographers to examine the behaviours of their samples while varying environmental variables such as temperature, pressure and applied fields, as well as in-situ monitoring of reactions and processes using specialised sample cells such as the work described in Chapter 5. While these types of experiment can also be performed using laboratory diffractometers, the time required to measure a diffraction pattern is much greater, limiting the resolution with respect to time. Greater intensity also allows for experiments to be performed in transmission geometry (Figure 1.8). In this geometry, powder samples are loaded into glass capillaries rather than on flat-plate holders. Transmission geometry has several benefits over reflection geometry: much smaller sample volumes are required to fill a capillary, and capillary loading, in conjunction with spinning the sample in the X-ray beam, can reduce the likelihood of preferred orientation occurring compared to reflection geometry. In general, the resolution in measurement space (Δθ/θ) is also better in transmission geometry and sample displacements errors are small. The geometry of the high-resolution powder diffraction beamline I11 at Diamond Light Source, which was used frequently for experiments described later in this thesis, is arranged such that the polarisation of the incident X-rays is perpendicular to the plane of the scattering, improving the intensity of the data at high angles.
Despite the predominant use of transmission geometry at synchrotron diffraction beamlines, transmission geometry also carries difficulties: air-sensitive samples must be carefully handled to prevent degradation, and if a powder is hygroscopic or prone to static electricity it may stick to the inside of a capillary tube. This can cause the appearance of a properly filled capillary without sufficient powder inside to produce a complete diffraction pattern, resulting in a form of texturing. Since atoms with high atomic numbers absorb X-rays more readily than lighter atoms, an absorption correction is sometimes required for transmission geometry. Without the absorption correction, peak intensities in the resultant diffraction pattern may be attenuated, making analysis more challenging. The amount of absorption may be estimated using the Cromer and Liberman\(^8\) algorithm and used to select an appropriate capillary diameter for a given X-ray wavelength.\(^*\) For example, the X-ray diffraction experiments at I11 on the $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ phase described in Chapter 2 were performed using 0.3 mm capillaries based on the results of the absorption calculation.

In both laboratory X-ray diffraction and synchrotron X-ray diffraction, detrimental effects such as preferred orientation may occur. Preferred orientation is a phenomenon in which the crystallites of a powder tend to be aligned in a specific direction rather than being randomly oriented. It can arise during the synthesis process, during grinding or as a result of the sample loading process. It is sometimes confused with texturing, which is a result of an experiment having too few crystallites and so the diffraction rings produced by textured samples appear spotty or otherwise incomplete. However, both phenomena have a similar effect on a diffraction pattern: the intensities of the Bragg peaks show large variations compared to non-textured, randomly-oriented samples, making phase identification and refinement of atomic coordinates difficult. This effect resulted in the data in Chapters 4 and 5 being unsuitable for Rietveld refinement, so Pawley refinements were used instead. These

\(^*\)Several web utilities exist to expedite calculations, such as the Argonne National Laboratory Absorb utility (https://11bm.xray.aps.anl.gov/absorb/absorb.php)
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effects may be somewhat mitigated by rotating the sample holder, which allows a greater number of orientations of crystallite grains to be sampled.

1.3.1.4 Neutron Diffraction

As mentioned in Section 1.2.4, neutrons also display diffraction and are suitable for structure determination, providing complementary information to X-ray diffraction experiments. The wavelength of a neutron is the de Broglie wavelength, \( \lambda_{dB} \):

\[
\lambda_{dB} = \frac{h}{mv}
\]

Where \( h \) is the Planck constant, \( m \) is the mass of the neutron and \( v \) is its velocity.

Since neutrons are neutral, massive particles, their interactions with the electron density surrounding a nucleus are relatively insignificant compared to X-rays, which are massless photons. Instead, neutrons interact with atomic nuclei via the strong nuclear force. Since the range of the strong nuclear force is much shorter than the wavelength of a neutron which is interacting with an atom, neutron diffraction is a type of point scattering. This results in one of the main differences between X-ray diffraction and neutron diffraction: X-ray atomic form factors, \( f_j \), are proportional to the atomic number, \( Z \), and \( Q \), where:

\[
Q = \frac{\sin \theta}{\lambda}
\]

Where \( \theta \) is the scattering angle and \( \lambda \) is the wavelength of the X-ray.

The dependence of the X-ray form factor on \( Q \) results in a loss of diffracted X-ray intensity at higher angles. Instead of a form factor, neutrons have a scattering length, \( b \), which is independent of \( Z \) and \( Q \) and varies apparently randomly from atom to atom and from isotope to isotope\(^9\). Since the scattering length does not vary monotonically with \( Z \), neutrons allow for better diffraction from lighter elements than X-rays in many instances. The
scattering lengths of certain atoms — such as vanadium — are close to zero; these atoms are effectively invisible to neutrons for the purposes of coherent diffraction experiments and are not readily analysed using neutron diffraction techniques. Some atoms — such as hydrogen, lithium, titanium and manganese — have negative scattering lengths. Materials which are composed of appropriate combinations of these elements can be useful: for example, a sample container made from an alloy of titanium (with a negative neutron scattering length) and zirconium (with a positive scattering length) will not contribute significantly to the diffraction pattern of the contained sample.

In addition to interacting with nuclei via the strong nuclear force, neutrons possess a spin value of \( \frac{1}{2} \) and may therefore interact with the magnetic fields resulting from the spins of unpaired electrons. In the paramagnetic regime, neutrons are scattered incoherently and contribute to the background of the diffraction pattern. When the spins of the electrons have long-range order, coherent diffraction is observed; for ferromagnetic order the magnetic Bragg peaks are observed on top of nuclear peaks, while for antiferromagnetic order the diffraction may be commensurate or incommensurate (i.e. indexed on the nuclear cell or a supercell). These peaks may then be analysed to identify the configuration of the magnetic moments using representation analysis (see Section 1.3.4). Since magnetic reflections involve electrons, they have a scattering form factor, and the intensity of magnetic reflections decreases with increasing diffraction angle. As such, magnetic peaks are most likely to be observed at lower angles in a diffraction pattern.

There are two main methods by which neutrons are generated for diffraction experiments: nuclear reactors and spallation sources. Nuclear reactors operate on the principle of nuclear fission, colliding neutrons with fissile nuclei such as \(^{235}\text{U}\) or \(^{239}\text{Pu}\) in a controlled reaction. 2-3 neutrons are produced per fission event; some of these neutrons proceed to perpetuate the fission reaction and some are used in diffraction. The emitted neutrons are polychromatic; they are passed through a moderator material such as water, heavy water, liquid hydrogen or solid methane to narrow their range of energies. They then pass through a monochromator crystal and collimator before being directed to a sample of interest for diffraction and detection. The Institut Laue-Langevin (ILL) High Flux Reactor is an example of a nuclear reactor neutron source. The neutrons produced by the reactor are continuous and are monochromated as they reach the various instruments, so the diffracted neutrons may be measured as a function of scattering angle \(2\theta\) in a similar way to X-ray diffraction. Examples of continuous-source diffraction experiments performed at beamlines D2B and D20 at the ILL may be found in Chapter 2.
Spallation sources operate by accelerating pulses of protons to an energy of approximately 1 GeV and colliding them with a heavy metal target such as tantalum or tungsten, chosen for the large number of neutrons in their nuclei. In each spallation event, a pulse of 20-30 neutrons are produced which pass through a moderator, followed in some cases by a ‘chopper’\textsuperscript{10}. The chopper is a device which periodically interrupts the neutron beam to produce well-defined pulses of neutrons and control the wavelength range. The ISIS Neutron and Muon source is an example of a pulsed spallation source, which operates at 50 Hz.

For some experiments, non-monochromated neutrons are preferred, such as when using neutrons from a spallation source for a time-of-flight (TOF) diffraction experiment. In each pulse, there is a broad distribution of energies. The neutrons with less energy take longer to travel from the source to the sample, so reflection intensities may be recorded as a function of the time between the beginning of the pulse and its detection (after diffraction by a sample). This method has several advantages over fixed-wavelength diffraction: collection times are shorter as more of the neutron flux is measured in each pulse than is measured for a fixed wavelength experiment, a wide range of diffraction angles may be measured simultaneously using multiple detectors, and in high-pressure powder diffraction experiments, the experiment can be arranged such that the high-pressure cell has a negligible contribution to the diffraction pattern. However, the low-angle detectors in TOF instruments have poorer resolution than high-angle detectors, and the arrangement of detectors and samples can usually only be optimised for high resolution or high intensity, but not both. Examples of data produced using the PEARL and GEM TOF instruments may be found in Chapter 2 and Chapter 3, respectively.

The greater relative sensitivity of neutron diffraction to lighter elements — such as oxygen in the phases presented in this thesis — and the possibility of performing magnetic structure analysis are significant advantages over X-rays. However, neutron diffraction also suffers from certain disadvantages. Due to the lower probability of interactions between neutrons and nuclei compared to X-rays and electron clouds (i.e. high penetration), a larger volume of sample is required. Typical experiments may require as much as 1 gram of sample as a minimum, with small sample volumes extending the already very long counting times for a single sample relative to X-ray diffraction. This may be leveraged as an advantage in some experiments: since the use of a Paris-Edinburgh press in a high-pressure diffraction experiment requires that the diffracted beam be passed through a pair of anvils as well as gasket materials, the high penetration and range of energies afforded by TOF neutrons help to mitigate the issue of diffraction by these materials. Further, neutrons result in essentially
no sample degradation, unlike X-rays which damage samples by ionisation over extended or repeated exposures. Another disadvantage of neutron diffraction compared to X-ray diffraction is cost. Small-scale neutron sources may be used to produce ‘cold’ (low-energy) neutrons by accelerating a proton beam at a \(^9\)Be target to produce \(^9\)B and neutrons in pulses. However, these are currently not widely used as they are expensive to produce, operate and maintain, as are nuclear reactors and spallation sources. As such, access to neutron diffraction equipment is relatively limited compared to X-ray diffraction.

1.3.2 Diffraction Data Analysis
As described above, crystal diffract incident X-rays and neutrons into patterns with specific geometries and amplitudes which are characteristic to their structure. The Fourier transform of the observed amplitudes gives the electron density of the crystal. In order to convert between these, the relative phases of the incident waves must be known; however, these are not measurable. In a single-crystal diffraction experiment, the phases may be calculated using a variety of methods\textsuperscript{11–12}. Discussion of the specifics of these methods is beyond the scope of this thesis, except to draw attention to the fact that they rely on precise measurements of the individual reflection intensities as a starting point. For powder diffraction data, the key difference is that the individual reflections observed in single-crystal data are overlapped into diffraction rings, which are converted into a plot of observed intensity, \(y_{\text{obs}}\), against 2\(\theta\) by measuring a ‘slice’ through the rings (Figure 1.10). The convolution of the reflection intensities with one another precludes the possibility of calculating the phases using the data. Instead, a starting model must be used to represent the structure which is then refined using the available data.

![Conversion of powder diffraction rings to a 1-dimensional plot of intensity against 2\(\theta\).

1.3.2.1 Non-Linear Least-Squares Refinement
A whole-pattern fitting method is used to model the structure, incorporating a structural model, description of peak shapes and parameters to describe the background simultaneously. The calculated intensity at each step in 2\(\theta\), \(y_{\text{calc},i}\), is then compared to the observed intensity, \(y_{\text{obs},i}\), and various parameters can be adjusted to improve the model.
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This is done using a least-squares refinement minimising the difference between the observed and calculated intensities, \( \Delta \):

\[
\Delta = \sum_{i=1}^{N} w_i (y_{obs,i} - y_{calc,i})^2
\]

1.13

Where \( w_i \) is a weighting factor (often set to \( \frac{1}{y_{obs,i}} \)) and \( N \) is the number of observed data points. More specifically, this is a case of non-linear least-squares refinement as \( \Delta \) is non-linear in terms of various instrumental and structural parameters. The minimum is found where each of the partial derivatives with respect to each parameter, \( p_j \) is zero. For \( M \) parameters, there are \( M \) equations of the form:

\[
\left( \frac{\partial \Delta}{\partial p_j} \right)_k = \sum_{i=1}^{N} \left\{ 2w_i (y_{obs,i} - y_{calc,i}) \left( \frac{\partial y_i}{\partial p_j} \right)_k \right\} = 0
\]

1.14

If a crystallographic model is close to satisfying all \( M \) equations, but the parameters differ from those of the true minimum by some amount \( \delta p_j \), an improvement to the model may be found using a Taylor expansion. Generally, the value of a function at \( x + \Delta x \) can be calculated using the Taylor series if the value of the function at \( x \) is known:

\[
f(x + \Delta x) = f(x) + \Delta x \frac{df(x)}{dx} + \frac{(\Delta x)^2}{2!} \frac{d^2 f(x)}{dx^2} + \frac{(\Delta x)^3}{3!} \frac{d^3 f(x)}{dx^3} + \cdots
\]

1.15

If the initial model is close to the true structure, \( \Delta x \) is small and the expansion may be safely truncated at the linear term. This is a key assumption in non-linear least-squares refinement of crystallographic data; if the initial model is too different from the true structure, more terms are needed to approximate the true function and the refinement will fail. Applying the first-order Taylor expansion to the multi-parameter function:

\[
y_{calc,i} = y_i(p_1 \ldots p_M) + \sum_{k=1}^{M} \delta p_k \left( \frac{\partial y_i}{\partial p_k} \right)_j
\]

1.16

Substituting Equation 1.16 into 1.14 produces:

\[
\sum_{i=1}^{N} \sum_{k=1}^{M} w_i \delta p_k \left( \frac{\partial y_i}{\partial p_k} \right)_j \left( \frac{\partial y_i}{\partial p_j} \right)_k = \sum_{i=1}^{N} \left\{ w_i [y_{obs,i} - y_i(p_1 \ldots p_M)] \left( \frac{\partial y_i}{\partial p_j} \right)_k \right\}
\]

1.17
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This is better visualised in matrix form:

$$\mathbf{A} \times \mathbf{S} = \mathbf{V} \quad 1.18$$

Where \( \mathbf{A} \) is an \( M \times M \) symmetric square matrix and \( \mathbf{S} \) and \( \mathbf{V} \) are column matrices with \( M \) rows. The elements of \( \mathbf{A} \) are the sum of the products of the partial derivatives:

$$A(j, k) = \sum_{i=1}^{N} w_i \left( \frac{\partial y_i}{\partial p_k} \right) \left( \frac{\partial y_i}{\partial p_j} \right) \quad 1.19$$

The elements of \( \mathbf{S} \) are the shifts \( \delta p_j \) that will be added to each parameter and the elements of \( \mathbf{V} \) contain information regarding the observed data:

$$\mathbf{V} = \sum_{i=1}^{N} \left\{ w_i \left[ y_{obs,i} - y_i(p_1 \ldots p_M) \right] \left( \frac{\partial y_i}{\partial p_j} \right) \right\} \quad 1.20$$

To calculate the values of the shifts, the square matrix \( \mathbf{A} \) must be inverted:

$$\mathbf{S} = \mathbf{A}^{-1} \times \mathbf{V} \quad 1.21$$

By applying the calculated shifts to the initial model, a new model is generated, and the whole process repeats iteratively until the shifts are reduced to negligibly small values. Equation 1.21 highlights a key feature of the non-linear least-squares refinement process: any faults in the model will become apparent if the matrix \( \mathbf{A} \) cannot be inverted. Similarly, if the model is good but the data are poor, the calculated shifts in \( \mathbf{S} \) will be poorly-defined. 'Good' data in this context refers to a large number of observed data points, and a good model will typically fit the data well with as few parameters as possible. Several whole-pattern methods to parameterise a structural model for powder diffraction data are in common use, including the Pawley method\textsuperscript{14} and the Rietveld method\textsuperscript{15–17}.

1.3.2.2 Pawley Refinement

A primitive whole-pattern fit could be performed using a combination of a function to describe the background of the diffraction pattern, the measured integrated intensities, \( I_n \), of all of the \( n \) peaks and a function to describe the peak shapes, \( P_k(2\theta_n) \), such as a Gaussian, Lorentzian or Pseudo-Voigt function (a summation of both), or a more complex function:

$$Whole \ Pattern = Background + \sum_{1}^{n} I_n P_k(2\theta_n) \quad 1.22$$
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However, assuming a flat background function and constant peak widths, this would require a total of $2n + 2$ parameters. A Pawley refinement improves on this method by describing the pattern in terms of $2\theta$ positions of each reflection, $2\theta_{hkl}$, instead of individual peak intensities, using only $n$ parameters to describe the whole diffraction pattern in addition to the background and zero-point parameters:

$$\text{Whole Pattern (Pawley)} = \text{Background} + \sum_{1}^{n} I_n P k (2\theta_{hkl} - 2\theta_{zp})$$  \hspace{1cm} 1.23

Where $2\theta_{zp}$ is a correction for the zero-point error of the diffractometer. The values of $2\theta_{hkl}$ are determined by a set of lattice parameters. This requires a knowledge of the symmetry of the phase being studied, so the diffraction pattern must be indexed before refinement. Indexing is the process of assigning Miller indices to the observed reflections using their observed $2\theta$ positions. For high-symmetry systems such as cubic phases, this process is relatively straightforward and can be performed by hand, but for lower-symmetry systems the process is usually automated using software.

The general form of the relationship between interplanar spacing and lattice parameters is given by the metric tensor equation:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} + \frac{2kl}{bc \cos \alpha} + \frac{2hl}{ac \cos \beta} + \frac{2hk}{ab \cos \gamma}$$  \hspace{1cm} 1.24

Where $d$ is the interplanar spacing, $h$, $k$ and $l$ are the Miller indices of each reflection and $a$, $b$, $c$, $\alpha$, $\beta$ and $\gamma$ are the lattice parameters. The equation is simplified by the inclusion of symmetry. For a cubic system, Equation 1.24 becomes:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2}$$  \hspace{1cm} 1.25

Combining Equation 1.24 with the squared Bragg equation (Equation 1.3) shows the relationship between the $2\theta$ position of a reflection and the associated Miller indices (again for a cubic system):

$$\sin^2 \theta = \frac{n^2 l^2}{4a^2} \cdot (h^2 + k^2 + l^2)$$  \hspace{1cm} 1.26

The list of $hkl$ reflections generated by the indexing can then be used to calculate accurate lattice parameters. Values of $I_{hkl}$ can also be extracted using a least-squares refinement process and used to calculate $F_{hkl}^2$ values. The use of lattice parameters to generate a structural model helps to mitigate the problem of correlations due to peak overlap, as the
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$hkl$ values associated with two overlapping peaks can be held separate by peaks which do not overlap. However, the scope of Pawley refinement is limited to the extraction of lattice parameters and $hkl$ intensities (as well as peak shape and strain if a peak shape model is added). For lower-symmetry structures with a greater number of structural degrees of freedom, it is useful to be able to extract additional information.

1.3.2.3 Rietveld Refinement

Using the Rietveld method, the intensity of each diffraction peak, $I_{hkl}$, is modelled directly via the structure factor, $F_{hkl}$. The relationship between the two properties is calculated according to:

$$I_{hkl} = \text{scale factor} \times LP \times \text{multiplicity} \times F_{hkl}^2$$  \hspace{1cm} (1.27)

Where $LP$ is the Lorentz and polarisation factor and $m$ is the multiplicity of the reflection (the number of reflections which are equivalent according to the symmetry of the unit cell). The Lorentz factor accounts for imperfections in crystals which allow the Bragg condition to be satisfied over a range of values. The polarisation correction arises because only the component of the polarisation of the X-rays which is perpendicular to the diffracted beam is fully conserved, while polarisation in the plane of the scattering is reduced by $\cos^2 2\theta$. This is important for laboratory X-ray data as these sources are usually not polarised or only partially polarised, so high-angle data has a reduced intensity, while synchrotron X-rays are highly polarised and the geometry of the experiment is arranged such that the polarisation is perpendicular to the plane of the scattering, improving the intensity of high-angle data. The overall $LP$ correction is:

$$LP = \frac{1 + \cos^2 2\theta_{mono} \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$ \hspace{1cm} (1.28)

Where $2\theta_{mono}$ is the angle of the monochromator in the experiment. The structure factor equation provides a means to identify how well an incident wave of a given frequency samples a given $hkl$ plane of electron density. For X-rays reflecting from the set of planes with indices $(h\ k\ l)$, the phase difference, $\delta$, between X-rays reflecting from atoms at the origin of a unit cell and a given position with fractional coordinates $(x, y, z)$ is calculated according to:

$$\delta = 2\pi(hx + ky + lz)$$ \hspace{1cm} (1.29)
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Each diffracted wave is a sinusoidal wave and the resultant diffracted intensity is calculated as the sum of all waves. The individual waves may be written in complex notation as:

\[ F_j = f_j (\cos \delta_j + i \sin \delta_j) = f_j \exp(i\delta_j) \]  \hspace{1cm} 1.30

Where \( f_j \) is the atomic form factor of atom \( j \) and \( \delta_j \) is the phase of each wave.

Combining Equations 1.29 and 1.30 across all waves gives the equation used to calculate the structure factor for a given \( hkl \):

\[ F_{hkl} = \sum_{j=1}^{N} t_j f_j \exp \left[ 2\pi i \left( hx_j + ky_j + lz_j \right) \right] \]  \hspace{1cm} 1.31

Where \( N \) corresponds to the number of atoms in the unit cell and \( t_j \) is a correction factor to account for thermal vibrations of atoms about their average positions reducing the observed intensity. It is usually referred to as an atomic displacement parameter and has the form:

\[ t_j = \exp \left( -B_j \sin^2 \frac{\theta}{\lambda^2} \right) \]  \hspace{1cm} 1.32

Where the values of \( B_j \) are experimentally determined for each atom in the structure. The mean-squared atomic displacement, \( U_{iso} \), is equal to \( B_j/8\pi^2 \). As with the Pawley method, these parameters are combined with functions to describe the background and zero-point error. Additional parameters such as a resolution function (to describe the instrument and beam characteristics) and parameters for the size and strain of the crystallites may also be included to produce a full model of the structure. Rietveld refinements also offer the flexibility to incorporate distortion modes via representation analysis and are a powerful method of modelling structures. Table 1.5 highlights some of the parameters which may be refined in Pawley and Rietveld refinements.
1.3.3 SQuID Magnetometry

A superconducting quantum interference device (SQuID)\(^{16}\) is a type of magnetometer which is useful for measuring extremely subtle magnetic behaviours, whether that is due to a small quantity of available sample or weak magnetic interactions. The key component of a SQuID consists of two superconductors through which a small current is passed. The superconductors are separated by thin insulating layers, resulting in a supercurrent (a current which flows continuously without an applied voltage) flowing between the superconductors via quantum tunnelling. By introducing a magnetic material between the superconductors, an additional current is induced which produces a measurable voltage, which may be converted to a measure of magnetic susceptibility in the magnetic sample.

Experiments may be performed to measure susceptibility as a function of temperature or at fixed temperature while varying an applied magnetic field. Direct current (DC) or alternating current (AC) may be used to infer different properties from magnetometry experiments using a SQuID: DC measurements provide equilibrium values of magnetisation, whereas AC measurements provide information on the dynamics of the magnetisation. Examples of the characteristic shapes of magnetic susceptibility curves acquired using DC SQuID magnetometry for different types of magnetic order are shown in Figure 1.11.
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1.3.4 Representation Analysis

Representation analysis and group theory are of fundamental importance in understanding the chemistry of solid-state materials. This section will provide an overview of the concepts involved in applying these mathematical constructions to crystallography. A more complete description of group theory and representation analysis may be found in a variety of textbooks.1,2

1.3.4.1 Mathematical Concepts

In mathematics, groups are defined as collections of elements (abstract mathematical objects) which obey four axioms as summarised in Table 1.6. The ‘order’ of a group is the number of objects within it; in the context of crystallographic space groups, the order is equal to the number of symmetry operations within a group and can be used to understand the relative symmetry of one group with respect to another. For example, the cubic $\overline{m}3m$ point group contains 48 symmetry operations and possesses higher symmetry than the monoclinic $2/m$ point group with 4 symmetry operations.

<table>
<thead>
<tr>
<th>Axiom</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closure</td>
<td>If $x$ and $y$ are elements in a group $G$, a binary operation combining $x$ and $y$ (i.e. $x \cdot y$) must also be in $G$.</td>
</tr>
<tr>
<td>Identity</td>
<td>There exists an element $e$ in a group $G$ such that, for every element $x$ in $G$, $e \cdot x = x$ and $x \cdot e = x$. The element $e$ is the identity element.</td>
</tr>
<tr>
<td>Invertibility</td>
<td>For every element $x$ in a group $G$, there exists some element $y$ such that $x \cdot y = y \cdot x = e$, where $e$ is the identity element.</td>
</tr>
<tr>
<td>Associativity</td>
<td>If $x, y$ and $z$ are elements in a group $G$, then $(x \cdot y) \cdot z = x \cdot (y \cdot z)$.</td>
</tr>
</tbody>
</table>

Elements of a group may be categorised into classes, which are sets of conjugate elements. Conjugate elements are similarity transforms of one another, meaning that if $y = A^{-1}xA$ for any $A$ that is also an element in the group, $x$ and $y$ are conjugate and belong to the same
class. In the context of crystallography, this refers to sets of symmetry operations which may be interconverted by the application of another symmetry operation from the group. For example, the 4 and $4_3$ rotations in a cubic group are related to one another by mirror planes, so they belong to the same class.

A representation of a group is any method by which the action of an operation within the group on an object is described. For example, the actions of a set of symmetry operations on a molecule may be displayed as a set of matrices acting on a matrix of the atoms in the molecule: this is a matrix representation. Representations are useful when considering how particular distortions may affect the symmetry of a space group. For point symmetry, the conservation or ‘flipping’ of a symmetry element under the effect of a particular symmetry operation is indicated by a positive or negative integer, while violation of the symmetry element is indicated by a zero in a character table (which are readily available for any point group). As an example, the character table for the $E_g$ ($Γ^+_3$ using Miller and Love’s notation, see Section 1.3.4.2 below) irrep of the $m3m$ point group are shown in Table 1.7. An irrep (short for ‘irreducible representation’) is representation of a group which cannot be described by a combination of other representations. A distortion which transforms as the $E_g$ irrep breaks the threefold rotation axis but retains the twofold rotation, inversion symmetry and mirror plane perpendicular to the [100] direction.

![Table 1.7 Character table of selected irreps of the m3m point group.](image)

The number of irreps for a given group is equal to the number of classes. In terms of crystallography, the irreps of a point group are the complete set of ways in which the symmetry of a structure with that point group may be broken. All distortions of a structure form a basis for either an irrep or for a linear combination of a set of irreps.

**1.3.4.2 Notation**

The irreps of point group symmetry use Mulliken notation\(^{19,20}\). This notation consists of a letter (A, B or E depending on whether the irrep is symmetric or antisymmetric with respect to rotation about the principal rotation axis or degenerate if there is a higher-order principal axis) followed by a subscripted number (1 or 2 depending on symmetry or anti-symmetry with respect to a vertical mirror plane perpendicular to the principal axis) and a subscripted letter (g or u depending on symmetry or anti-symmetry with respect to a centre of symmetry). Where appropriate, a prime or double prime symbol may also appear.
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depending on symmetry or anti-symmetry with respect to a mirror plane horizontal to the principal rotation axis.

For crystallography, the addition of translation symmetry necessitates the use of a different notation, described by Miller and Love\textsuperscript{21}. These take the form $K_n^+/-$, where $K$ is the Bradley-Cracknell\textsuperscript{22} symbol for the high-symmetry point in reciprocal space (see Section 1.2.4.3), $n$ is a number to distinguish the irrep from others with the same label and the + or – symbol indicates whether or not inversion symmetry is retained. The precise irrep label used is dependent on the setting of the unit cell.

1.3.4.3 Applications of Representation Analysis and Group Theory

Representation analysis and group theory are particularly useful in describing phase transitions. At a phase transition, a more ordered phase and a more disordered phase of the same material are in thermal equilibrium with one another and the chemical potential, $\mu$, of each phase is equal. Phase transitions may take a variety of forms, including changes of state (melting, boiling, etc.), transitions between magnetic orderings, structural phase transitions and displacive phase transitions. They can be described as first- or second-order, referring to the differential of the Gibbs free energy, $G$, for which a step is observed. First-order phase transitions typically exhibit an abrupt change in the free energy of the system at the transition point, resulting in a discontinuity in the first derivative of $G$ (known as a latent heat when the state variable is temperature). The coexistence of two phases over a range of temperatures around a phase transition is often indicative of a first-order transition, an example of which is the evaporation of water at its boiling point, where the discontinuity would be in the first derivative of the free energy with respect to temperature. In second-order phase transitions, the free energy evolves continuously across the transition, leading to an turning point in the first derivatives of $G$ and a discontinuity in the second derivatives (such as heat capacity).

Landau theory\textsuperscript{23}, in conjunction with representation analysis, can be used to generalise the theory of second-order phase transitions and as a quantitative model for first-order transitions. The essential premise of Landau theory is the definition of an order parameter (OP), typically noted with the symbol $Q$: a measurable property that may be used to monitor a phase transition. OPs are normalised such that $Q = 0$ above a phase transition, evolving either continuously or discontinuously to $Q = 1$ below it as the temperature approaches 0 K. When Landau theory was originally formulated it was a phenomenological theory (i.e. unconcerned with the details of atomic interactions which should govern the behaviour of a system, as opposed to a microscopic theory) and any observable property could be used as an OP. However, in modern usage it is combined with detailed crystallographic studies.
and irrep analysis. Since phase transitions in crystals typically occur as displacive transformations — a coordinated movement of atoms within the unit cell which do not involve the breaking of chemical bonds but which change the symmetry of the structure — modern Landau theory uses distortions which transform as specific irreps as primary OPs, allowing coupling between the irreps and higher-order terms in the expansion to be enumerated using invariants analysis: the identification of coupled secondary OPs according to whether or not they are invariant under the symmetry operators of the parent space group.

The Landau free energy, $\mathcal{F}$, describes the energy of a system near to a symmetry-lowering phase transition. It is similar to the Gibbs free energy and depends on similar parameters such as temperature and pressure; the key difference is that the Landau free energy also depends on the OPs of relevant modes in the system. For a given set of parameters, the stable phase of a system is the one for which the Landau free energy is minimised as a function of all internal degrees of freedom. It can be described as the sum of the internal energy due to parameters which are not involved with a phase transition, $\mathcal{F}_0$, parameters and some function of the energy which arises due to the OPs, $\Delta \mathcal{F}(Q^i)$:

$$\mathcal{F} = \mathcal{F}_0 + \Delta \mathcal{F}(Q^i)$$

1.33

Where $\Delta \mathcal{F}(Q^i)$ is small near the phase transition. For a simple one-dimensional OP, the Taylor expansion (referred to as a Landau expansion) of the free energy in terms of the OP has the form:

$$\Delta \mathcal{F} = -HQ + \frac{a}{2}Q^2 + \frac{c}{3}Q^3 + \frac{b}{4}Q^4 + \cdots$$

1.34

Where $H$ refers in this instance to a general external field (not specifically a magnetic field). Different terms in the Landau expansion provide different information on the nature of the phase transition. Terms which are linear in the OP must couple to the external field but are permitted only if the OP is translationally invariant. Phase transitions occur when one of the coefficients of the quadratic term changes sign while all of the other coefficients remain positive. For a temperature-driven phase transition, the quadratic term is usually written as $a'(T - T_c)Q^2$, where $T_c$ is the transition temperature. If a cubic term is present in the expansion, the transition must be first-order.

In order to use OPs to describe phase transitions, the order parameter direction (OPD) must also be specified. The OPD is a vector in representation space which defines the direction of and (if more than one distortion is present) magnitudes of distortions. For a given phase,
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the combination of an OPD with a space group (referred to as the parent structure) and setting above a phase transition is sufficient to identify the structure and symmetry of the phase below the transition (referred to as the child structure). Specifically, a space group which results from the action of specific OPs on a parent group is referred to as an isotropy subgroup and contains a subset of the same irreps.

The notation used by the ISODISTORT\textsuperscript{24,25} software suite will be used in this thesis. This comprises an irrep label in the style of Miller and Love, the OPD vector components in representation space, the space group type of the resulting subgroup, the basis vectors and origin shift of the resulting sublattice (in the same units as the parent cell), and the size \(s\) and index \(i\) of the primitive unit cell of the subgroup relative to the parent space group. For convenience, once these have been noted for a given distortion, only the irrep label will be used. The periodicity of the distortion mode is described by the number of ‘k-actives’. As an example, the out-of-phase tilting of oxide octahedra (with irrep \(X_3^-\)) in a \(\text{Ca}_3\text{Mn}_2\text{O}_7\) Ruddlesden-Popper structure with the parent space group \(I4/mmm\) may have OPD \((a,0)\), \((a,a)\) or \((a,b)\), resulting in the isotropy subgroups \(Amam\), \(P4_2/mmm\) or \(Pnmm\), respectively\textsuperscript{26}. The letter indicates the magnitude of the distortion and its direction is given by which position in the label is occupied.

1.4 Ferroics

The term ‘ferroics’ refers to materials which display any combination of the three ferroic properties: ferromagnetism, ferroelectricity and ferroelasticity. These properties all share a particular feature: a critical temperature at which a phase transition occurs from a non-ferroic phase to a phase which exhibits a spontaneous polarisation (which may be magnetisation, electrical polarisation or strain). This is referred to as the ferroic transition, in which the OP is the polarisation. For ferromagnetism and ferroelectricity the critical temperature is referred to as the Curie temperature, while for antiferromagnetic (AFM) materials it is the Néel temperature. Each type of ferroic material has a different OP at the phase transition: magnetisation in ferromagnets, polarisation in ferroelectrics and strain in ferroelastics. Ferroelasticity is defined as a spontaneous strain which may be switched by the application of a stress field across a ferroelastic phase. This thesis focuses on materials in which ferromagnetic (FM) and ferroelectric (FE) orderings are significant and, though some of the phase transitions may have ferroelastic secondary OPs (such as orthorhombic strain in the \(A2_1am\) phase of \(n = 2\) Ruddlesden-Popper phases), ferroelasticity will not be considered further. The following sections will describe the underlying theory behind ferromagnetism and ferroelectricity.
1.4.1 General Properties of Ferroic Materials

1.4.1.1 Domains

Polarisation in materials (magnetic, electric or otherwise) occurs along a specified crystallographic direction. On the length scale of multiple unit cells, it is often the case that the dipole moments of one region are aligned differently to those of another region. These regions of homogeneous polarisation are referred to as domains and occur to minimise the magnetostatic or electrostatic energy of the ferroic system as a whole, which result in strain in the crystal. They form arrangements such that the dipole moments of two neighbouring domains meet at either 90° or 180° relative to one another. For small enough crystal grains (such as those found in a powder sample), a single domain may occur per grain, while larger single-crystal structures may have multiple domains. Domains are useful in memory storage applications as the dipole moments on them may be switched to encode binary information.

1.4.1.2 Hysteresis

Reversibility (or ‘switchability’) is a key characteristic of ferroic properties via the application of an appropriate field: magnetic fields for ferromagnets, electric fields for ferroelectrics and stress fields for ferroelastics. A key consequence of the ability of ferroics to switch is hysteresis: the dependence of the state of a material on its history. Figure 1.12 shows an example of a hysteresis loop for a generic ferromagnetic material; the y-axis shows the magnetic induction, $B$, of the material and the x-axis shows the applied magnetic field, $H$. At zero field the material is unmagnetised (i.e. all of its domains cancel one another); the induction then increases with the field in the positive direction until it reaches a saturation point at $B_s$, where all of its domains are aligned with the field. When the applied field is returned to zero, the material remains magnetised; this is the residual magnetic induction, $B_r$. The additional reversed field required to remove the magnetic induction is the coercivity, $H_c$.

![Figure 1.12 Example responses to an applied magnetic field of diamagnetic, paramagnetic and ferromagnetic materials. A superparamagnetic response is shown with a dotted green line. The coercive fields and residual and saturation magnetisations are marked on the ferromagnetic hysteresis loop. Not to scale.](image_url)
By continuing to increase the magnetic field in the opposite direction, the magnetic induction will be reversed until it reaches an opposite value to its initial saturation point, \(-B_s\), and by once again returning the field to zero, then to its initial value, magnetic induction values of \(-B_r\), zero and \(B_s\) can be recovered. The hysteresis curve is generalisable to any ferroic property: for an FE material the axes would change to polarisation, \(P\), and applied electric field, \(E\).

### 1.4.2 Ferromagnetism

Ferromagnetism is the oldest-known ferroic property, having been known to ancient people in the form of the iron-based mineral, magnetite (Fe\(_3\)O\(_4\); this is the source of the ‘ferro-’ prefix applied to the other ferroic properties). *In modern use, the term ‘ferromagnetism’ refers specifically to a phenomenon resulting from unpaired electronic spins aligning with each other in the absence of an applied field, so the shortened form ‘magnetism’ is used to describe the general phenomenon. This section will outline some of the mathematical concepts required to understand magnetism. Note that all equations quoted here use centimetre-gram-second (cgs) units rather than Système International (SI) units, as this is the conventional system used to analyse the SQuID data in Chapters 2 and 3. Switching to SI units would incur some alterations to the following equations, such as including a factor of \(\mu_0\) (the permeability of free space) in Equation 1.35.

For a singular electron bound to an atom, the orbital angular momentum quantum number, \(l\), must be greater than zero in order for the electron to contribute to the magnetic dipole of the atom. The magnetic quantum number of the electron, \(m_l\), may take integer values in the range \(-l\) to \(l\) and determines the orientation of the orbital angular momentum with respect to an applied field. The energy, \(E\), of an electron in a magnetic field \(H\) is given by:

\[
E = \mu_B m_l H
\]

Where \(\mu_B\) is the Bohr magneton, the elementary unit of orbital magnetic moment in an atom, calculated according to:

\[
\mu_B = \frac{e\hbar}{2m_e c}
\]

Where \(e\) is the charge on the electron, \(\hbar\) is the reduced Planck constant, \(m_e\) is the mass of the electron and \(c\) is the speed of light. The change in energy of an electron when a magnetic field is introduced is known as normal Zeeman splitting.

*Though strictly, magnetite is a ferrimagnet as it contains two non-cancelling AFM sublattices.
The other key component of magnetism in a single-atom system is the spin of the electron around its own axis. This is the spin quantum number, $s$, which always has a value of $\frac{1}{2}$. In a magnetic field, the spin angular momentum is quantised (analogous to the quantisation of the orbital angular momentum in a magnetic field); referred to as $m_s$, it may take values from $-s$ to $+s$. For atoms containing more than a single electron, spin-orbit coupling must be considered. This is the interaction between the magnetic moment from the electron’s spin with the magnetic field from its orbital motion. The magnitude of spin-orbit coupling is proportional to $Z^4$, where $Z$ is the atomic number, but as this thesis will only consider phases containing lighter atoms, the result of spin-orbit coupling in heavier atoms will not be considered here. For light atoms, the coupling between the individual orbital angular momenta and the individual spins is stronger than the spin-orbit coupling, so in order to calculate the magnetic moment of the atom, the total angular momentum of the system is calculated. This is done by combining the total orbital angular momentum, $L$, and the total spin angular momentum, $S$, of all the individual electrons via vector addition. For a two-electron system, $L$ is given by the Clebsch-Gordan series:

$$L = l_1 + l_2, l_1 + l_2 - 1, ..., |l_1 - l_2|$$  \hspace{1cm} 1.37

$S$ is calculated according to:

$$S = s_1 + s_2, s_1 - s_2$$  \hspace{1cm} 1.38

The total angular momentum quantum number, $J$, is then found by vector addition of these values:

$$J = L + S, L + S - 1, ..., |L - S|$$  \hspace{1cm} 1.39

The total magnetic moment of the atom, $\mu_{\text{eff}}$, is then given by:

$$\mu_{\text{eff}} = g \mu_B \sqrt{J(J + 1)}$$  \hspace{1cm} 1.40

Where $g$ is the Landé g-factor:

$$g = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}$$  \hspace{1cm} 1.41
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For first-row transition metal oxides, angular momentum is often ‘quenched’, meaning that the degeneracy of the d orbitals is removed via crystal field splitting and/or Jahn-Teller distortions. This results in situations in which \( J = S \), wherein the effective magnetic moment is known as the ‘spin-only’ moment, calculated according to:

\[
\mu_{\text{eff}} = 2 \mu_B \sqrt{S(S + 1)}
\]

It is worthwhile to note here that the spin-only approximation has been appropriate for all of the systems studied in this thesis. Materials in a magnetic field behave differently depending on whether or not they have a net magnetic moment (Figure 1.13). In the following sections, the different cases will be summarised according to these behaviours.

1.4.2.1 Diamagnetism

Diamagnetism refers to the repulsion of an applied magnetic field by a material. This phenomenon occurs in all materials but is negligible in magnitude compared to the other types of magnetism, so only materials which lack any other magnetic ordering are referred to as diamagnetic. The mechanism of diamagnetism can be understood as being due to an induced magnetic field in the electrons of a material as a result of their orbital angular momentum. Diamagnets are of particular interest due to their relationship with superconductivity: superconductors can be considered perfect diamagnets due to their complete expulsion of a magnetic field (the Meissner effect).

![Depiction of basic magnetic phenomena in a 1-dimensional chain of electrons](image)

*Figure 1.13* Depiction of basic magnetic phenomena in a 1-dimensional chain of electrons; in each example the direction of an imaginary external magnetic field is pointed upwards.

1.4.2.2 Paramagnetism

In paramagnetic materials, the magnetic moments are weakly coupled to one another (ideal paramagnets have completely independent magnetic moments). As a result of thermal energy they are randomly oriented in the absence of an applied field and when a field is applied, only a small percentage of them will align with it. The susceptibility, \( \chi \), of insulating paramagnetic materials (the degree to which the magnetisation of a material is affected by
an applied magnetic field) is usually well-modelled by the Curie-Weiss law, which states that the susceptibility $\chi$, of paramagnetic phases varies linearly with respect to temperature until $T = T_C$, whereupon there is a divergence from linearity:

$$\chi = \frac{C}{T - T_C}$$  \hspace{1cm} 1.43

Where $T$ is the temperature, $T_C$ is the Curie temperature and $C$ is the Curie constant:

$$C = \frac{Ng^2(J + 1)\mu_B^2}{3k_B}$$  \hspace{1cm} 1.44

Where $N$ is the number of magnetic atoms (or molecules) per unit volume and $k_B$ is the Boltzmann constant. In conducting materials, a different behaviour known as Pauli paramagnetism occurs which arises due to the formation of electron bands. As this thesis deals primarily with insulating materials, this behaviour will not be discussed further here.

1.4.2.3 Ferromagnetism and Antiferromagnetism

As mentioned above, ferromagnetic materials are those in which the magnetic moments spontaneously align parallel to one another. Antiferromagnetic materials also exhibit spontaneous alignment of the magnetic moments, but each parallel moment is balanced with an antiparallel moment such that the resulting net magnetic moment in the bulk sample is zero. This may be achieved in various ways, as detailed in Figure 1.14. The determining factor in whether ferromagnetism or antiferromagnetism will occur in an insulating material is the type of exchange interaction which dominates.

![Figure 1.14 Archetypal antiferromagnetic orderings which may be observed in a primitive unit cell.](image)

The exchange interaction is a quantum mechanical electrostatic term which arises as a result of the Pauli exclusion principle and Hund’s rule. The basic types of exchange interaction are summarised in Figure 1.15. In direct exchange, the energy of a pair of
magnetic ions in close proximity to one another is minimised by aligning their spins parallel or antiparallel. Ferromagnetic or antiferromagnetic ordering is favoured depending on the d orbital occupancy of the neighbouring species. For the two ions to be in close enough proximity for direct exchange, the coordination polyhedral (i.e. oxide octahedra) are often face- or edge-sharing. In the superexchange interaction, intermediate anions such as oxides facilitate the coupling of electron spins. The relative orientations of the orbitals determines whether ferromagnetic or antiferromagnetic ordering is favoured: a 180° metal-anion-metal angle results in antiferromagnetic interactions, while 90° angles result in ferromagnetism.

The abovementioned types of magnetism are not the only possibilities. For species which behave antiferromagnetically, there exists a possibility that the opposing magnetic moments of neighbouring atoms or ions may become canted following a structural phase transition, resulting in a small net magnetic moment which is referred to as weak ferromagnetism. This is illustrated in Figure 1.16.

Materials which contain multiple magnetic species with different magnetic moments may display ferrimagnetism, in which the magnetic moments of one species align parallel to an
applied field and the magnetic moments of the other species align antiparallel. This results in a ferromagnet-like response to the field, though one in which the net magnetic moment is weaker than if only the greater magnetic moments were present.

1.4.2.4 Shubnikov Groups

Defining a space group with magnetic moments included requires an additional level of complexity. This is achieved using Shubnikov groups, which account for the fact that magnetic moments behave as axial vectors. These vectors may be visualised as a current loop which follows a right-hand rule relative to the direction of the electron spin. Certain symmetry operations, such as reflection in a plane parallel to the direction of the vector, reverse the direction of the loop. However, reflection in a plane perpendicular to the direction of the vector causes the corresponding polar vector to reverse, but not the axial vector; this phenomenon is visualised in Figure 1.17. A mirror operator reversing a perpendicular axial vector is known as time reversal symmetry and is indicated by the addition of a prime symbol to the space group symbol. Combining time reversal symmetry to the 230 crystallographic space groups produces the 1651 Shubnikov groups. This type of space group symbol has been used sparingly in Chapters 2 and 3; the majority of the magnetic orderings have been described using the irrep formalism in which magnetic vectors are assigned labels similarly to distortion modes.

1.4.3 Ferroelectricity

First described in Rochelle salt, ferroelectricity is defined as a spontaneous polarisation which may be switched by the application of an electric field. For a pair of particles of charge $q$ separated by a distance $r$, the dipole moment, $\mu$, between them is simply:

$$\mu = q \cdot r$$

In an FE material, there is a net permanent dipole moment, which is calculated from the vector sum of dipole moments in each unit cell, $\sum \mu$. This net moment requires a unit cell
which is non-centrosymmetric (i.e. lacking inversion symmetry), as the dipole moments in a centrosymmetric unit cell cancel one another out. Macroscopic polarisation can only be achieved in 10 crystal classes: 1, 2, \( m \), \( mm2 \), 4, \( 4mm \), 3, \( 3m \), 6 and \( 6mm \). There must also be a spontaneous local dipole moment to result in bulk polarisation, \( P \). One way in which polarisation may be defined is as the total dipole moment per unit volume, \( V \):

\[
P = \frac{\sum \mu}{V}\n\]

FE materials are distinguished from dielectrics by the hysteretic behaviour of the polarisation: while both are polarised by an applied electric field, dielectrics return to an unpolarised state upon removal of the field. A further comparison may be made with paraelectric (PE) materials, which display an enhanced polarisation in response to an applied field but which return to an unpolarised state in the absence of an applied field. The responses are very similar to those of magnetic materials to an applied field, shown in Figure 1.12. Materials which display a spontaneous electrical polarisation below a phase transition temperature but which cannot be switched by the application of an applied electric field are referred to as pyroelectrics. Finally, materials which exhibit an electrical polarisation when under the influence of an applied strain are known as piezoelectrics. All FE materials are also pyroelectric, and all pyroelectric materials are also piezoelectric, but not all piezoelectrics are pyroelectric and not all pyroelectrics are FE materials.

Different types of ferroelectricity are categorised according to the primary OP of the FE phase transition. Broadly, two main types exist: ‘proper’ and ‘improper’ ferroelectricity. In proper ferroelectricity, the primary OP of the PE-FE phase transition is the onset of switchable polarisation; if any other property is the primary OP, improper ferroelectricity is present. Where proper ferroelectricity was first described in 1921, improper ferroelectricity was not discovered until 1968 in \( \text{Gd(MnO}_4\text{)}_2 \). These two categories are further subdivided according to the specific mechanism by which the polarisation arises, and the following sections will summarise several of these with examples from the literature.

\subsection{Proper Ferroelectricity}

Arguably the best-known example of a proper FE phase is the perovskite \( \text{BaTiO}_3 \), which exhibits a phase transition from a cubic \( Pm\bar{3}m \) structure to a tetragonal \( P4mm \) structure around 393 K. In the transition, the \( \text{Ti}^{4+} \) cation undergoes an off-centre displacement which is stabilised by hybridisation of the O 2p orbitals with the Ti 3d orbitals. This distortion removes the Ti\(^{4+}\) cation from the centre of the unit cell, breaking the inversion symmetry.
and resulting in a bulk polarisation (Figure 1.18). This type of mechanism is referred to as a second-order Jahn-Teller (SOJT) distortion. Upon further cooling, additional orthorhombic and rhombohedral phases may be accessed in which the direction of the Ti\(^{4+}\) distortion changes but the polarisation remains. These phase transitions are inconsistent with a traditional second-order displacive phase transition model and have instead been rationalised using an order-disorder model\(^3\text{5-37}\), in which symmetry-breaking distortions on a local scale dominates the mechanism.

![Figure 1.18 Visualisation of the SOJT mechanism producing proper ferroelectricity in BaTiO\(_3\). Green spheres indicate Ba\(^{2+}\) cations, blue spheres indicate Ti\(^{4+}\) cations and red spheres indicate O\(^{2-}\) cations. The black arrow indicates the off-centre displacement direction of the Ti\(^{4+}\) cation.](image)

### 1.4.3.2 Improper Ferroelectricity

The hexagonal manganites (AMnO\(_3\); A: Sc, Y, In, Dy, Ho, Er, Tm, Yb, Lu) are a family of compounds with the same apparent underlying formula as traditional perovskites, but a hexagonal unit cell. Unlike their cubic perovskite relatives, these phases allow for face-sharing metal-oxide polyhedra, which has led to particular interest in their magnetic structures for quantum materials\(^3\text{8}\). Instead of Mn\(^{4+}\) cations located in O\(^{2-}\) octahedra, Mn\(^{3+}\) cations are found in MnO\(_5\) trigonal bipyramids, and the A-site cations are located in 7-fold coordination instead of 12-fold. The crystal field splitting is therefore also different to octahedral field splitting in these materials: instead of a triplet \(t_{2g}\) and doublet \(e_g\) state, the d-orbitals split into a pair of doublets and a higher-energy singlet. The four d-electrons in an Mn\(^{3+}\) cation occupy the two doublet states and so the Mn\(^{3+}\) cation is not Jahn-Teller active\(^3\text{9}\).

The \(h\)-YMnO\(_3\) composition exhibits a type of improper ferroelectricity which is sometimes referred to as geometric ferroelectricity. At 1258±15 K, \(h\)-YMnO\(_3\) exhibits a phase transition from a centrosymmetric structure with \(P6_3/mmc\) symmetry to an improper FE \(P6_3cm\)
structure (Figure 1.19)\textsuperscript{40,41}. The phase transition contains two distortions. The first distortion is the primary OP and has the irrep label $K_3$; it causes the MnO$_5$ bipyramids to tilt and displaces the Y$^{3+}$ cations, tripling the unit cell. However, the displacement of the cations is antiferrodistorvive and the resultant dipoles cancel one another. The FE phase in $h$-YMnO$_3$ arises due to a secondary distortion mode with irrep $\Gamma_2^-$ triggered by the $K_3$ mode, which causes a polar displacement of the Y$^{3+}$ cations. Since this distortion is a secondary OP of the phase transition, $h$-YMnO$_3$ is described as an improper FE. An additional transition has been observed around 920 K which does not change the space group but does involve a polar shift of the Mn-O equatorial planes, resulting in a reduction in the polarisation. It has been theorised that this transition is related to hybridisation between the Y$^{3+}$ centre and an axial O$_2^-$ centre\textsuperscript{42,43}. Below this transition $h$-YMnO$_3$ is strictly best described as ferrielectric, as there are two inequivalent Y$^{3+}$ sites with differing polarisations aligned antiparallel to one another. Recent work has shown that the FE domains in $h$-YMnO$_3$ may be switched locally and returned to their initial state by varying temperature, suggesting that novel functionalities may yet be discovered in improper FEs\textsuperscript{44}.

![Figure 1.19 Centrosymmetric and polar structures of YMnO$_3$. Blue spheres indicate Y$^{3+}$ ions, purple polyhedra indicate YMnO$_5$ trigonal bipyramids and red spheres indicate O$_2^-$ ions.](image)

In phases such as magnetite (Fe$_3$O$_4$)\textsuperscript{45,46}, half-doped manganites (Pr$_{0.5}$Ca$_{0.5}$MnO$_3$) and certain rare-earth nickelates (ANiO$_3$; A: Y, Lu)\textsuperscript{47}, FE properties may arise as a result of charge ordering. The specifics of the ferroelectricity vary from structure to structure, but for the perovskite-like structures the following mechanism has been proposed: upon charge ordering, either the charge on the sites within a structure become inequivalent, or the charge distribution in the bonds between the sites become inequivalent. Neither of these regimes result in ferroelectricity on their own, but upon simultaneous site- and bond-
centred charge ordering, inversion symmetry is broken and a net dipole moment develops. This is illustrated in Figure 1.20. For magnetite, an alternative model has been proposed in which the localised electrons are distributed over three Fe sites, forming a quasiparticle referred to as a ‘trimeron’\textsuperscript{48–50}. This distribution of the electrons results in significant off-centre displacements and couple the polarisation to the magnetic structure.

\[ \text{Figure 1.20 A proposed mechanism of charge-ordering-induced ferroelectricity in perovskite-like materials. Simultaneous ordering of charges on sites and bonds produces an overall polarisation, which is absent when only one type of ordering is present.} \]

A special case of improper ferroelectricity results from the simultaneous condensation of multiple non-polar distortion modes with a polar mode. This is referred to as hybrid improper ferroelectricity; this is the basis of the investigations in Chapters 4 and 5 and will be described in greater detail in those chapters.

1.4.4 Multiferroics

1.4.4.1 Definitions

A multiferroic material is any phase which is capable of exhibiting two or more ferroic properties. The term ‘multiferroic’ is strictly ambiguous as to which ferroic properties are present, but conventionally it refers specifically to those materials in which both magnetic ordering and ferroelectric ordering are simultaneously present. It is important to distinguish ferromagnetic ferroelectric multiferroics from magnetoelectric materials. The magnetoelectric effect refers to any coupling between magnetic and electric properties of a material but is not limited to the switchable polarisation and magnetisation of ferroic materials. A material may possess both magnetic and ferroelectric orderings (and therefore
be referred to as a multiferroic), but if they are not coupled, the material is not a magnetoelectric multiferroic.

![Venn diagram of ferroic properties](image)

*Figure 1.21 Venn diagram of ferroic properties. Any area in which two or three properties overlap is a form of multiferroic.*

Multiferroics may be classified into two groups. In type-I multiferroics, the mechanisms of magnetism and ferroelectricity are independent of one another. The two properties therefore have different phase transition temperatures, and the coupling is weak. Type-I multiferroics comprise the majority of the earliest-discovered multiferroics. In type-II multiferroics, one type of ordering drives the other, leading to strong coupling between the two. However, the magnitudes of the orderings are typically smaller than those in type-I multiferroics, and significantly smaller than those of non-multiferroic phases. These phases are the ones which are typically targeted in current research due to the variety of potential applications which arise from the strong coupling of the magnetic and ferroelectric properties. Such applications have been proposed in the emerging field of spintronics as well as for data storage, sensor technologies and multiferroic refrigeration, to name a few.

1.4.4.2 The d⁰ Rule

Early descriptions of multiferroics include that of Ni₃B₂O₁₃I by Ascher and co-workers in 1966, but it is only since the mid-nineties that research into these phases has become more widespread. This is due to a number of factors, including advances in analytical techniques such as high-resolution X-ray diffraction, and theoretical breakthroughs in understanding the scarcity of naturally-occurring multiferroic materials. Among these was Spaldin’s description of the “d⁰ rule” for ABO₃ perovskites, which states that ferroelectric displacements of the B cation are inhibited if the formal charge does not equate to a d⁰ electronic configuration. As partially-occupied d (or f) shells are mandatory for magnetic...
cations, this would appear to prohibit any form of coupling between ferromagnetic and ferroelectric properties. However, several mechanisms by which the d⁰ rule may be circumvented have been discovered and the goals of research in multiferroics have shifted towards increasing the magnitude of both the FE and FM properties, improving the coupling between the two and tuning the phase transition temperatures to produce functional materials.

1.4.4.3 Examples of Multiferroic Phases
Possibly the best-known type-I multiferroic is BiFeO₃, which is one of only a small number of known room-temperature multiferroics⁵⁷,⁵⁸. This phase is rhombohedral at room temperature with the R₃c space group⁵⁹. BiFeO₃ exhibits proper ferroelectricity due to ordering of the Bi 6s² lone pair which is aligned with the [111] direction. The FE phase transition occurs at approximately 1100 K from an orthorhombic phase with Pbnm symmetry⁶⁰–⁶³. A report by Ramesh and co-workers⁶⁴ suggested that the polarisation was greatly enhanced in a thin-film deposited on to SrTiO₃ substrates. Though the polarisation was eventually shown to be intrinsic to the phase⁶⁵, this resulted in a surge of interest in multiferroic phases. The onset of magnetic ordering occurs around 643 K and arises entirely due to the Fe³⁺ centres.⁶⁶ The ordering is approximately G-type AFM, with each Fe³⁺ spin surrounded by six antiparallel spins on its nearest neighbours, however a weak canting moment occurs as a result of magnetoelectric coupling to the polarisation. Additionally, an incommensurate spin cycloid⁶⁷ is superimposed on the unit cell-scale magnetic ordering which averages out the canting. Under a sufficiently high magnetic field, the cycloid is destroyed and the canted magnetisation is dominant. Further magnetic phase transitions have also been reported at 200 K⁶⁸ and 140 K⁶⁹ which have been proposed to be due to spin reorientations or due to a spin-glass state⁷⁰.

Another well-known type-I multiferroic is h-YMnO₃. The high-temperature geometric FE mechanism of the hexagonal polymorph of this composition is described above. A single FM transition is observed for h-YMnO₃ at 76 K⁷¹. Observations of coupling between the magnetic and electric domains (though not on a unit cell scale) in h-YMnO₃⁷² was likely one of the key driving forces behind the surge in multiferroic research in the last two decades. Curiously, an extremely similar mechanism for geometric ferroelectricity as that observed in h-YMnO₃ has been proposed for the hexagonal perovskite 2H-BaMnO₃⁷³ in spite of its different atomic arrangement, cation sizes and Mn valence. Coupled with its AFM transition at 59±2 K, 2H-BaMnO₃ is another example of type-I multiferroicity⁷⁴,⁷⁵.

Type-II multiferroics were first described more recently than type-I and encompass two main subcategories. The first category consists of phases with a spiral-type
incommensurate magnetic structure (in other words, a magnetic structure without inversion symmetry), while the second category consists of phases for which FE properties appear alongside collinear magnetic structures. Examples of phases of the former type include AMnO$_3$ (A: Gd, Tb, Dy)\textsuperscript{77,78}, TbMn$_2$O$_5$\textsuperscript{79} and MnWO$_4$\textsuperscript{80-82}. The last of these is particularly interesting as it has been demonstrated that the FE and AFM orderings are very strongly coupled\textsuperscript{83-85} and that an FE polarisation state is memorised and can be recovered from the PE phase by application of a magnetic field\textsuperscript{86}. At room temperature MnWO$_4$ exists in the $P2_1/c$ space group and three magnetic transitions are observed at approximately 13.5 K, 12.5 K and 7.6 K, respectively\textsuperscript{87}. The first transition is from a paramagnetic state to an incommensurate spin-density wave state with a wavevector $Q = (-0.214, 0.5, 0.457)$\textsuperscript{88} in which the spins are collinear in the $ac$ plane. Below the next transition, a spin component develops in $b$, resulting in an elliptical spiral spin structure. The final transition is to a commensurate magnetic structure with collinear spins and wavevector $Q = (±0.25, 0.5, 0.5)$. It is in the middle of these magnetic phases that the polarisation develops as a result of a mechanism first described by Balatsky and co-workers\textsuperscript{89} which takes into account the Dzyaloshinskii-Moriya (DM) interaction\textsuperscript{90,91}. In short, the mechanism describes the polarisation, $P$, in the following way:

$$P \propto e_{ij} \times (\vec{S}_i \times \vec{S}_j)$$

Where $i$ and $j$ are two magnetic sites in a structure, $\vec{S}$ represents the non-collinear magnetic moment on each site, and $e_{ij}$ is the vector between the sites $i$ and $j$. The cross product $(\vec{S}_i \times \vec{S}_j)$ is proportional to the spin current, $j_{sc}$. In the case of a cycloidal spin spiral, as is found in MnWO$_4$, the polarisation is forced to vary with the magnetic field. Very recent work\textsuperscript{92} has suggested an alternative mechanism in which competition between the DM interaction and an isotropic exchange interaction causes an inequivalence between the two Mn sublattices which are present in MnWO$_4$, breaking inversion symmetry. The recent discovery that application of high pressure to a sample of TbMnO$_3$ results in significant enhancement of the polarisation shows that this type of multiferroic may still be explored for unexpected functionalities\textsuperscript{93}.

Under high-pressure conditions, an orthorhombic polymorph of YMnO$_3$ (sometimes referred to as the perovskite structure, $\alpha$-YMnO$_3$) with space group $Pnma$ may be stabilised. In contrast to the single FM transition observed for $h$-YMnO$_3$, $\alpha$-YMnO$_3$ has a pair of AFM magnetic transitions at 39±3 K and 29 K\textsuperscript{94}. The former of these indicates the onset of a magnetic structure which is incommensurate with the nuclear structure, with the magnetic moments oriented parallel to the propagation vector $k = (k_x, 0, 0)$. The initial value
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$k_x = 0.420$ increases to a maximum value $k_x = 0.435$ around the second transition. The magnetic structure is the second sub-category of type-II multiferroic, referred to as collinear E-type: Mn atoms with parallel spins form chains in the $ab$ plane, with alternating planes along $b$ possessing opposing spins. The chains are stacked antiferromagnetically in $c$. The onset of AFM ordering has been shown to drive FE ordering in $o$-YMnO$_3$\textsuperscript{95,96}. The mechanism for this is described as exchange striction\textsuperscript{97}, which relies on the fact that the exchange constant $J$ (a physical constant measuring the degree to which the electronic charge distributions of two magnetic atoms in a material overlap one another, not to be confused with the total angular moment quantum number) is strongly correlated with the distance between the two atoms. When the spins of the two atoms order (i.e. at the magnetic phase transition), the exchange magnetic energy produces a change in the elastic energy of the structure, and the atoms rearrange themselves to minimise these energies. For YMnO$_3$, this results in an alternating ‘up-up-down-down’ alternation of the Mn-O-Mn bonds, lowering the symmetry to $P2_1/nm$ to produce spontaneous polarisation along the $a$ axis. A similar mechanism is proposed for AMnO$_3$ (A: Ho, Er, Tm, Yb, Lu)$^{94,98}$, Ca$_3$CoMnO$_6$\textsuperscript{99} and the AMn$_2$O$_5$ (A: Ho, Er, Tm, Yb, Lu) series\textsuperscript{100}, though the latter series exhibit charge-ordering-based ferroelectricity rather than geometric ferroelectricity.

1.5 Thesis Outline

This thesis consists of four main research chapters with a theme of investigating structure-property relationships in the solid state, with particular emphasis on improper ferroelectric orderings. Chapter 2 is concerned with the solid solution Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$ (A: Ca, Ba; 0 $\leq$ $x$ $\leq$ 7), initially exploring a variety of synthetic techniques to produce structures substituted to varying degrees by Ca$^{2+}$ and Ba$^{2+}$ cations, before characterising the resulting phases by powder synchrotron X-ray diffraction, powder neutron diffraction and SQuID magnetometry. Special attention is paid to the unusual asymmetric and anisotropic substitution patterns of the two cations. Chapter 3 focuses on the synthesis and characterisation of the Ba-substituted end member of the solid solution, Ba$_3$Mn$_4$O$_{15}$, a novel binary metal oxide compound. Powder synchrotron X-ray diffraction, powder neutron diffraction techniques and SQuID magnetometry are used to characterise the phase, and careful symmetry-adapted structural refinements provide evidence that the phase possesses a multiferroic ground state.

The latter half of the experimental chapters examine the $n$ = 2 Ruddlesden-Popper phases Ca$_3$Ti$_2$O$_7$ and Ca$_3$Mn$_2$O$_7$. In Chapter 4, a high-pressure powder synchrotron X-ray diffraction experiment and \textit{ab initio} calculations are used to investigate the effect of increasing pressure on the phase transitions of both compounds, finding unexpectedly that high
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pressure acts to stabilise the polar $A2_1 am$ phase. This contradicts the expected result for proper FE materials, in which the polar phase is destabilised by increasing pressure. In Chapter 5, the switching mechanism of the hybrid improper ferroelectric (HIF) $n = 2$ Ruddlesden-Popper (RP) phases are explored. A novel in situ synchrotron X-ray diffraction experiment is performed on sintered powder samples of $\text{Ca}_{2.15}\text{Sr}_{0.85}\text{Ti}_2\text{O}_7$, and careful analysis is performed to extract the intensities of superstructure reflections relevant to the switching process. In conjunction with symmetry-adapted modelling, a mechanism for the switching is proposed involving the rotation mode with irrep $X_2^+$ present in the structure. Finally, Chapter 6 reviews the experimental work in this thesis and proposes possible future research based on the results in the context of current research trends.
Chapter 2. Synthesis and Characterisation of $\text{Sr}_{7-x}\text{A}_x\text{Mn}_4\text{O}_{15}$

2.1 Introduction

The manganite family of compounds are a well-studied group of solid-state phases and are known to exhibit a variety of phenomena, including FM and FE orderings, multiferroicity\textsuperscript{101} and colossal magnetoresistance\textsuperscript{102,103}. The $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ structure was first described by Kriegel et al.\textsuperscript{104} in 1992. It is a monoclinic crystal structure with the space group $P2_1/c$ which is unlike the more commonly-seen perovskite or Ruddlesden-Popper phases described elsewhere in this thesis. The unit cell of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ is shown in Figure 2.1, and its asymmetric unit consists of four Sr sites, two Mn sites and eight O sites; all but two of these (the Sr(3) and O(6) sites) are on general positions. The Sr(1) site is small, having an average Sr-O bond length of approximately 2.56 Å compared with approximately 2.68 Å for the other three Sr sites. The two Mn sites are close together and form $\text{Mn}_2\text{O}_9$ face-sharing octahedral dimer motifs. These dimers are connected in the $ac$-plane to form strings, which themselves form layers by stacking along $a$. Put together, these dimers form a quasi-2-dimensional structure.

![Figure 2.1 Unit cell of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ showing the $\text{Mn}_2\text{O}_9$ face-octahedral dimers in the $bc$- and $ac$-planes, as well as a $(2 \times 1 \times 2)$ supercell to illustrate the strings of dimers](image)

Compared to the more ubiquitous perovskites, relatively little literature exists exploring the structural and magnetic behaviour of $\text{Sr}_7\text{Mn}_4\text{O}_{15}$. The first work published after its discovery explored its potential for use in high-temperature negative temperature coefficient...
thermistors; that is, electrical resistors which exhibit a reduction in their resistance with increasing temperatures\textsuperscript{105}. Both this work and a later investigation\textsuperscript{106} of the high-temperature properties of Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15} found that the phase would be an effective candidate for such an application.

The first major work investigating the structure and properties of Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15} were performed by Vente \textit{et al.}\textsuperscript{107} In their first paper, samples of Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15}, Sr\textsubscript{6}CaMn\textsubscript{4}O\textsubscript{15}, Sr\textsubscript{6}BaMn\textsubscript{4}O\textsubscript{15} and Sr\textsubscript{5}BaCaMn\textsubscript{4}O\textsubscript{15} were produced via standard solid-state synthetic methods. They showed that Ca\textsuperscript{2+} substituted preferentially on to the smaller Sr(1) site, which sits between the layers of Mn\textsubscript{2}O\textsubscript{9} dimer strings, with Ba\textsuperscript{2+} substituting on to the larger Sr(3) and Sr(4) sites, which are in the centre and edge of each layer. The Sr(2) site is central in the layers on the opposite side of the dimer to Sr(1). The unit cell volume varied linearly with the average ionic radius of the A-site cation. The relationship between the individual lattice parameters and the cation radius in Sr\textsubscript{5}BaCaMn\textsubscript{4}O\textsubscript{15} was more complex than anticipated; with the average cation radius on each site being more important for determining the change in a given parameter than the overall average cation radius. This work was followed by a powder neutron diffraction (PND) and magnetic susceptibility investigation into the non-substituted Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15}\textsuperscript{108}. The magnetic structure was found to be AFM, though a divergence in the DC magnetic susceptibility zero-field-cooled and field-cooled curves below 150 K was observed. This was rationalised as being due to the formation of clusters of AFM-ordered unit cells over short range, which grow to form long-range order by approximately 75 K. This result was corroborated by Li and co-workers\textsuperscript{109}, who used electron spin resonance and dielectric spectroscopy techniques to show AFM spin pairing in the Mn\textsubscript{2}O\textsubscript{9} dimers, with a transition around 370 K indicating an approximate onset temperature. Their work also found a strong correlation between the magnetic and dielectric properties in the form of spin-lattice coupling. Craddock and Senn\textsuperscript{110} later found that the synthesis of samples substituted by Ca\textsuperscript{2+} up to 50\% (i.e. Sr\textsubscript{3.5}Ca\textsubscript{3.5}Mn\textsubscript{4}O\textsubscript{15}) was achievable and proposed an alternative explanation for the divergence in the magnetic susceptibility. Their theory proposed that the AFM spins may undergo a small canting. Not only would this result in weak FM properties, but it would also couple to a structural phase transition below the magnetic ordering temperature to the lower-symmetry \textit{P}2\textsubscript{1} space group in which the O(6) site is displaced from its high-symmetry position, resulting in a multiferroic structure.

Several researchers have also performed work to investigate the anion ordering in Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15}. Hayward\textsuperscript{111} showed that Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15} undergoes topotactic reduction by heating the phase in the presence of NaH, forming the metastable Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{12} phase. The apex-shared
Chapter 2. Synthesis and Characterisation of Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$

O$^{2-}$ anions were selectively eliminated from the structure (as opposed to the face-sharing anions), producing isolated Mn$_2$O$_6$ dimers consisting of a distorted square-based pyramid which shared a face with a highly distorted tetrahedron. The reduced phase exhibited no long-range magnetic ordering, showing the significance of the dimer strings in producing ordered magnetic behaviour. The average effective paramagnetic moment on each Mn$^{2.5+}$ (mean oxidation state) was found to be 2.1 μB; strong intra-dimer Mn-Mn coupling and low-spin configurations were both proposed as reasons for the low value. Later experiments found that compositions Sr$_7$Mn$_4$O$_{15-x}$ ($x = 1, 2, 3$) were attainable by controlling the temperature of the reduction reaction and careful reoxidation using KMnO$_4$. Observations from these experiments showed that the reason for the selective elimination of the apical O$^{2-}$ anions was to maintain the most ideal coordination environments for both the Mn and Sr sites in the structure. This selectivity extended to the Sr$_6$CaMn$_4$O$_{15}$ and Sr$_6$BaMn$_4$O$_{15}$ compositions. Finally, Saratovsky et al. demonstrated that the reduced Sr$_7$Mn$_4$O$_{12}$ phase could be reacted with F$_2$ to produce Sr$_7$Mn$_4$O$_{13}$F$_2$. In this phase, the F$^-$ anions are found on a site similar to the O(8) site in Sr$_7$Mn$_4$O$_{15}$, though displaced from its original position, implying a degree of charge ordering.

In summary, the Sr$_7$Mn$_4$O$_{15}$ phase has been demonstrated to possess a certain degree of flexibility to chemical substitution, with remarkable changes to its structural and magnetic behaviour shown to be possible. The aim of the work presented in this chapter was to extend the cation substitution of the phase, and to investigate the resultant changes in the structure and magnetic behaviour, with aspirations towards triggering a phase transition to a novel multiferroic phase.

2.2 Experimental

2.2.1 Solid-State Synthesis

Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$ ($A$: Ca, Ba; $0 \leq x \leq 5$) samples were synthesised using standard solid-state methods. Stoichiometric quantities of the appropriate combinations of carbonates (SrCO$_3$, CaCO$_3$ and BaCO$_3$, all $> 99.9\%$ pure) were ground in an agate mortar with MnO$_2$ until homogeneous, then pressed into 13 mm-diameter pellets using 7.5 tonnes of applied pressure. These pellets were calcined at 900 °C for 20-24 hours, then reground and fired between 900-1200 °C for various time periods depending on the A-site cation and degree of substitution. The heating temperatures and durations which were found to produce the purest samples are summarised in Table 2.1. All samples were prepared with frequent intermediate regrindings.
Table 2.1 Heating temperatures and durations required to synthesise substituted Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$ phases and impurity phases identified for each composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>T (°C)</th>
<th>Time (days)</th>
<th>Impurity phase(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_7$Mn$<em>4$O$</em>{15}$</td>
<td>1000</td>
<td>6</td>
<td>4H-SrMnO$_3$ (maximum 3.71%)</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Sr$_6$CaMn$<em>4$O$</em>{15}$</td>
<td>1000</td>
<td>40</td>
<td>4H-SrMnO$_3$ (4.92%)</td>
</tr>
<tr>
<td>Sr$_5$Ca$_2$Mn$<em>4$O$</em>{15}$</td>
<td>1000</td>
<td>37</td>
<td>4H-SrMnO$_3$ (3.53%)</td>
</tr>
<tr>
<td>Sr$_4$Ca$_3$Mn$<em>4$O$</em>{15}$</td>
<td>1000</td>
<td>37</td>
<td>4H-SrMnO$_3$ (3.11%)</td>
</tr>
<tr>
<td>Sr$_3$Ca$_4$Mn$<em>4$O$</em>{15}$</td>
<td>1000</td>
<td>86</td>
<td>Ca$<em>{4/3}$Sr$</em>{2/3}$MnO$_4$ (24.46%)</td>
</tr>
<tr>
<td>Sr$_2$Ca$_5$Mn$<em>4$O$</em>{15}$</td>
<td>1000</td>
<td>90</td>
<td>Ca$_2$MnO$_4$ (5.17%)</td>
</tr>
<tr>
<td>Sr$_5$BaMn$<em>4$O$</em>{15}$</td>
<td>1050</td>
<td>3</td>
<td>4H-SrMnO$_3$ (1.71%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2H-BaMnO$_3$ (0.83%)</td>
</tr>
<tr>
<td>Sr$_5$Ba$_2$Mn$<em>4$O$</em>{15}$</td>
<td>1050</td>
<td>3</td>
<td>2H-BaMnO$_3$ (0.62%)</td>
</tr>
<tr>
<td>Sr$_4$Ba$_3$Mn$<em>4$O$</em>{15}$</td>
<td>1050</td>
<td>5</td>
<td>2H-BaMnO$_3$ (0.72%)</td>
</tr>
<tr>
<td>Sr$_3$Ba$_4$Mn$<em>4$O$</em>{15}$</td>
<td>1050</td>
<td>5</td>
<td>None identified</td>
</tr>
<tr>
<td>Sr$_2$Ba$_5$Mn$<em>4$O$</em>{15}$</td>
<td>1050</td>
<td>5</td>
<td>None identified</td>
</tr>
<tr>
<td>Ba$_7$Mn$<em>4$O$</em>{15}$</td>
<td>900</td>
<td>6</td>
<td>BaCO$_3$ starting material (8.31%)</td>
</tr>
</tbody>
</table>

2.2.2 Diffraction Experiments

2.2.2.1 Laboratory Powder X-Ray Diffraction

Laboratory powder diffraction experiments were performed to monitor the progress of the various synthetic attempts. These experiments were performed using a Panalytical X-Pert Pro MPD in reflection geometry equipped with a Johansson monochromator to produce Cu K$_{α1}$ X-ray radiation, and a Panalytical Empyrean diffractometer in reflection geometry equipped with a Co target and Fe filter to produce Co K$_{α1}$ and K$_{α2}$ radiation. All diffraction data were analysed using TOPAS Academic v6.

2.2.2.2 Synchrotron Powder X-Ray Diffraction

High-resolution X-ray powder diffraction experiments were performed on all samples at Beamline I11 at Diamond Light Source, making use of the position-sensitive detector (PSD) and multi-analyser crystal (MAC) detector at room temperature. The samples were loaded in transmission geometry in borosilicate glass capillaries which were 0.3 mm in diameter. The beam energy was ~15 keV, equating to an X-ray wavelength of ~0.825 Å. The precise experimental wavelength and instrumental contribution to the peak profile were determined against a NIST 640 Si standard and fixed for subsequent analysis. All diffraction data were analysed using TOPAS Academic v6.
2.2.2.3 Powder Neutron Diffraction

High-resolution neutron powder diffraction experiments were performed on samples of Sr$_7$Mn$_4$O$_{15}$, Sr$_2$Ba$_5$Mn$_4$O$_{15}$ and Sr$_2$Ca$_5$Mn$_4$O$_{15}$ at Beamline D2B at the ILL. The neutron wavelength was 1.594251(1) Å (calculated using a NAC (Na$_2$La$_3$Al$_2$F$_{14}$) standard), and experiments were performed at 1.5 K, 100 K and 300 K. Additional variable-temperature neutron diffraction experiments were performed on samples of Sr$_2$Ba$_5$Mn$_4$O$_{15}$ and Sr$_2$Ca$_5$Mn$_4$O$_{15}$ at Beamline D20 (ILL) in the temperature range 1.5 – 100 K, using a neutron wavelength of ~2.409 Å. All diffraction data were analysed using TOPAS Academic v6. Combined X-ray and neutron refinements were performed for Sr$_7$Mn$_4$O$_{15}$, Sr$_2$Ca$_5$Mn$_4$O$_{15}$ and Sr$_2$Ba$_5$Mn$_4$O$_{15}$, and these were found to be robust. For these refinements, the background, lattice parameters, atomic coordinates and Sr site occupancies were allowed to freely refine, and the B$_{iso}$ values were constrained such that one value was refined per atom type. Significant anisotropic peak strain was modelled by using a Stephens’ anisotropic peak broadening model consistent with monoclinic geometry. Empirically it was found that only refining coefficients S220, S022 and S121 produced a satisfactory fit while keeping the number of additional parameters introduced into the refinement to a minimum.

Due to the large number of degrees of freedom in the model, refinements against X-ray diffraction data for the intermediate compositions where neutron data were not available were performed with the following constraints: a linear interpolation was performed between the values in the combined refinements for the atomic coordinates and B$_{iso}$ values, and Stephens’ anisotropic peak broadening parameters were fixed to the Sr$_7$Mn$_4$O$_{15}$ values. The background, lattice parameters and Sr site occupancies were allowed to refine freely.

High-pressure TOF neutron powder diffraction data were collected on the PEARL diffractometer at the ISIS Neutron and Muon Facility by Dr Nick Funnell. Details on the PEARL instrument and associated experimental and data-correction procedures are described by Bull et al. A powder sample of Sr$_2$Ca$_5$Mn$_4$O$_{15}$ was loaded into a null-scattering, encapsulated titanium-zirconium alloy gasket, and a lead pellet was added to serve as a pressure calibrant. Hydrostatic compression conditions were achieved by using a methanol-ethanol pressure-transmitting medium in a 4:1 volume ratio. The gasket was loaded in a V3 Paris-Edinburgh press equipped with single-toroid zirconia-toughened alumina ceramic anvils. Data were collected at 5-tonne load increments with an additional measurement at 12 tonnes. Collection times for most load points were approximately 4 hours, except at 15, 40, 55 and 60 tonnes which collected data for 8, 9, 6, and 8 hours respectively. The unit cell volume of the lead calibrant was determined using Rietveld refinement and was used during the experiment to determine the pressure in GPa from a
previously-determined Murnaghan equation of state\textsuperscript{115}. For additional higher-pressure measurements, the gasket was loaded into a Paris-Edinburgh press equipped with single-toroid sintered diamond anvils. Collection times for these measurements were 8, 10 and 13 hours at 70, 80 and 90 tonnes respectively. The maximum pressure achieved in these experiments was 8.07(6) GPa.

\textbf{2.2.3 SQuID Magnetometry}

Field-cooled (FC) and zero field-cooled (ZFC) DC magnetic susceptibility measurements were performed using a Quantum Design MPMS-5S SQuID magnetometer in the temperature range 5 – 325 K with an applied field of 100 Oe. Powder samples were loaded into gel capsules for measurements.

\section*{2.3 Results and Discussion}

\subsection*{2.3.1 Synthesis Conditions}

Initial attempts to synthesise the solid solution phases focussed entirely on traditional solid-state techniques, with early successes up to \(x = 3\) for both substituting cations. However, as the degree of substitution of the phase increased, the progress of the solid-state reaction to produce Ca-substituted phases became increasingly slow as monitored by laboratory X-ray diffraction, and impurity phases (noted in Table 2.1) were found to be extremely difficult to eliminate. Attempts to accelerate the synthesis of Ca-substituted phases by increasing the reaction temperatures resulted in phases which were dominated by impurity phases. As such, reactions below 1100 °C were attempted to mitigate the formation of impurities such as perovskites and \(n = 1\) Ruddlesden-Popper phases. These syntheses were extremely time-intensive and require a large number of regrinding steps to promote complete reaction. A variety of other synthetic approaches were investigated in an attempt to synthesise higher-substituted compositions.

\subsection*{2.3.1.1 Citrate Precursor Method}

The methods known variously in the literature as the ‘Pechini process’\textsuperscript{116}, ‘citrate precursor’\textsuperscript{117,118} or ‘sol-gel’\textsuperscript{119} syntheses has previously been shown to permit access to phases and compositions which are not readily prepared by traditional solid-state techniques. The general method involves dissolving an appropriate combination of metal-containing starting materials in a solution of an appropriate acid (such as metal nitrates and nitric acid), then adding citric acid and ethylene glycol before drying the solution to a gel. The gel is then heated to around 100-200 °C to drive off water and produce a powder, which is then heated to > 600 °C to decompose the citrates and any other organic material in the sample. The formation of a solution and gel results in a homogeneous mixture of the metal
cations throughout the eventual powder. It was hoped that this precursor procedure would allow for both faster reactions and a greater control of the impurity phases. The method had previously been demonstrated as a synthesis route for Sr$_7$Mn$_4$O$_{15}$ and so it was also hoped that it would prove possible to produce Ca$_7$Mn$_4$O$_{15}$ in this manner. Additionally, the morphology and oxygen content of samples produced by citrate precursor methods has been demonstrated to vary from those produced by traditional techniques to the extent that magnetic properties may be affected, so the potential for this synthesis technique to affect possible multiferroic orderings was also of interest.

To attempt to synthesise Sr$_7$Mn$_4$O$_{15}$ and Ca$_7$Mn$_4$O$_{15}$ by the citrate precursor method, stoichiometric quantities of Sr(NO$_3$)$_2$, Ca(NO$_3$)$_2$ and Mn(NO$_3$)$_2$ were dissolved in a 30% solution of HNO$_3$. Separately, 100 mL of anhydrous ethanol and 10 mL of glacial acetic acid were mixed. The two solutions were mixed and 5 molar equivalents of citric acid was added and mixed to dissolve. The solution was heated on a hotplate at 200 °C with stirring until a gel formed. Heating was then increased to 300 °C until the gel was dried completely to a black powder. This powder was dried at 200 °C for 20 hours, then pressed at 7.5 tonnes into 13-mm diameter pellets. These pellets were heated initially at 500 °C for 12 hours, then re-ground, pressed into pellets and sintered at 750 °C for 48 hours. Attempts to produce Sr$_7$Mn$_4$O$_{15}$ and Ca$_7$Mn$_4$O$_{15}$ using the citrate precursor process were unsuccessful, with powder X-ray diffraction patterns containing a variety of different Sr-Mn-O and Ca-Mn-O compositions. Several of these compositions were identified including SrO, CaO, 4H-SrMnO$_3$ and Sr$_3$Mn$_2$O$_7$, however several peaks remained unidentified, and the overall structures were quite amorphous. Additional heating of the powder sample did not produce the desired phases, instead resulting in an increase in the crystallinity of the perovskite and RP phases.

2.3.1.2 Solvothermal Synthesis

An attempt to produce Sr$_7$Mn$_4$O$_{15}$ was also made using a solvothermal route. This technique involves the use of a solid reagents suspended in a solvent contained within a sealed reaction vessel to produce high reaction pressures at relatively low temperatures compared to traditional syntheses. The solvothermal process has been shown to produce metastable binary metal oxides which were otherwise unattainable by solid-state methods with the benefit of reduced energy costs and less hazardous solvents than the citrate precursor method described above. MnSO$_4$ and KMnO$_4$ were made into separate 0.35 mol dm$^{-3}$ solutions and combined in a ratio of 1.5:1. KOH was also dissolved to produce a 4 mol dm$^{-3}$ solution and these solutions were combined in a 25 mL polytetrafluoroethylene autoclave reaction vessel. SrSO$_4$ was then added, and the autoclave
was sealed before being placed into an oven at 200 °C for 24 hours. Once cooled, the resultant black powder was washed with deionised water and dried at 74 °C for 24 hours. Laboratory powder X-ray diffraction experiments performed on the powder indicated that the desired reaction had not occurred. The diffraction pattern was largely dominated by unreacted SrSO₄, with a small amount of unreacted MnSO₄ and several oxides of manganese. The reason for this failed synthesis is unclear, as the hexagonal perovskite 4H-SrMnO₃ has been reportedly synthesised via a similar solvothermal route. It is possible that the mixed solubilities of the Mn-containing reagents limited the reaction.

### 2.3.1.3 High-Pressure Synthesis

Following the initial synthesis of a Ba₇Mn₄O₁₅ sample containing only Ba₄Mn₃O₁₀ as an impurity phase of around 10% (the details of which are discussed in Chapter 3), it was realised that the calculated density of Ba₇Mn₄O₁₅ was approximately 6.2 g cm⁻³. Given that the density of Ba₄Mn₃O₁₀ was calculated at 6.14 g cm⁻³, it was hoped that by performing a high-pressure treatment of this mixed powder sample, the reaction could be forced to completion. The high-pressure treatment was performed by Dr Wei-Tin Chen at the Center for Condensed Matter Sciences at the National Taiwan University. Two samples, one containing a mixture of Ba₇Mn₄O₁₅ (90% by mass according to Rietveld refinements of high-resolution X-ray powder diffraction) and Ba₄Mn₃O₁₀ (10%) and the other containing a 75%:25% mixture of the same phases were subjected to the same high-pressure treatment: 5 GPa of hydrostatic pressure and 900 °C for 30 minutes. High-resolution X-ray powder diffraction performed on these samples post-treatment indicated that the Ba₇Mn₄O₁₅ phase was not favoured. Instead, both samples exhibited a switch in the majority phase to Ba₄Mn₃O₁₀ along with the development of an additional unwanted phase which was identified as Ba₂MnO₃; the first sample was found to have a Ba₇Mn₄O₁₅:Ba₄Mn₃O₁₀:Ba₂MnO₃ ratio of approximately 12:80:8, while the second sample switched to 32:61:7. The calculated density of Ba₂MnO₃ is 5.84 g cm⁻³, suggesting that the density of the phase is less important to the effectiveness of the high-pressure treatment than the Ba:Mn ratio, since the two impurity phases detailed here have the most similar ratio to Ba₇Mn₄O₁₅ of all of the binary Ba-Mn-O phases listed on the Inorganic Crystal Structure Database (ICSD) (at the time of writing).

### 2.3.2 Impurity Phases

None of the above methods were especially successful at reducing the reaction time and monitoring by X-ray powder diffraction indicated that most of these methods failed to produce the desired phases at all. Indeed, even traditional solid-state syntheses of Sr₆CaMn₄O₁₅, Sr₅Ca₂Mn₄O₁₅ and Sr₃Ca₄Mn₄O₁₅ suffered from competition between the
desired phases and 4H-SrMnO₃ hexagonal perovskite impurities. The Sr₃Ca₄Mn₄O₁₅ and Sr₃Ca₃Mn₄O₁₅ compositions contained slightly different impurities which were identified as Ca₄/₃Sr₂/₃MnO₄ and Ca₃MnO₄. The precise reason for the appearance of the n = 1 Ruddlesden-Popper phase in place of the hexagonal perovskite impurity is unknown but may be related to the increased Ca²⁺ content of the reaction, as Ca-rich perovskites tend towards the traditional cubic structure while Sr-rich perovskites tend to form hexagonal structures. Due to the extremely long reaction times required to produce these compositions, repeated syntheses with small variations in reaction conditions were of limited value. The phases detailed in Table 2.1 represent the results from samples with the smallest impurity concentrations and totally pure samples were not achieved for most compositions; nevertheless, the impurities were minimal and well-characterised in terms of their structure and properties and hence did not preclude a thorough investigation of the structure-property relationships across the Sr₇₋ₓAₓMn₄O₁₅ solid solution.

Syntheses of the Sr₇₋ₓBaₓMn₄O₁₅ compositions did not suffer from the same quantity of impurity phases. In place of the 4H-SrMnO₃ phase identified for the Ca-containing compositions, the key impurity for these phases was found to be 2H-BaMnO₃. The concentration of this phase was generally lower than that of the Ca-containing phase impurities, possibly indicating the relative ease with which Ba²⁺ is incorporated into the Sr₇Mn₄O₁₅ structure. For the Sr₂Ba₃Mn₄O₁₅ phase, a very small peak was observed around 2θ = 15.2° which was never successfully identified in spite of extensive database searching. Due to a lack of further peaks which remained unidentified, the peak at 15.2° may be the result of highly strained unreacted starting material.

The SrCa₄Mn₄O₁₅, Ca₇Mn₄O₁₅ and SrBa₆Mn₄O₁₅ compositions were not found to be accessible, despite several attempts at synthesising each phase. For the Ca-substituted compositions, the products of the syntheses were mixtures of perovskites (CaMnO₃ and SrMnO₃) and RP phases (Ca₃MnO₄ and Ca₃Mn₂O₇) with no identifiable quantity of the desired product in the laboratory powder X-ray diffraction patterns. For SrBa₆Mn₄O₁₅, a mixture of hexagonal perovskites (SrMnO₃ and 2H-BaMnO₃) and layered phases (Ba₄Mn₃O₁₀ and Ba₆Mn₃O₁₆) were the main phases identified from the diffraction experiments.

In summary, standard solid-state synthesis techniques were found to be the best methods for accessing higher-substituted phases in the Sr₇₋ₓAₓMn₄O₁₅ solid solution. Though the products of these syntheses were not always phase-pure, they were sufficiently pure as to facilitate further study.
2.3.3 Structural Analysis

A plot of the fit achieved by combined Rietveld refinements to a synchrotron X-ray powder diffraction pattern recorded using the high-resolution MAC detector at I11 at Diamond Light Source and a neutron powder diffraction pattern recorded at the D2B beamline at the ILL is shown in Figure 2.2. The .cif produced using this refinement is summarised in Table 2.2, with the constraints described in Section 2.2.2.3. For the sake of brevity, tables of the structural information for other compositions in the solid solution Sr\(_7\)Mn\(_4\)O\(_{15}\)-xA\(_x\)Mn\(_4\)O\(_{15}\) (A: Ca, Ba; 0 ≤ x ≤ 5) are contained in Appendix 1.

Figure 2.2 Combined Rietveld refinement fit (R\(_{wp}\): 7.98\%, R\(_p\): 6.40\%, \(\chi^2\): 8.39) to (a) powder synchrotron X-ray diffraction pattern (\(\lambda = 0.826341(5)\) Å) for Sr\(_7\)Mn\(_4\)O\(_{15}\) at 300 K recorded using I11 MAC detector and (b) neutron powder diffraction pattern (\(\lambda = 1.594596(5)\) Å) for Sr\(_7\)Mn\(_4\)O\(_{15}\) at 300 K recorded using D2B detector. Blue ticks indicate reflections present in the main phase, green ticks indicate reflections resulting from the 4H-SrMnO\(_3\) impurity. The small misfit intensity at approximately 2\(\theta\): 17° in the X-ray pattern and 2\(\theta\): 45° is possibly due to incompletely-modelled anisotropic peak broadening.
Table 2.2 Lattice parameters and atomic coordinates extracted from combined refinement of I11 (powder synchrotron X-ray diffraction, $\lambda = 0.826341(5)$ Å) and D2B (neutron powder diffraction) data for Sr$_7$Mn$_4$O$_{15}$ at 300 K.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Space group</th>
<th>Sr$_7$Mn$<em>4$O$</em>{15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P2_1/c$</td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td></td>
<td>6.81514(3)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td></td>
<td>9.62423(4)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td></td>
<td>10.38158(4)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
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<td>90</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td></td>
<td>91.8560(2)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
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<td>90</td>
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</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
<th>$B_{ISO}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr1</td>
<td>0.99631(12)</td>
<td>0.18438(8)</td>
<td>0.46573(7)</td>
<td>1</td>
<td>0.632(7)</td>
</tr>
<tr>
<td>Sr2</td>
<td>0.35054(13)</td>
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<td>0.19565(7)</td>
<td>1</td>
<td>0.632(7)</td>
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<tr>
<td>Sr3</td>
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<tr>
<td>Mn2</td>
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<td>0.16713(13)</td>
<td>0.72099(11)</td>
<td>1</td>
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<td>0.5033(6)</td>
<td>0.1011(4)</td>
<td>0.7519(4)</td>
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<td>0.544(19)</td>
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<td>0.6789(7)</td>
<td>0.1763(4)</td>
<td>0.3359(4)</td>
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<td>0.544(19)</td>
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<td>1</td>
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<td>0.0834(40)</td>
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<td>0</td>
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<td>0.544(19)</td>
</tr>
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<td>0.7105(4)</td>
<td>1</td>
<td>0.544(19)</td>
</tr>
</tbody>
</table>

Rietveld refinements were also performed against the powder diffraction data for the other compositions in the solid solution. As with Sr$_7$Mn$_4$O$_{15}$, combined refinements were performed for Sr$_2$Ca$_5$Mn$_4$O$_{15}$ and Sr$_2$Ba$_5$Mn$_4$O$_{15}$ against both I11 powder synchrotron X-ray diffraction data and D2B PND data, while for the remaining compositions, only I11 powder synchrotron X-ray diffraction data were available. As such, a linear interpolation of the atomic coordinates and $B_{ISO}$ values was performed for the non-end member compositions, but their lattice parameters and the occupancies of the Sr sites were permitted to refine. This was performed on the basis that the $O^2-$ positions were less well-resolved by X-ray diffraction alone and the near-linear behaviour of the lattice parameters. The lattice parameters of the solid solution are plotted in Figure 2.3. The $a$, $b$, and $c$ parameters all vary essentially in a linear fashion with substitution, with a slight tendency for plateauing as higher substitution by Ca is reached. The value of $\beta$ behaves differently depending on the choice of substituting cation: for Ca-substituted samples’ $\beta$ decreases with increasing substitution. With increasing Ba substitution, the same decrease is initially observed but reverses as Ba becomes the majority cation on the so-called A-site. The value of $\beta$ for
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Sr$_2$Ba$_5$Mn$_4$O$_{15}$ is still slightly less than that of Sr$_7$Mn$_4$O$_{15}$, but data for Ba$_7$Mn$_4$O$_{15}$ (replicated from Chapter 3) shows that it continues to increase with Ba substitution until it exceeds its ‘initial’ value.

To understand this unexpected behaviour and elucidate its impact on the structure as a whole, the refined site occupancy results for the solid solution were examined.

2.3.3.1 Site Occupancy Preferences

Figure 2.4 shows the refined site occupancy values extracted from the Rietveld refinements at 300 K for the solid solution Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$ (A: Ca, Ba; 0 ≤ x ≤ 5). Filled symbols indicate that the data source was a combined powder synchrotron X-ray diffraction and PND refinement, empty symbols indicate that the source was solely synchrotron data. Data for Ba$_7$Mn$_4$O$_{15}$ is replicated from Chapter 3. Error bars for all data were within the scale of the markers and are therefore not displayed.

Figure 2.3 Lattice parameters extracted from Rietveld refinements at 300 K for the solid solution Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$ (A: Ca, Ba; 0 ≤ x ≤ 5). Filled symbols indicate that the data source was a combined powder synchrotron X-ray diffraction and PND refinement, empty symbols indicate that the source was solely synchrotron data. Data for Ba$_7$Mn$_4$O$_{15}$ is replicated from Chapter 3. Error bars for all data were within the scale of the markers and are therefore not displayed.

To understand this unexpected behaviour and elucidate its impact on the structure as a whole, the refined site occupancy results for the solid solution were examined.

2.3.3.1 Site Occupancy Preferences

Figure 2.4 shows the refined site occupancy values extracted from the Rietveld refinements at 300 K for the solid solution. The left side of the plot shows the fractional occupancy of Ca$^{2+}$ cations on each of the four Sr sites for each composition and the right side of the plot shows the same results for Ba$^{2+}$ cations. In line with early reports on Sr$_6$CaMn$_4$O$_{15}$ and Sr$_6$BaMn$_4$O$_{15}$, we observe the greatest amount of Ca$^{2+}$ substitution occurring on the small Sr(1) site and the greatest amount of Ba$^{2+}$ substitution occurring on the Sr(3) and Sr(4) sites. The Sr(2) site displays a very similar degree of substitution by both cations. At low degrees of substitution, Ca$^{2+}$ cations do not substitute on to the Sr(3) and Sr(4) site at all, only
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beginning to do so when the Sr(1) and Sr(2) sites are already occupied by a majority of Ca$^{2+}$
cations.

Figure 2.4 Sr site occupancy data extracted from Rietveld refinements at 300 K for the solid
solution Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$ (A: Ca, Ba; 0 ≤ x ≤ 5). The left side indicates the fractional occupancy
on each site of the Ca$^{2+}$ cation and the right side indicates the fractional occupancy on each
site of the Ba$^{2+}$ cation. Filled symbols indicate that the data source was a combined powder
synchrotron X-ray diffraction and PND refinement, empty symbols indicate that the source
was solely synchrotron data. Data for Ba$_7$Mn$_4$O$_{15}$ is replicated from Chapter 3. Error bars for
all data were within the scale of the markers and are therefore not displayed.

A deeper understanding of the substitution behaviour of the solid solution may be gained
by examining the bond valence sums (BVS) for each site which may be occupied by Ca$^{2+}$, Sr$^{2+}$
or Ba$^{2+}$ at each composition (for convenience these sites will be referred to as Sr sites
henceforth). These were calculated according to Equation 2.1:

\[
\text{BVS} = \sum \exp\left(\frac{R_0 - R_i}{b}\right)
\]

Where $R_0$ is the ‘ideal’ bond length for an element $i$ with a valence of exactly 1 and a given
oxidation state, $R_i$ is the observed bond length extracted from powder diffraction experiments and $b$ is an empirical parameter. The parameters for these calculations were taken from the 2020 version of the IUCr Bond Valence Parameters webpage. The ideal BVS value for an A-site in Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$ is equal to the nominal valence value, $V_i$, of 2; a higher value indicates that the site is ‘overbonded’ and that the bonds are compressed, while a lower value indicates that the site is ‘underbonded’ and the bonds are stretched.$^{127}$

The difference between the BVS and the nominal valence of the site is the discrepancy factor, \( d_i \):

\[
d_i = \text{BVS} - V_i
\]

2.2

The results of the BVS calculations are pictured in Figure 2.5. The red, green and blue lines indicate the results for each site and composition using only the parameters for Sr\(^{2+}\), Ca\(^{2+}\) and Ba\(^{2+}\) respectively; the Ca\(^{2+}\)-only and Ba\(^{2+}\)-only results are confined to the left and right sides of the plots. The purple lines indicate the average of the Sr\(^{2+}\) and Ca\(^{2+}\) or Sr\(^{2+}\) and Ba\(^{2+}\) calculations, weighted according to the occupancy of the site in the given composition. The black horizontal lines indicate the ideal BVS value of 2. The data suggest that the curve observed for the \( \beta \) parameters of the Ba-substituted samples may be attributed to substitution on to the different Sr sites in the structure; as the larger Sr\((3)\) and Sr\((4)\) sites outside the Mn\(_2\)O\(_9\) layers are filled, the Ba\(^{2+}\) cations are forced on to the smaller Sr\((1)\) and Sr\((2)\) sites between the layers. Given their positions within the unit cell, the \( \beta \) behaviour begins to make sense, with the larger Ba\(^{2+}\) cation forcing the unit cell to open to accommodate shifts of the dimer chains. If samples of the Sr\(_3\)Ca\(_4\)Mn\(_4\)O\(_{15}\) and Ca\(_7\)Mn\(_4\)O\(_{15}\) compositions were to be prepared, one might expect a corresponding downturn in \( \beta \) as the unit cell contracts to accommodate the smaller cation on the Sr\((3)\) and Sr\((4)\) sites.

It can be seen that the Ca\(^{2+}\)-only calculations result in BVS results which are underbonded in all cases except for Sr\(_3\)Ca\(_4\)Mn\(_4\)O\(_{15}\) and Sr\(_2\)Ca\(_5\)Mn\(_4\)O\(_{15}\), while the Ba\(^{2+}\)-only calculations result in overbonding in all cases. The degree to which a given site is under- or overbonded is related to the size of the site and the cation involved. As such, the Ca\(^{2+}\)-only substitutions tend to be closer to ideal in the Sr\((1)\) and Sr\((2)\) sites, while the Ba\(^{2+}\)-only substitutions are closer to ideal in the Sr\((3)\) and Sr\((4)\) sites. For all sites, the Sr\(^{2+}\)-only substitutions are generally more overbonded for Ca-substituted samples and underbonded for Ba-substituted samples. The results which are generally closest to ideal are found by calculating the occupancy-weighted average of the BVS for the substituting cations on each site. The maintenance of ideal Sr-site BVS values in the structure is another reason for the substitution preferences of the sites. The only exception to this is the Sr\((1)\) site in Ba\(_7\)Mn\(_4\)O\(_{15}\), for which full occupation by Ba\(^{2+}\) cations results in a large degree of overbonding. The larger size of these cations compared to Sr\(^{2+}\) results in compression of the Ba-O bonds in the polyhedra, but since there are no other sites on which the cations can be placed, they are forced into the same structure as Sr\(_7\)Mn\(_4\)O\(_{15}\). The discrepancies between the calculated BVS results and the ideal values could therefore indicate a large degree of strain in the structures. It is also likely that the results for the compositions which were not part of a
combined synchrotron and neutron refinement are biased by the linear interpolation of the atomic coordinates described above.

Figure 2.5 Bond valence sums calculated for the Sr sites of the Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$ solid solution using single-cation calculations and an occupancy-averaged calculation. The black line indicates the ideal value of 2.

2.3.3.2 Split-Site Model

Early work on the synthesis of Sr$_7$Mn$_4$O$_{15}$ by Vente et al.\textsuperscript{108} described a significant improvement in the fitting statistics of their PND data at 29 K by permitting displacements of the Sr(3) and O(6) sites. In spite of attempts at refining Sr$_7$Mn$_4$O$_{15}$ models using the 1.5 K PND data from D2B in which some combination of the Sr(3) and O(6) sites were either permitted to freely refine or manually displaced in combinations of the $a$, $b$ and $c$ directions, this result has not been replicated. Further tests were also performed using ISODISTORT to investigate modes transforming as the $\Gamma_1^+$, $\Gamma_1^-$, $\Gamma_2^+$ and $\Gamma_2^-$ irreps. An example of the results gathered from these refinements is pictured in Figure 2.6. Depicted is the change in the $R_{\text{wp}}$ of refinements with manual variation the $\Gamma_4^-$ modes of the O(6) site, generating a structure with $P2_1$ symmetry. The three modes (with ISODISORT labelling) are as follows: P2$_1$/c[0,0,0]GM1-(a)[O6:b: dsp] Au$_1$(a), P2$_1$/c[0,0,0]GM1-(a)[O6:b: dsp] Au$_2$(a) and P2$_1$/c[0,0,0]GM1-(a)[O6:b: dsp] Au$_3$(a). These correspond to a displacement of O(6) along $c$, in the $ac$-plane and along $b$, respectively. It is clear that, while the latter two do cause a very small improvement in $R_{\text{wp}}$, none of these modes provides a significant improvement in the fitting statistics. Similar results were found for displacement tests of the Sr(3) site.
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2.3.4 Magnetic Analysis

In addition to the room-temperature structural analysis, all samples in the solid solution (except Sr\textsubscript{3}Ca\textsubscript{4}Mn\textsubscript{4}O\textsubscript{15} due to significant contamination by an n = 1 RP phase) were investigated for their magnetic properties via SQuID magnetometry. Neutron powder diffraction experiments were performed on the Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15}, Sr\textsubscript{5}Ca\textsubscript{3}Mn\textsubscript{4}O\textsubscript{15} and Sr\textsubscript{3}Ba\textsubscript{3}Mn\textsubscript{4}O\textsubscript{15} compositions at Beamline D2B at the ILL at 1.5 K, 100 K and 300 K, with the latter two compositions being carried through to additional variable-temperature neutron powder diffraction experiments on Beamline D20 at the ILL in the 3 – 92 K temperature range.

2.3.4.1 SQuID Data

The DC SQuID magnetometry results acquired for the purest compositions in the solid solution Sr\textsubscript{7-x}A\textsubscript{x}Mn\textsubscript{4}O\textsubscript{15} (A: Ca, Ba; 0 ≤ x ≤ 5) are shown in Figure 2.7. Though there is some obvious variation between the compositions, they all share the same general shape: a steady increase in the $\chi_{\text{mol}}$ value with decreasing temperature between 300-100 K, followed by a pair of turning points in the 80-50 K region and a sharp increase in $\chi_{\text{mol}}$ below 20 K. The FC and ZFC curves separate below approximately 85 K in the Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15} phase, and the maximum FC susceptibility remains similar across the entire solid solution between 0.016-0.022 emu mol\textsuperscript{-1} Oe\textsuperscript{-1}.

The Ca-containing compositions have sharper inflection points (both maxima and minima) than Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15}. These compositions also exhibit separation of the FC and ZFC curves at a higher temperature than the rest of the solid solution, with Sr\textsubscript{5}CaMn\textsubscript{4}O\textsubscript{15} separating around 100 K and Sr\textsubscript{5}Ba\textsubscript{2}Mn\textsubscript{4}O\textsubscript{15}, Sr\textsubscript{4}Ca\textsubscript{3}Mn\textsubscript{4}O\textsubscript{15} and Sr\textsubscript{3}Ba\textsubscript{3}Mn\textsubscript{4}O\textsubscript{15} separating around 125 K. Since the behaviour does not appear to evolve consistently with the degree of Ca substitution in
the phase, it was assumed that it is not intrinsic to the solid solution and is the result of an
impurity. The most obvious possibility is that the 4H-SrMnO₃ impurity phase identified in
all except Sr₂Ca₃Mn₄O₁₅ has a long-range magnetic transition coincident with this feature.
However, several sets of previous experiments on the 4H-SrMnO₃ phase indicate that
its Néel temperature is around 280 K, and the FC and ZFC curves both decrease with cooling
between 400-10 K. Searching for plausible alternatives, the next most likely candidate is
CaMnO₃ which has a Néel temperature of 125 K, consistent with our observations.
While no evidence of CaMnO₃ was found in the Rietveld refinements, it remains the most
likely culprit for the observed magnetic behaviour. A SQuID magnetometry experiment
performed by Gil de Muro and co-workers under a coercive field of 100 Oe demonstrates
that the magnetic susceptibility of a pure sample of CaMnO₃ can reach around
0.6 emu mol⁻¹ Oe⁻¹, approximately 30 times higher than that observed in Sr₇-xCaₓMn₄O₁₅. Thus, even an impurity concentration of <1 % (which is likely below the detection limit of
the X-ray diffraction experiments) will give an appreciable contribution to the observed
magnetic susceptibility.

Figure 2.7 DC SQuID magnetometry results for the solid solution Sr₇-xAₓMn₄O₁₅ (A: Ca, Ba;
0 ≤ x ≤ 5) excluding Sr₃Ca₃Mn₄O₁₅ due to excessive magnetic impurity.
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The relative purity of the Ba-containing compositions yields greater confidence in the SQuID results representing trends in the solid solution. In addition to having sharper local maxima, these phases have small peak features which begin at 63 K for Sr$_6$BaMn$_4$O$_{15}$ and decrease to approximately 47 K for Sr$_2$Ba$_2$Mn$_4$O$_{15}$. The Sr$_2$Ba$_2$Mn$_4$O$_{15}$ composition shows the greatest difference to Sr$_7$Mn$_4$O$_{15}$: in place of the pair of inflection points, the ZFC susceptibility rises smoothly with decreasing temperature and the FC susceptibility has a very subtle peak in place of the more obvious feature for the less-substituted compositions.

Plots of the maximum and minimum temperatures and susceptibilities at the turning points for each member of the solid solution are shown in Figure 2.8. The turning points were calculated by performing differentiation of a polynomial fit to the observed susceptibility. The temperature at which the FC and ZFC upper turning points occur decreases from 85 K immediately upon substitution by either Ca or Ba, stabilising around 70 K for Ca-containing samples and continuing to decrease to 50 K as Ba content increases, indicative of a decrease in the magnetic ordering temperature for the substituted phases. The lower turning points follow a similar trend, decreasing from around 40 K for Sr$_7$Mn$_4$O$_{15}$ to around 25 K for the substituted compositions. The values of the magnetic susceptibility at the turning points do not vary with any obvious trends. If the separation of the FC and ZFC curves in the Sr$_5$Ca$_2$Mn$_4$O$_{15}$ and Sr$_4$Ca$_3$Mn$_4$O$_{15}$ SQuID results can be assumed to be extrinsic, then the variation in the susceptibility maxima is very small, within approximately 0.02 emu mol$^{-1}$ Oe$^{-1}$. 
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Figure 2.8 Properties of the DC SQuID magnetometry turning point plots extracted for Sr$_7$Mn$_4$O$_{15}$-xA$_x$Mn$_4$O$_{15}$ (A: Ca, Ba; 0 ≤ x ≤ 5). Due to the difference in the shape of the curve for Sr$_2$Ba$_5$Mn$_4$O$_{15}$ its data are not included here.

Curie-Weiss fits to the 200-300 K regions of the ZFC DC magnetic susceptibility data are shown in Figure 2.9. All compositions obey Curie’s law in this temperature region, with the Ca-containing phases remaining linear to lower temperatures than the Ba-containing phases. Included in each plot are the gradient and constant values required for the straight-line fit, which are used to calculate the Curie constants according to the relationship:

\[ C = \frac{1}{m} \]

Where \( C \) is the Curie constant and \( m \) is the gradient of the inverse molar susceptibility. The effective magnetic moments per unit cell and per site are then calculated according to:

\[ \mu_{\text{eff}} (\text{formula unit}) \approx \sqrt{8C^2} \]

\[ \mu_{\text{eff}} (\text{per Mn}^{4+}) = \sqrt{\frac{\mu_{\text{eff}} (\text{formula unit})^2}{4} = \frac{\mu_{\text{eff}} (\text{formula unit})}{2}} \]
Calculated values of the Curie constant, effective paramagnetic moments per unit cell and effective paramagnetic moments per Mn$^{4+}$ are summarised in Table 2.3 and Figure 2.10. The results presented here are in closest agreement with those reported by Kriegel et al. These values are generally slightly higher than the expected result of 3.87 $\mu_B$ according to the spin-only formula for Mn$^{4+}$ cations (given in Equation 2.6 below). These deviations may be the result of strong magnetic correlations, even as high as 300 K arising due to mixing of the assorted orbitals within the Mn$_2$O$_9$ dimers. More realistic values may be recovered by measuring the magnetic susceptibilities to higher temperatures.

\[ \mu_{SO} = 2\sqrt{S(S + 1)} = 2\sqrt{\frac{3}{2}(\frac{3}{2} + 1)} = 3.87 \mu_B \]  

Figure 2.9 Curie-Weiss fits to the 200-300 K region of the ZFC susceptibility curves. The values on each plot are the gradient and constant factor for the straight-line fit, truncated to three decimal places.
Table 2.3 Curie constants, Weiss constants and effective paramagnetic moments calculated from DC ZFC SQuID results. Additional results from literature are also included for Sr\textsubscript{7-x}A\textsubscript{x}Mn\textsubscript{4}O\textsubscript{15}.

<table>
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<tr>
<th>Composition</th>
<th>Curie constant (K)</th>
<th>Weiss constant, θ (K)</th>
<th>$\mu_{\text{eff}}$(per formula unit) (μB)</th>
<th>$\mu_{\text{eff}}$(per Mn\textsuperscript{4+}) (μB)</th>
</tr>
</thead>
<tbody>
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<td>Sr\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15}</td>
<td>7.029</td>
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<td>7.499</td>
<td>3.749</td>
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<td></td>
<td>-426\textsuperscript{104}</td>
<td></td>
<td>3.62\textsuperscript{104}</td>
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<tr>
<td></td>
<td></td>
<td>-490\textsuperscript{108}</td>
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<td></td>
<td>-401\textsuperscript{109}</td>
<td></td>
<td>4.40\textsuperscript{109}</td>
</tr>
<tr>
<td>Sr\textsubscript{6}CaMn\textsubscript{4}O\textsubscript{15}</td>
<td>8.682</td>
<td>-460.5</td>
<td>8.333</td>
<td>4.167</td>
</tr>
<tr>
<td>Sr\textsubscript{5}Ca\textsubscript{2}Mn\textsubscript{4}O\textsubscript{15}</td>
<td>9.543</td>
<td>-455.4</td>
<td>8.737</td>
<td>4.369</td>
</tr>
<tr>
<td>Sr\textsubscript{4}Ca\textsubscript{3}Mn\textsubscript{4}O\textsubscript{15}</td>
<td>9.471</td>
<td>-436.3</td>
<td>8.704</td>
<td>4.352</td>
</tr>
<tr>
<td>Sr\textsubscript{2}Ca\textsubscript{5}Mn\textsubscript{4}O\textsubscript{15}</td>
<td>9.338</td>
<td>-344.7</td>
<td>8.643</td>
<td>4.322</td>
</tr>
<tr>
<td>Sr\textsubscript{6}BaMn\textsubscript{4}O\textsubscript{15}</td>
<td>8.356</td>
<td>-435.6</td>
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<td>4.088</td>
</tr>
<tr>
<td>Sr\textsubscript{5}Ba\textsubscript{2}Mn\textsubscript{4}O\textsubscript{15}</td>
<td>9.063</td>
<td>-434.5</td>
<td>8.515</td>
<td>4.258</td>
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<tr>
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<td>9.292</td>
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<td>4.311</td>
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<tr>
<td>Sr\textsubscript{3}Ba\textsubscript{4}Mn\textsubscript{4}O\textsubscript{15}</td>
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<td>4.520</td>
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<tr>
<td>Sr\textsubscript{2}Ba\textsubscript{5}Mn\textsubscript{4}O\textsubscript{15}</td>
<td>9.896</td>
<td>-463.5</td>
<td>8.898</td>
<td>4.449</td>
</tr>
</tbody>
</table>

Figure 2.10 Left: $\mu_{\text{eff}}$ per Mn\textsuperscript{4+} site calculated using Curie-Weiss fits to DC ZFC SQuID results. The red line indicates the expected result for an Mn\textsuperscript{4+} cation according to the spin-only formula. Right: $R^2$ quality-of-fit values for the Curie-Weiss fits to the SQuID results.

Values of the $R^2$ residual calculated for the Curie-Weiss fits to the SQuID data are also shown in Figure 2.10. The results for Sr\textsubscript{2}Ca\textsubscript{5}Mn\textsubscript{4}O\textsubscript{15} show the greatest deviation from a linear fit in the 250-300 K region, possibly as a result of the very short Mn-Mn distances due to the small unit cell allowing for increased short-range correlations at higher temperatures than the
other compositions. The other feature of this plot is the turning point observed for the Ba-containing compositions, with the \( \text{Sr}_4\text{Ba}_3\text{Mn}_4\text{O}_{15} \) composition having the highest \( R^2 \) value. The reason for this behaviour is unknown, though it appears to correlate with the \( \beta \) parameter or the Mn(1)-O(5)-Mn(2) angle (shown below in Figure 2.19) for these compositions.

### 2.3.4.2 Powder Neutron Diffraction Refinements

To further investigate the magnetic structure of the \( \text{Sr}_{7-x}\text{A}_x\text{Mn}_4\text{O}_{15} \) phases, three compositions were taken to the D2B beamline at the ILL for PND experiments at 300, 100 and 1.5 K. The compositions selected were \( \text{Sr}_7\text{Mn}_4\text{O}_{15} \), \( \text{Sr}_2\text{Ca}_3\text{Mn}_4\text{O}_{15} \) and \( \text{Sr}_2\text{Ba}_3\text{Mn}_4\text{O}_{15} \), as these were the most-substituted compositions at the time and were expected to display the greatest variation in properties, which could then be interpolated to generate an understanding of the solid solution as a whole. The results of Rietveld refinements of the \( \text{Sr}_7\text{Mn}_4\text{O}_{15} \), \( \text{Sr}_2\text{Ca}_3\text{Mn}_4\text{O}_{15} \) and \( \text{Sr}_2\text{Ba}_3\text{Mn}_4\text{O}_{15} \) combined powder synchrotron X-ray diffraction and PND data at 300 K are shown in Figure 2.11.

![Rietveld refinement of D2B PND data for \( \text{Sr}_7\text{Mn}_4\text{O}_{15} \), \( \text{Sr}_2\text{Ca}_3\text{Mn}_4\text{O}_{15} \) and \( \text{Sr}_2\text{Ba}_3\text{Mn}_4\text{O}_{15} \) at 300 K. Blue ticks indicate reflections present in the main phase, green ticks indicate reflections resulting from the 4H-\( \text{SrMnO}_3 \) impurity and purple ticks indicate reflections resulting from the \( \text{Ca}_2\text{MnO}_3 \) impurity.](image-url)

Figure 2.11 Rietveld refinement of D2B PND data for \( \text{Sr}_7\text{Mn}_4\text{O}_{15} \), \( \text{Sr}_2\text{Ca}_3\text{Mn}_4\text{O}_{15} \) and \( \text{Sr}_2\text{Ba}_3\text{Mn}_4\text{O}_{15} \) at 300 K. Blue ticks indicate reflections present in the main phase, green ticks indicate reflections resulting from the 4H-\( \text{SrMnO}_3 \) impurity and purple ticks indicate reflections resulting from the \( \text{Ca}_2\text{MnO}_3 \) impurity.
Chapter 2. Synthesis and Characterisation of Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$

Upon cooling to 1.5 K, each of the samples exhibited magnetic Bragg peaks at low values of 2θ. These peaks could be indexed on the nuclear cell, with the greatest intensity observed for the (1 0 1), (1 1 0), (0 0 2), (0 1 2) and (1 0 2) reflections. Plots of the indexed reflections are shown in Figure 2.12 with the y-axes of the 300 K and 1.5 K data for each composition normalised to make the overlap of the nuclear peaks and the appearance of the magnetic peaks more visible. To fit these peaks, models were tested using a single magnetic propagation vector $k = [0 0 0]$, which was selected as each of the peaks could be indexed on the nuclear cell. The four irreps at this $k$-point transform as $m\Gamma_1^+, m\Gamma_2^+, m\Gamma_1^-$ and $m\Gamma_2^-$ according to the convention used in ISODISTORT$^{24,25}$. Figure 2.13, Figure 2.14 and Figure 2.15 show the results of the models constructed by considering spin orderings which transform as each of these irreps for each composition. In all cases, the models were constrained such that the Mn$^{4+}$ centres in the Mn$_2$O$_9$ dimer systems were AFM-ordered as their proximity to one another made direct exchange the most plausible ordering; for half-filled $t_{2g}$ orbitals this favours strong antiparallel coupling. The initial refinements of the $m\Gamma_2^-$ models were constrained only by the AFM ordering described above, but it was found that the spins tended to align along the symmetry-unique $b$ direction. As such, further refinements were performed in which the spins were constrained along this direction. The quality of the fits were not significantly harmed by this constraint. The fitting statistics for each of these models are summarised in Table 2.4; for all three compositions, the $m\Gamma_2^-$ model was found to have both the best fit by visual inspection as well as the lowest $R_{wp}$. This model produces the $P2_1/c$ magnetic space group and the spin configuration is shown in Figure 2.16.
Figure 2.12 Indexing of magnetic Bragg peaks in D2B 1.5 K data compared to 300 and 100 K data ($\lambda = 1.594251(1) \text{ Å}$) for Sr$_7$Mn$_4$O$_{15}$, Sr$_2$Ca$_5$Mn$_4$O$_{15}$ and Sr$_2$Ba$_5$Mn$_4$O$_{15}$. Note that the background intensity baseline for each composition is normalised such that the appearance of the magnetic peaks is more visible.
**Figure 2.13** Comparison of different magnetic models used to fit PND data ($\lambda = 1.594251(1)$ Å) of Sr$_7$Mn$_4$O$_{15}$ at 1.5 K. Blue ticks indicate reflections present in the main phase, green ticks indicate reflections resulting from the 4H-SrMnO$_3$ impurity.

**Figure 2.14** Comparison of different magnetic models used to fit PND data ($\lambda = 1.594251(1)$ Å) of Sr$_2$Ca$_5$Mn$_4$O$_{15}$ at 1.5 K. Blue ticks indicate reflections present in the main phase, purple ticks indicate reflections resulting from the Ca$_2$MnO$_4$ impurity.
Chapter 2. Synthesis and Characterisation of Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$

Figure 2.15 Comparison of different magnetic models used to fit PND data ($\lambda = 1.594251(1)$ Å) of Sr$_2$Ba$_5$Mn$_4$O$_{15}$ at 1.5 K. Blue ticks indicate reflections present in the main phase.

Figure 2.16 Visualisation of the spin configuration resulting from the $m\Gamma_2^-$ irrep in Sr$_7$Mn$_4$O$_{15}$. The magnetic moments of the Mn(1) and Mn(2) sites are coloured red and blue, respectively, to distinguish them. The moments are constrained to the symmetry-unique $b$ direction as this constraint was found to result in the best fit to the data. The non-crystallographic constraint that the moments within a dimer are AFM with respect to one another is imposed as discussed in the main text.
Chapter 2. Synthesis and Characterisation of Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$

Table 2.4 Fitting statistics for Rietveld refinements using different models to fit magnetic Bragg peaks in D2B 1.5 K data for Sr$_7$Mn$_4$O$_{15}$, Sr$_2$Ca$_5$Mn$_4$O$_{15}$ and Sr$_2$Ba$_5$Mn$_4$O$_{15}$.

<table>
<thead>
<tr>
<th>Model</th>
<th>$R_{wp}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sr$_7$Mn$<em>4$O$</em>{15}$</td>
</tr>
<tr>
<td>$m\Gamma_1^+$</td>
<td>7.282</td>
</tr>
<tr>
<td>$m\Gamma_2^+$</td>
<td>7.244</td>
</tr>
<tr>
<td>$m\Gamma_1^-$</td>
<td>6.866</td>
</tr>
<tr>
<td>$m\Gamma_2^-$</td>
<td>6.779</td>
</tr>
<tr>
<td>$m\Gamma_2^-$ (b only)</td>
<td>6.781</td>
</tr>
</tbody>
</table>

The values of the ordered magnetic moment calculated from the PND experiments at 1.5 K for each composition are summarised in Table 2.5. All of the results are very similar at around 2.1-2.2 $\mu_B$ implying that the structural variation resulting from the chemical pressure has little impact on the long-range magnetic ordering. These values are also slightly below the expected value of 3 $\mu_B$ for Mn$^{4+}$, suggesting that some degree of overlap between the Mn$^{4+}$ t$_{2g}$ orbitals is occurring and causing a reduction in the effective spin density. Given the variation in the forms of the magnetic susceptibilities of the phases in the solid solution, it was expected that the long-range magnetic ordering temperature would also change as a function of the composition. In an effort to investigate this, the Sr$_2$Ca$_5$Mn$_4$O$_{15}$ and Sr$_2$Ba$_5$Mn$_4$O$_{15}$ compositions were taken to the D20 beamline at the ILL for variable-temperature neutron powder diffraction (VT-PND) experiments in the 3-93 K (for Sr$_2$Ca$_5$Mn$_4$O$_{15}$) and 5-85 K (for Sr$_2$Ba$_5$Mn$_4$O$_{15}$) temperature ranges. Lattice parameters for both compositions are plotted in Figure 2.17. All of the lattice parameters vary monotonically with temperature and there is no evidence of structural phase transitions.

Table 2.5 Values of ‘b-only’ ordered magnetic moment calculated from D2B PND data at 1.5 K for Sr$_7$Mn$_4$O$_{15}$, Sr$_2$Ca$_5$Mn$_4$O$_{15}$ and Sr$_2$Ba$_5$Mn$_4$O$_{15}$.

<table>
<thead>
<tr>
<th>Ordered magnetic moment ($\mu_B$)</th>
<th>Sr$_7$Mn$<em>4$O$</em>{15}$</th>
<th>Sr$_2$Ca$_5$Mn$<em>4$O$</em>{15}$</th>
<th>Sr$_2$Ba$_5$Mn$<em>4$O$</em>{15}$</th>
</tr>
</thead>
</table>
Figure 2.17 Lattice parameters for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ and $\text{Sr}_2\text{Ba}_5\text{Mn}_4\text{O}_{15}$ extracted from Rietveld refinements of D20 VT-PND data.

The variation of the $m\Gamma_2^-$ mode amplitude (for refinements in which only the $b$ component is refined) with temperature is plotted in Figure 2.18. It can be seen that, despite the difference in their SQuID DC magnetic susceptibility results, both compositions exhibit a dramatic increase in the amplitude of the magnetic mode beginning at approximately 50 K and increasing as the temperature falls. The $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ result in Figure 2.18 has been normalised: the mode amplitude recovered from the refinement (in cyan) is greater at the lowest temperature than is expected for the $d^3$ Mn$^{4+}$ cation and is greater than zero above 80 K (which is above the transition temperature). Comparing these data to the D2B PND data, it is clear that no evidence of magnetic intensity remains at 100 K (see Figure 2.12). It is possible that correlation with a non-magnetic peak such as (0 2 1) or (1 1 2) may have caused the refinement to overestimate the magnetic mode amplitude in the VT data, suggesting that this overestimation is an artifact of the poorer resolution of the D20 PND data. The correction factor simply subtracts 1 $\mu_B$ from the mode amplitude, bringing it in line with the expected values and very close to the values for $\text{Sr}_2\text{Ba}_5\text{Mn}_4\text{O}_{15}$. The reason for selecting 1 $\mu_B$ as the normalisation was to bring the maximum mode amplitude to the maximum permitted value for the Mn$^{4+}$ cation.
Both $\text{Sr}_2\text{Ba}_3\text{Mn}_4\text{O}_{15}$ and $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ display an increase in the $m\Gamma_2^-$ mode amplitude which begins around 50 K and reaches a plateau just below 3 $\mu_B$ at 5 K. At the onset of magnetic ordering $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ demonstrates a faster initial increase in the mode amplitude than $\text{Sr}_2\text{Ba}_3\text{Mn}_4\text{O}_{15}$ but (accounting for the normalisation) both compositions reach the same saturation amplitude at similar temperatures, suggesting that the short-range correlations between Mn centres in the Mn$_2$O$_9$ dimers are the most significant in the structure.

![Figure 2.18 Amplitude of $m\Gamma_2^-$ mode in b direction for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ and $\text{Sr}_2\text{Ba}_3\text{Mn}_4\text{O}_{15}$ extracted from Rietveld refinements of D20 VT-PND data. The data in cyan markers are the results from the D20 data for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ without a correction factor.](image)

**2.3.4.3 Discussion**

Examining the results of the SQUID magnetometry and PND experiments, it appears that the Mn$_2$O$_9$ dimers dominate the magnetic behaviour of the solid solution phases. This is not enormously surprising, since these dimers contain the shortest-range Mn-Mn neighbours. What is somewhat unexpected, however, is the observation of how little changing the A-site cation impacts the long-range magnetic ordering temperature as determined by VT-PND, while still having a significant effect on various features in the FC and ZFC magnetic susceptibility data. The distances between assorted Mn sites in the solid solution are plotted in Figure 2.19, including data from the Ba$_7$Mn$_4$O$_{15}$ composition in Chapter 3. The Mn(1)-Mn(1) and Mn(1)-Mn(2) distances are strongly correlated with the lattice parameters and, as a result of the linear interpolation of these parameters in the Rietveld refinements, are also linear between the end members. The main deviation from this is seen in the intradimer distances, which are likely to be more strongly correlated with the atomic coordinates and size of the cations on the Sr sites than with the lattice parameters. For the Ba-containing compositions, the intradimer distance increases with increasing Ba$^{2+}$ content,
Chapter 2. Synthesis and Characterisation of \( \text{Sr}_7\text{A}_x\text{Mn}_4\text{O}_{15} \)

while for Ca-containing compositions, an initial decrease in the intradimer Mn(1)-Mn(2) distance with increasing Ca\(^{2+}\) content is slightly reversed at the \( \text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15} \) composition. The angle between the Mn(1) and Mn(2) sites, which share an intermediate O(5) site, remains unchanged with increasing Ca\(^{2+}\) content, but shows a curved response to increasing Ba\(^{2+}\) content. This change in angle is likely related to the \( \beta \) behaviour of the Ba-containing compositions, which is related to the site occupancies as described in Section 2.3.3.

In other phases containing examples of face-sharing MnO\(_6\) octahedra such as 2H-BaMnO\(_3\)\(^{134}\), 4H-SrMnO\(_3\)\(^{74,129,135}\) and 6H-SrMnO\(_3\)\(^{138}\) and the layered \( \text{Ba}_3\text{Mn}_3\text{O}_{10} \) and \( \text{Ba}_3\text{Mn}_5\text{O}_{16} \) phases\(^{136-138}\), AFM ordering is common, and doping by \( \text{A}^{2+} \) cations at the A-site tends to either have little effect on magnetism or to slightly reduce its magnitude and ordering temperature\(^{139,140}\). Doping by aliovalent cations is known to have a different effect, for example La\(^{3+}\) producing FM clusters within the BaMnO\(_3\) and \( \text{Ba}_3\text{Mn}_3\text{O}_{10} \) structures by introducing a secondary La\(^{3+}\)/Mn\(^{3+}\) sublattice\(^{141}\). These results show that the A-site substitution has a significant effect on the short-range magnetic correlations, but little effect on the long-range ordering.

Figure 2.19 Distances and angles between Mn sites in the \( \text{Sr}_7\text{A}_x\text{Mn}_4\text{O}_{15} \) (A: Ca, Ba; \( 0 \leq x \leq 7 \)) solid solution as a function of composition. Calculated errors were within the markers and error bars are therefore omitted.
2.3.5 High-Pressure PND Analysis

Following several unsuccessful synthetic attempts towards Ca$_7$Mn$_4$O$_{15}$, it was hypothesised that the $P2_1/c$ structure was not capable of supporting additional Ca without undergoing a structural transition. A sample of Sr$_{2}\text{Ca}_5\text{Mn}_4\text{O}_{15}$ was selected for investigation in a high-pressure neutron diffraction experiment using the PEARL instrument at the ISIS Neutron and Muon Source. This phase was selected as it contained the largest amount of Ca and therefore possessed the smallest unit cell of the family of substituted Sr$_7$Mn$_4$O$_{15}$ phases, such that it might be the most susceptible to a phase transition with applied pressure. The experimental details for this are described in Section 2.2.2.3. A diffraction pattern recorded at 0.077 GPa is shown in Figure 2.20 with additional reflections arising due to the Paris-Edinburgh cell marked with star symbols. There is clearly a significant contamination of the diffraction pattern by the cell, which impeded data analysis and limited the results to the calculation of lattice parameters and assignment of a space group. The rest of the diffraction patterns from these measurements are shown in Figure 2.21 and Figure 2.22. The measurements at the three highest pressure points were performed using a Paris-Edinburgh press equipped with sintered diamond anvils and, as such, exhibits greater attenuation than the lower-pressure data. The plots at these pressures are on a smaller scale than the plots at lower pressures.

![Diffraction pattern](image)

*Figure 2.20 PND pattern recorded for Sr$_{2}\text{Ca}_5\text{Mn}_4\text{O}_{15}$ at 0.077 GPa at the PEARL instrument at ISIS. Blue ticks indicate reflections present in the main phase, green ticks indicate reflections resulting from the Ca$_2$MnO$_4$ impurity, red ticks indicate reflections resulting from the lead pressure marker, purple ticks indicate reflections due to the alumina components of the Paris-Edinburgh cell and orange ticks indicate reflections due to the zirconia components of the cell. Stars above peaks in the diffraction pattern indicate strong reflections arising from these impurities, colour-coded to the colour noted for the reflection ticks. The time-of-flight range shown is approximately equivalent to a d-spacing range of 0.3-4.1 Å.*
Figure 2.21 PND patterns recorded for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ with increasing pressure at the PEARL instrument at ISIS. Measurements below 5.4 GPa were performed using a Paris-Edinburgh press equipped with zirconia-toughened alumina gaskets. The time-of-flight range shown is approximately equivalent to a $d$-spacing range of 0.3-4.1 Å.

Figure 2.22 PND patterns recorded for $\text{Sr}_2\text{Ca}_5\text{Mn}_4\text{O}_{15}$ with increasing pressure at the PEARL instrument at ISIS. Measurements above 5.4 GPa were performed using sintered diamond anvils and suffer from greater beam attenuation and thus reduced intensity and resolution, and these plots are on a smaller scale than those in Figure 2.21. The time-of-flight range shown is approximately equivalent to a $d$-spacing range of 0.3-4.1 Å.
Chapter 2. Synthesis and Characterisation of Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$

There is no strong evidence for a phase transition up to the maximum pressure in this experiment (8.074 GPa). The variation of the lattice parameters of Sr$_2$Ca$_5$Mn$_4$O$_{15}$ with increasing pressure are shown in Figure 2.23. The $a$, $b$, and $c$ parameters decrease linearly with pressure, while $\beta$ increases. This was unexpected as the impact of increasing Ca$^{2+}$ content on the Sr$_{7-x}$Ca$_x$Mn$_4$O$_{15}$ structure was to cause $\beta$ to decrease, as observed in Figure 2.3, so further reduction in the unit cell volume was predicted to continue that trend.

![Figure 2.23 Evolution of lattice parameters of Sr$_2$Ca$_5$Mn$_4$O$_{15}$ with increasing isotropic pressure, measured on PEARL instrument at ISIS. Filled symbols indicate that the lattice parameters were extracted from Rietveld refinements of data measured using zirconia-toughened alumina gaskets, hollow symbols indicate that sintered diamond anvils were used. Calculated errors were within the markers and error bars are therefore omitted.](image)

Principal axis strain calculations were performed on the PEARL PND data for Sr$_2$Ca$_5$Mn$_4$O$_{15}$ using the Principal Axis Strain Calculator (PAScal) web tool\textsuperscript{142}. The resultant compressibility parameters and Birch-Murnaghan coefficients are summarised in Table 2.6 and Table 2.7. In line with the lattice parameter contractions with increasing pressure, the compressibilities of each principal axis decrease in the order $X_1 > X_2 > X_3$. $X_2$ is aligned with the crystallographic $b$ axis and both $X_1$ and $X_3$ are split in the $ac$ plane, with $X_1$ being mostly aligned with $c$ with a large component in $a$ and $X_3$ being largely aligned with $a$ and having only a small component in $c$. These compressibilities can be rationalised by considering the structural motifs present in the unit cell: the Mn$_2$O$_9$ dimers are of limited compressibility,
but the stacks of strings they form in $a$ may be compressed together to a greater degree than they may be compressed in $c$.

**Table 2.6 Compressibility parameters for Sr$_2$Ca$_3$Mn$_4$O$_{15}$ calculated from PEARL PND data using PASCaL.**

<table>
<thead>
<tr>
<th>Axes</th>
<th>$K$ (TPa$^{-1}$)</th>
<th>$\sigma K$ (TPa$^{-1}$)</th>
<th>Direction</th>
<th>Empirical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$a$</td>
<td>$b$</td>
</tr>
<tr>
<td>$X_1$</td>
<td>3.1930</td>
<td>0.0466</td>
<td>0.4905</td>
<td>0</td>
</tr>
<tr>
<td>$X_2$</td>
<td>2.7546</td>
<td>0.0486</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$X_3$</td>
<td>1.7786</td>
<td>0.0295</td>
<td>-0.9772</td>
<td>0</td>
</tr>
<tr>
<td>$V$</td>
<td>7.6863</td>
<td>0.0833</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.7 Second- and third-order Birch-Murnaghan coefficients for Sr$_2$Ca$_3$Mn$_4$O$_{15}$ calculated from PEARL PND data using PASCaL.**

<table>
<thead>
<tr>
<th></th>
<th>$B_0$ (GPa)</th>
<th>$\sigma B_0$ (GPa)</th>
<th>$V_0$ ($\text{Å}^3$)</th>
<th>$\sigma V_0$ ($\text{Å}^3$)</th>
<th>$B'$</th>
<th>$\sigma B'$</th>
<th>$P_c$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2nd</td>
<td>117.0395</td>
<td>0.4453</td>
<td>633.8554</td>
<td>0.0585</td>
<td>4</td>
<td>n/a</td>
<td>0</td>
</tr>
<tr>
<td>3rd</td>
<td>116.7535</td>
<td>1.8051</td>
<td>633.8654</td>
<td>0.0869</td>
<td>4.1103</td>
<td>0.6735</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 2.24** Lattice parameters of Sr$_{7-x}$Ca$_x$Mn$_4$O$_{15}$ ($0 \leq x \leq 5$) plotted as a function of unit cell volume. Filled symbols indicate values of the lattice parameters for Sr$_2$Ca$_3$Mn$_4$O$_{15}$ measured with increasing pressure on PEARL instrument at ISIS. Crosses indicate values measured at standard pressure for the solid solution (conditions the same as in Figure 2.3). Markers for the end members are noted with the composition. Calculated errors were within the markers and error bars are therefore omitted.
Plotting the PEARL PND lattice parameter data as a function of the unit cell volume allows comparison with the data for the \( \text{Sr}_{7-x} \text{A}_x \text{Mn}_4 \text{O}_{15} \) (A: Ca, Ba; \( 0 \leq x \leq 5 \)) solid solution at standard pressure and reveals an interesting property. As shown in Figure 2.24, the \( a, b \) and \( c \) lattice parameters of the \( \text{Sr}_2 \text{Ca}_5 \text{Mn}_4 \text{O}_{15} \) composition decrease as anticipated with increasing pressure. However, the \( \beta \) parameter increases, mirroring the behaviour of the Ba-containing compositions as the unit cell volume increases above 720 \( \text{Å}^3 \). The observation of this behaviour in the absence of variation of the site occupancies casts doubt on the earlier hypothesis of the angle being related to the occupancies of the different Sr sites. Since the application of physical pressure acts in a similar way to the addition of the smaller Ca\(^{2+}\) cation to the structure, the upturn in \( \beta \) with decreasing unit cell volume is unexpected. Further computational and experimental work is necessary to understand this phenomenon.

**2.4 Conclusions**

In this chapter, the synthesis of substituted \( \text{Sr}_{7-x} \text{A}_x \text{Mn}_4 \text{O}_{15} \) has been extended to \( x = 5 \) for A: Ca, Ba. A variety of synthetic techniques were attempted but standard solid-state syntheses were found to be the most appropriate. Synchrotron PXRD and PND experiments show linear variation in the lattice lengths with substitution. The value of \( \beta \) appears to vary as a function of unit cell volume, as shown by the high-pressure PND. The diffraction experiments also reveal that the entire solid solution remains in the \( P2_1/c \) space group and that asymmetric anisotropic substitution on the four Sr sites occurs depending on the ionic radius of the substituting cation. SQuID DC magnetic susceptibility results suggest that short-range magnetic interactions can be tuned to some extent by chemical substitution, but the long-range magnetic ordering observed by VT-PND experiments remains nearly fixed at approximately 50 K. For all compositions tested, an AFM \( m\Gamma_2^- \) model has been found to provide the best fit to the magnetic Bragg peaks.
Chapter 3. Synthesis and Characterisation of Ba$_7$Mn$_4$O$_{15}$

3.1 Introduction

Following the successful expansion of the solid solution Sr$_{7-x}$A$_x$Mn$_4$O$_{15}$ ($A$: Ca, Ba; $0 \leq x \leq 7$) to include greater quantities of Ca$^{2+}$ and Ba$^{2+}$ cations described in Chapter 2, efforts were made to produce the end members Ca$_7$Mn$_4$O$_{15}$ and Ba$_7$Mn$_4$O$_{15}$. Though the former was not achieved, this chapter will describe the development of a consistent synthetic procedure towards Ba$_7$Mn$_4$O$_{15}$ and the characterisation techniques which were used to elucidate the structure and magnetic properties of this phase. A complex magnetoelectric ground state is uncovered via symmetry-motivated analysis, identifying Ba$_7$Mn$_4$O$_{15}$ as a potential multiferroic material.

![Figure 3.1 Unit cell of Ba$_7$Mn$_4$O$_{15}$ with sites labelled.](image)

3.2 Experimental

3.2.1 Synthesis

Samples of Ba$_7$Mn$_4$O$_{15}$ were synthesised using standard solid-state methods. BaCO$_3$ and MnO$_2$ were ground in an agate mortar until homogeneous, then pressed into 13 mm-diameter pellets using 7.5 tonnes of applied pressure. A 10% molar excess of BaCO$_3$ was used to mitigate impurity formation (discussed in Section 3.3.1). These pellets were calcined at 900 °C under an atmosphere of flowing N$_2$ gas for 20-24 hours, then reground, pressed and fired again a total of five times. Heating was always performed under an atmosphere of flowing N$_2$. 
3.2.2 X-ray Powder Diffraction

High-resolution powder synchrotron X-ray diffraction experiments were performed at Beamline I11 at Diamond Light Source, with diffraction patterns recorded at 300 and 100 K using the multi-analyzer crystal (MAC) detector for both Ba$_7$Mn$_4$O$_{15}$ and Sr$_7$Mn$_4$O$_{15}$, and variable-temperature measurements performed between these temperatures using the mythen detector for Ba$_7$Mn$_4$O$_{15}$. The beam wavelength was 0.82683(1) Å for the Ba$_7$Mn$_4$O$_{15}$ experiment and 0.82634(1) Å for the Sr$_7$Mn$_4$O$_{15}$ experiment, refined using NIST 640c Si standards.

3.2.3 Neutron Powder Diffraction

Powder neutron diffraction experiments were performed using the GEM instrument at the ISIS Neutron and Muon Source at 80 K and 10 K for Ba$_7$Mn$_4$O$_{15}$ and using the D2B instrument at the ILL at 300, 100 and 1.5 K for Sr$_7$Mn$_4$O$_{15}$.

3.2.4 SQuID Magnetometry

Magnetisation measurements were performed using a Quantum Design MPMS SQuID magnetometer. Magnetic susceptibility versus temperature data were collected between 10 and 325 K in an applied field of 100 Oe under ZFC warming and FC cooling conditions. Magnetisation versus field curves were collected in applied fields of up to 50 kOe at temperatures between 2 and 300 K.

3.2.5 Powder Diffraction Analysis

Rietveld refinements were performed using TOPAS Academic v6. A starting model for the refinement was based on the crystal structure of the related Sr$_7$Mn$_4$O$_{15}$ phase with space group $P2_1/c$. Combined Rietveld refinements were performed using the 100 K dataset from the I11 MAC detector and the 80 K dataset from the GEM experiment. These refinements excluded detector bank 1 and bank 6 from the GEM dataset due to poor signal-to-noise ratios. To model the broad peaks of the BaCO$_3$ impurity, separate peak shape parameters were refined for this phase. The isotropic displacement parameters were constrained to be equal for a given atom type. Refinements of the low-temperature magnetic structure were performed within the symmetry-adapted formalism of the ISODISTORT suite and as implemented through the linear constraints language of TOPAS.

3.3 Results and Discussion

3.3.1 Synthesis

Early attempts to synthesise Ba$_7$Mn$_4$O$_{15}$ using stoichiometric quantities of reagents were unsuccessful and produced a mixture of 4H-BaMnO$_3$ and material which was identified as Ba$_9$Mn$_2$O$_8$. This phase contains Mn$^{5+}$ cations, leading to an interesting magnetic structure...
and a dark green colour\textsuperscript{145-147}. This phase was identified by a search of the ICSD in which the impurity pattern was compared to a variety of patterns of other Ba-Mn-O phases; the unexpected colour change helped to identify an oxidation of the Mn\textsuperscript{4+} present in the MnO\textsubscript{2} starting material. To prevent the oxidation of the Mn\textsuperscript{4+} cations in the MnO\textsubscript{2} reagent, further synthetic attempts were performed using a tube furnace under an atmosphere of flowing N\textsubscript{2}. With this impurity phase suppressed, the next obstruction to a pure sample of Ba\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15} was identified using laboratory PXRD experiments as the layered hexagonal phase Ba\textsubscript{4}Mn\textsubscript{3}O\textsubscript{10}\textsuperscript{125}. This impurity contains Mn in the 4+ oxidation state, supporting the use of an inert N\textsubscript{2} atmosphere to facilitate the reaction. Assorted reaction temperatures were tested between 850-1200 °C to minimise the appearance of this impurity, and the most success was found for a 900 °C reaction, which produced a sample containing only 12.5% Ba\textsubscript{4}Mn\textsubscript{3}O\textsubscript{10} by mass. As it was unknown at this juncture whether a purer sample would be achievable, a SQuID DC magnetic susceptibility experiment was performed using this impure sample. The results were not readily analysed as the susceptibility of the Ba\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15} was contaminated by the greater susceptibility of the Ba\textsubscript{4}Mn\textsubscript{3}O\textsubscript{10} content, which has been postulated to arise due to a weak FM component below 40 K. Following the published synthesis\textsuperscript{125}, a pure sample of Ba\textsubscript{4}Mn\textsubscript{3}O\textsubscript{10} was produced and a SQuID experiment was performed to identify the DC magnetic susceptibility of the phase when not mixed with the magnetic response of Ba\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15}. Attempts to deconvolute the magnetic susceptibilities of both phases by subtracting the Ba\textsubscript{4}Mn\textsubscript{3}O\textsubscript{10} response from that of Ba\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15} (normalised to their relative concentration within the sample) were unsuccessful, possibly due to coupling between the domains of both phases.

![Figure 3.2](image-url)  

*Figure 3.2 DC magnetic susceptibility as a function of temperature for Ba\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15} and Ba\textsubscript{4}Mn\textsubscript{3}O\textsubscript{10}, and a plot calculating the difference between them, normalised to the composition of the sample.*
An attempt to separate the two phases by their magnetic responses was also made. The powder sample was suspended in a vial of dry ethanol and subjected to ultrasonic vibration before a strong permanent magnet was held to the side of the vial. Some of the powder was observed to be attracted to the magnet and it was hoped that this represented the impurity phase. The sample was separated using this method and, after drying, was investigated by laboratory powder X-ray diffraction. Unfortunately, the resultant diffraction pattern was found to be identical to the rest of the sample, indicating that the domains of the main and impurity phases may be intergrown.

Attempts to synthesise a purer sample of $\text{Ba}_7\text{Mn}_4\text{O}_{15}$ continued and were eventually successful. Due to the higher Ba:Mn ratio in $\text{Ba}_7\text{Mn}_4\text{O}_{15}$ (1.75:1) compared with $\text{Ba}_4\text{Mn}_3\text{O}_{10}$ (1.33:1), a reaction was performed at 900 °C which included a 10% molar excess of $\text{BaCO}_3$. The resultant product was almost phase-pure and contained only a small amount of unreacted $\text{BaCO}_3$. As this impurity is non-magnetic it cannot significantly affect the SQuID results. The impurity became quite amorphous due to the heating and is identifiable in the diffraction pattern (Figure 3.4) with a broad peak around $2\theta = 13^\circ$.

Figure 3.3 Rietveld refinement ($R_{wp}$: 4.37%, $R_p$: 3.31%, $\chi^2$: 2.69) of laboratory PXRD data of $\text{Ba}_4\text{Mn}_3\text{O}_{10}$ at 300 K ($\text{Cu Ka}_1$ source: $\lambda = 1.5406$ Å). Blue ticks indicate reflections resulting from the main phase, green ticks represent reflections resulting from a minor 2H-$\text{BaMnO}_3$ impurity.
Chapter 3. Synthesis and Characterisation of Ba$_7$Mn$_4$O$_{15}$

Figure 3.4 Rietveld refinement ($R_{wp}$: 11.26%, $R_p$: 8.90%, $\chi^2$: 5.76) against powder synchrotron X-ray diffraction ($\lambda = 0.82683(1)$ Å) data at 300 K. Blue tick marks indicate reflections for Ba$_7$Mn$_4$O$_{15}$; green tick marks indicate reflections for residual reagent BaCO$_3$.

The intricate combination of unusually low temperature, inert atmosphere and excess BaCO$_3$ required to successfully synthesise Ba$_7$Mn$_4$O$_{15}$ took significant effort to identify, and likely form a significant part of the reason that this phase remained unidentified until now. The refined structure of Ba$_7$Mn$_4$O$_{15}$ is summarised in Table 3.1; isotropic displacement parameters were constrained to be equal for a given atom.
### Table 3.1 Lattice parameters and atomic coordinates of \( \text{Ba}_7\text{Mn}_4\text{O}_{15} \) refined using powder synchrotron X-ray diffraction data at 300 K (\( \lambda = 0.82683(1) \)).

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### 3.3.2 X-ray Powder Diffraction

The temperature-dependent variations in the lattice parameters of \( \text{Ba}_7\text{Mn}_4\text{O}_{15} \) between 300-100 K are shown in Figure 3.5. The lattice lengths all decrease linearly with temperature; the \( a \) parameter decreases by the smallest amount, approximately 0.15% across the temperature range, while the \( b \) and \( c \) parameters both decrease by a very similar amount at 0.23% and 0.22% respectively. The \( \beta \) parameter increases linearly, by 0.06%. There is no evidence of a phase transition in this temperature range.
3.3.3 SQuID Magnetometry

The DC magnetic susceptibility results for Sr$_7$Mn$_4$O$_{15}$ (recreated from Chapter 2 for comparison) and Ba$_7$Mn$_4$O$_{15}$ are shown in Figure 3.6. Above 100 K, both compositions display a similarly featureless curve, with a steady increase in susceptibility with decreasing temperature. However, below 100 K, the Sr$_7$Mn$_4$O$_{15}$ susceptibility shows a clear, broad peak centred at approximately 80 K with a turning point in both the FC and ZFC curves. Below this temperature, the FC and ZFC curves diverge from one another slightly before turning again at approximately 40 K and increasing rapidly towards 0 K. The broad peak is understood to be the result of short-range magnetic interactions building up as the temperature decreases, preceding the onset of the long-range magnetic phase transition at approximately 50 K. By contrast, the susceptibility of Ba$_7$Mn$_4$O$_{15}$ shows a relatively subtle divergence of the FC and ZFC curves at approximately 50 K, at which point a small peak is observed in the FC curve before it turns upwards towards 0 K. The ZFC curve has almost no observable peak but turns upwards at the same temperature. This implies that the short-range correlations observed in the other phases are not present for Ba$_7$Mn$_4$O$_{15}$. If it can be assumed that the same long-range magnetic ordering behaviour occurs in Ba$_7$Mn$_4$O$_{15}$ as is observed in Sr$_2$Ba$_3$Mn$_4$O$_{15}$ and Sr$_2$Ca$_3$Mn$_4$O$_{15}$ by powder neutron diffraction (Chapter 2,
Section 2.3.4.2, then the subtle FC peak near 50 K can be assumed to indicate the onset of magnetic ordering.

![Graph showing magnetic susceptibility as a function of temperature for Sr$_7$Mn$_4$O$_{15}$ and Ba$_7$Mn$_4$O$_{15}$](image)

*Figure 3.6 DC magnetic susceptibility as a function of temperature for Sr$_7$Mn$_4$O$_{15}$ and Ba$_7$Mn$_4$O$_{15}$. The lower figures indicate the Curie-Weiss fits of the inverse susceptibility for both phases between 200-300 K.*

Plots of the inverse magnetic susceptibility of both Sr$_7$Mn$_4$O$_{15}$ and Ba$_7$Mn$_4$O$_{15}$ are also shown in Figure 3.6. Curie-Weiss fits were calculated in the 200-300 K region of these data; the coefficients of the linear fit are noted on the plots and the derived Curie and Weiss constants, as well as effective paramagnetic moments, are summarised in Table 3.2. As with Sr$_7$Mn$_4$O$_{15}$, the expected spin-only value for the effective paramagnetic moment is 3.87 $\mu_B$, which agrees well with the calculated moment per Mn$^{4+}$ centre of 3.78 $\mu_B$. The large, negative Weiss constant indicates strong AFM interactions.
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Table 3.2 Curie constants, Weiss constants and effective paramagnetic moments calculated from DC ZFC SQuID results for $\text{Sr}_7\text{Mn}_4\text{O}_{15}$ (Chapter 2) and $\text{Ba}_7\text{Mn}_4\text{O}_{15}$.

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<th>Composition</th>
<th>Curie constant, $\theta$ (K)</th>
<th>Weiss constant, $\theta$ (K)</th>
<th>$\mu_{\text{eff}}$ (per formula unit) (µB)</th>
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3.3.4 Neutron Powder Diffraction

Further investigation of the structural and magnetic properties of $\text{Ba}_7\text{Mn}_4\text{O}_{15}$ was performed using the GEM instrument at ISIS. TOF neutron diffraction experiments were performed at 80 K and 10 K, well above and below the expected magnetic transition temperature. The higher-temperature data were refined in a combined Rietveld refinement with powder synchrotron X-ray diffraction data gathered at I11, Diamond Light Source at 100 K. The resulting structural information is shown in Table 3.3 and the fits to the GEM data are shown in Figure 3.7. The data from banks 1 and 6 were found to have poor signal-to-noise ratios and resolution and were therefore excluded from further analysis (though they are shown in Figure 3.7 and Figure 3.8 for completeness). While it is not ideal that the two data sets were not measured at the same temperature, the effects of thermal contraction over the 80-100 K temperature range were expected to be relatively small, and the neutron data were not expected to be sensitive to the subtle structural changes. To account for the larger differences, two sets of lattice parameters were refined: one for the X-ray diffraction data and one for the PND data. The lattice parameters reported in Table 3.3 are an average of these. This refinement, properly constrained as described in Section 3.2.3, was deemed sufficient to describe the structure given the available data.
Table 3.3 Lattice parameters and atomic coordinates of Ba\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15} as refined from combined powder synchrotron X-ray diffraction data at 100 K (\(\lambda = 0.82683(1)\)) and PND data at 80 K. The lattice parameters are an average of the values from each temperature as noted in the main text.

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Figure 3.7 Results of a combined Rietveld refinement ($R_{wp}$: 5.55%, $R_I$: 8.50%, $\chi^2$: 5.13) of the GEM and I11 powder diffraction data for Ba$_7$Mn$_4$O$_{15}$ at 80 K and 100 K respectively. Blue ticks indicate reflections resulting from Ba$_7$Mn$_4$O$_{15}$, green ticks indicate reflections resulting from BaCO$_3$.

Figure 3.8 shows the fits to the Ba$_7$Mn$_4$O$_{15}$ GEM data measured at 10 K (specifically using a $Pc$ model as described below). Magnetic Bragg peaks are evident in the data in the $d = 3\text{-}5$ Å range. This region of the diffraction pattern is shown in more detail in Figure 3.9, which compares the results at 80 K with those at 10 K. The clearest magnetic peaks index on the nuclear unit cell as $(0\ 1\ 2)$, $(1\ 0\ -2)$, $(1\ 1\ 2)$, $(1\ 2\ -1)$, $(1\ 2\ -2)$ and $(2\ 1\ -1)$.
Chapter 3. Synthesis and Characterisation of Ba$_7$Mn$_4$O$_{15}$

Figure 3.8 Results of Rietveld refinement ($R_{wp}$: 1.84%, $R_B$: 1.26%, $\chi^2$: 3.53) of the GEM neutron powder diffraction data for Ba$_7$Mn$_4$O$_{15}$ at 10 K. Blue ticks indicate reflections resulting from Ba$_7$Mn$_4$O$_{15}$, green ticks indicate reflections resulting from BaCO$_3$.

Figure 3.9 Comparison of the PND data for Ba$_7$Mn$_4$O$_{15}$ from GEM bank 3 at 80 K and 10 K, showing the magnetic Bragg peaks at low temperature. Note that the (0 2 1) reflection for Ba$_7$Mn$_4$O$_{15}$ is overlapped with the (1 1 0) and (0 2 0) reflections of the BaCO$_3$ impurity.
To fit these magnetic peaks, the nuclear structure refined using the combined 80 K GEM data and 100 K I11 data was used as a starting model in ISODISTORT. Since the magnetic peaks could all be indexed on the nuclear unit cell, the models generated using ISODISTORT considered a single magnetic propagation vector \( k = [0 \ 0 \ 0] \). At this \( k \)-point there are four irreps which transform as \( m\Gamma_1^+ \), \( m\Gamma_2^+ \), \( m\Gamma_1^- \) and \( m\Gamma_2^- \), respectively. The \( m\Gamma_1^+ \) irrep has FM components along [010] and AFM components along [100] and [001], \( m\Gamma_2^+ \) has FM components along [100] and [001] and AFM components along [010], and both \( m\Gamma_1^- \) and \( m\Gamma_2^- \) have only AFM components along all three lattice directions. These are visualised in Figure 3.10 with one constraint applied: the magnetic moments on the pair of symmetry-inequivalent Mn\(^{4+}\) sites in the asymmetric unit are constrained to be antiparallel with respect to one another. This is justified by the strong AFM direct exchange interactions anticipated in the face-sharing Mn\(_2\)O\(_9\) dimers as a result of the half-filled \( t_{2g} \) orbitals. Relaxation of the AFM constraint was tested in the final model, but did not lead to a significant improvement in the fitting statistics, nor a substantial deviation from the imposed anti-parallel configuration.

Figure 3.10 Visualisation of the spin configurations resulting from individual magnetic modes in Ba\(_7\)Mn\(_4\)O\(_{15}\). The magnetic moments of the Mn(1) and Mn(2) sites are coloured red and blue, respectively, to distinguish them. The moments are constrained to the \( bc \)-plane, with the \( m\Gamma_1^+ \) and \( m\Gamma_1^- \) mainly along \( c \) and \( m\Gamma_2^+ \) and \( m\Gamma_2^- \) mainly along \( b \), as this constraint was found to result in the best fit to the data. The non-crystallographic constraint that the moments within a dimer are AFM with respect to one another is imposed as discussed in the main text.
Chapter 3. Synthesis and Characterisation of Ba₇Mn₄O₁₅

Figure 3.11 Rietveld refinements to 10 K PND data from GEM bank 3 for Ba₇Mn₄O₁₅ using single-mode and dual-mode models, showing the failure of individual modes to capture all of the magnetic Bragg peak intensity. The Rwp’s of the refinements are as follows - \( m\Gamma_1^+: 1.87\% \), \( m\Gamma_1^- : 1.85\% \), \( m\Gamma_2^+: 1.87\% \), \( m\Gamma_2^- : 1.88\% \), \( m\Gamma_1^+ \oplus m\Gamma_2^- : 1.83\% \), \( m\Gamma_1^- \oplus m\Gamma_2^+ : 1.84\% \). The underfit intensity in the peak at 4.5 Å, marked with a star, is due to the BaCO₃ impurity.

In the 10 K refinements, the nuclear structure was fixed and the components of the magnetic modes were the only refined parameters. The fits to the magnetic peaks of the individual magnetic irreps are shown in in the first and second columns of Figure 3.11. It is clear that the models constructed using a single irrep fail to account for all of the magnetic peaks; the \( m\Gamma_n^- \) modes fail to capture the intensity of the (1 2 -2) and (2 1 -1) peaks, while the \( m\Gamma_n^+ \) modes fail to capture the (0 1 2) and (1 0 -2) peaks, so the next sets of refinements tested pairs of modes. The space group symmetries resulting from the binary combinations of modes are shown in Table 3.4. Following the symmetry requirements of the \( P2_1/c \) unit cell, the three basis vectors spanning each irrep which describe the possible spin orderings correspond to moments aligned with the symmetry-unique \( b \) direction or in the \( ac \)-plane. During the analysis, however, it was discovered that constraining the components of the modes to the \( b \) and \( c \) directions made a negligible difference to the quality of the fits, despite the magnetic ordering being unconstrained within the \( ac \)-plane according to symmetry.
Chapter 3. Synthesis and Characterisation of Ba\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15}

**Table 3.4 Space groups resulting from binary combinations of magnetic modes.**

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<tr>
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<td>P2\textsubscript{1}/c'</td>
<td>Pc'\textsuperscript{1}</td>
<td>P2\textsubscript{1}'</td>
</tr>
<tr>
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<td>Pc'\textsuperscript{1}</td>
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</tbody>
</table>

Table 3.5 shows the R\textsubscript{wp} values calculated for every possible binary combination of modes. The binary combinations of irreps produce different magnetic structures depending on the directions of the modes: if both modes are aligned with different directions (mΓ\textsuperscript{1+} in the ac-plane and mΓ\textsuperscript{-} along b, for example) a ‘spin-wave’ structure is produced in which the direction of the magnetic ordering varies between Mn\textsuperscript{4+} sites. If the pair of modes are both along b or both in the ac-plane a spin-density wave structure is produced in which both the direction and magnitude of the spins varies between the symmetry-inequivalent Mn\textsuperscript{4+} sites. Since both of the sites in Ba\textsubscript{7}Mn\textsubscript{4}O\textsubscript{15} are Mn\textsuperscript{4+}, a spin-wave solution was deemed to be more physically reasonable. Three binary combinations of magnetic modes were found to produce the best fits to the data. The first combination — mΓ\textsuperscript{1+} and mΓ\textsuperscript{-}, both constrained to the c direction — results in a structure with the P2\textsubscript{1} space group. Despite its good fit to the data, this model was discarded as it produces a spin-density wave structure with unreasonable magnetic moment magnitudes on different sites: the calculated moment on half of the Mn\textsuperscript{4+} sites was found to be 3.5 \( \mu_\text{B} \) and the moment on the remaining half of the sites was found to be 0.1 \( \mu_\text{B} \).
Chapter 3. Synthesis and Characterisation of Ba$_7$Mn$_4$O$_{15}$

Table 3.5 Fitting statistics ($R_{wp}$ values) of refinements of Ba$_7$Mn$_4$O$_{15}$ GEM data at 10 K, in which binary combinations of magnetic modes were permitted to refine in either the b direction or the c direction (following the realisation that allowing modes to refine in a made little difference to the quality of the fit). The combinations of modes marked with a box permit a magnetoelectric ground state. Blue cells indicate combinations of modes which produce a spin-wave magnetic structure and red cells indicate combinations of modes which produce a spin-density wave structure.

<table>
<thead>
<tr>
<th>Mode 1 →</th>
<th>$m\Gamma_2^+$</th>
<th>$m\Gamma_1^-$</th>
<th>$m\Gamma_2^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode 2 ↓</td>
<td>c</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>$m\Gamma_1^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>2.27</td>
<td>2.26</td>
<td>2.25</td>
</tr>
<tr>
<td>b</td>
<td>2.34</td>
<td>2.28</td>
<td>2.27</td>
</tr>
<tr>
<td>$m\Gamma_2^+$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>-</td>
<td>-</td>
<td>2.27</td>
</tr>
<tr>
<td>b</td>
<td>-</td>
<td>-</td>
<td>2.25</td>
</tr>
<tr>
<td>$m\Gamma_1^-$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The other two binary-mode models which result in a good fit to the data are $m\Gamma_1^+$ aligned with c and $m\Gamma_2^-$ aligned with b, and $m\Gamma_2^+$ aligned with b and $m\Gamma_1^-$ aligned with c. These result in structures with the space group $Pc$ and $Pc'$, respectively. The fits to the magnetic peaks are shown in the right-hand column of Figure 3.11 and the $R_{wp}$ values from these refinements are highlighted in bold font in Table 3.5. As is implied by the space groups, these two models differ only slightly in the arrangement of the magnetic moments, which are shown in Figure 3.12. The magnitude of the magnetic moment per Mn$^{4+}$ site is also similar in both models: 2.46 $\mu_B$ for the $Pc$ model and 2.34 $\mu_B$ for $Pc'$. These values are lower than the expected maximum value of 3 $\mu_B$ for the $d^3$ Mn$^{4+}$ centres, a phenomenon which has been observed in other Ba-Mn-O systems with face-sharing MnO$_6$ octahedra$^{74,108,125,137,148}$ and justified through a combination of covalency and zero-point effects, as well as frustration in the case of phases containing odd numbers of face-sharing octahedra in their layers (as in Ba$_4$Mn$_3$O$_{10}$). In Ba$_7$Mn$_4$O$_{15}$, overlap between the $t_{2g}$ orbitals of the Mn$^{4+}$ centres is expected to result in a degree of covalency, reducing the observed ordered magnetic moment. Of the two possibilities, the $Pc$ structure is believed to be the more plausible, as the $m\Gamma_2^-$ mode present in this structure was found to best describe the magnetic ordering in Sr$_7$Mn$_4$O$_{15}$ (Chapter 2) and the exchange pathways in both phases are expected to be similar.
The best-fitting models are remarkable in that they both contain a pair of magnetic irreps, one of which conserves inversion symmetry ($m_G^+$) and another in which inversion symmetry is violated ($m_G^-$). This combination of irreps produces a structural space group in which inversion symmetry is globally broken. Comparing the two-mode models which globally break inversion symmetry ($m_G^+ \oplus m_G^-$) with those in which inversion symmetry is retained ($m_G^+ \oplus m_G^-$), the former models always exhibit improved fits, suggesting that a non-centrosymmetric structure is the ground state of the phase. Figure 3.14 shows the results of the magnetisation versus applied field SQUID experiment for Ba$_7$Mn$_4$O$_{15}$. The magnetisation is linear in the 50 to 300 K range, but at low temperatures an enhanced magnetisation response is evident, accompanied by a subtle but clear hysteresis. The maximum moment is 0.083 μB per Mn$^{4+}$ at 2 K and 50 kOe. As this is significantly lower than the effective moment in the paramagnetic region, the ordering is most likely to be largely AFM in character with a small FM component. This can be attributed to a slight canting of the magnetic moments along b transforming as the FM irrep $m_G^+$, suggesting that there is a small incomplete cancellation of the magnetic moments within the Mn$_2$O$_9$ dimers along this lattice direction. These magnetisation results further support the proposed two-irrep magnetic structure and hence also the proposed multiferroic ground state as the magnetism is switchable.

Figure 3.12 Spin configurations for Ba$_7$Mn$_4$O$_{15}$ resulting from two-mode refinements constrained to the bc-plane. The two symmetry-unique Mn sites in P2$_1$/c are indicated by blue and red arrows; the coupling between them is constrained to be AFM as this was found to yield the best fit the experimental data.
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Figure 3.13 Magnetisation versus field results for Ba$_7$Mn$_4$O$_{15}$.

Figure 3.14 shows one of the possible distortion pathways by which the magnetoelastic coupling could be realised: a displacement of the O(6) position which transforms as the $\Gamma_2^-$ irrep. This irrep is responsible for displacive distortions leading to a reduction in the symmetry of the unit cell from $P2_1/c$ to a $Pc$ structure with basis $= \{(1,0,0),(0,1,0),(0,0,1)\}$ and origin shift $= (0,1/4,0)$ with respect to the parent cell. As the O(6) site is on a high-symmetry position in the $P2_1/c$ phase, the displacement would induce a polarisation. Notably, polar distortions appear irrespective of which of the two magnetic space groups ($Pc$ or $Pc'$) are assigned, and since the non-centrosymmetric ground state would be induced by the magnetic ordering, Ba$_7$Mn$_4$O$_{15}$ would be classified as a type II multiferroic. However, despite significant efforts, it was not possible to detect an off-centring of either of the high-symmetry positions (Sr(3) and O(6)) in the PND data. Since the proposed distortions are driven by magnetic ordering, the displacements are expected to be on the order of thousandths of an ångström. The PND experiment described in this chapter is not sensitive to displacements this small, and so nothing can be inferred about the magnitude of the $\Gamma_2^-$ distortion or any other symmetry-allowed displacements. However, the Landau expansion of the free energy at the magnetic phase transition may take the form:

$$
\mathcal{F} = \mathcal{F}_0 + \frac{1}{2} \alpha (T - T_c) \left( Q_{m1}^2 + Q_{m2}^2 \right) + \frac{1}{4} \beta \left( Q_{m1}^2 + Q_{m2}^2 \right)^2 + \frac{1}{6} \kappa \left( Q_{m1}^2 + Q_{m2}^2 \right)^3 + \gamma Q_{m1} Q_{m2} Q_{m1} Q_{m2} + \ldots
$$

The trilinear term in the Landau expansion implies that reversing the sign of either of the magnetic OPs may also serve to reverse the polar distortion.
Figure 3.14 Symmetry-allowed polar displacements (transforming as $I_2^-$) of the O6 anion in Ba$_7$Mn$_4$O$_{15}$ (green vectors) in the Pc space group (basis = \{\(110\),\(010\),\(001\)\}, origin shift = \(01/4\),0\) with respect to the \(P2_1/c\) parent cell).

Figure 3.15 Rietveld against PND data collected at D2B for Sr$_7$Mn$_4$O$_{15}$ at 300 K. Blue ticks indicate reflections for the Sr$_7$Mn$_4$O$_{15}$ phase, green ticks indicate reflections for a small SrMnO$_3$ impurity. Inset: magnetic reflections observed at 1.5 K (black crosses) and the same region of 2θ at 300 K (green crosses).

Comparing the low-temperature PND experiment results for Ba$_7$Mn$_4$O$_{15}$ with the results for Sr$_7$Mn$_4$O$_{15}$ as described in Chapter 2, it is apparent that the magnetic structures are related, though a magnetoelectric ground state does not seem to be evident in the data for Sr$_7$Mn$_4$O$_{15}$. Figure 3.15 shows the neutron diffraction pattern of Sr$_7$Mn$_4$O$_{15}$ at 300 K and the magnetic Bragg peaks which appear in the pattern at 1.5 K. The magnetic transition temperature is assumed to be 50 K, following the results obtained for Sr$_2$Ca$_5$Mn$_4$O$_{15}$ and Sr$_2$Ba$_5$Mn$_4$O$_{15}$. The best fit to the magnetic structure was achieved using a model which incorporated only the $m\Gamma_2^-$ irrep aligned with the b direction, which was consistent with
Chapter 3. Synthesis and Characterisation of Ba$_7$Mn$_4$O$_{15}$

previously-published models$^{108}$. This model results in an ordered magnetic moment of 2.249 $\mu_B$, very similar to the results calculated for Ba$_7$Mn$_4$O$_{15}$. Two-irrep models resulted in no improvement compared to the single $m\Gamma_2^-$ model, implying that the magnetoelectric ground state is specific to Ba$_7$Mn$_4$O$_{15}$. It is not straightforward to rationalise the origin of the difference in the magnetic structures of Sr$_7$Mn$_4$O$_{15}$ and Ba$_7$Mn$_4$O$_{15}$. Table 3.6 shows a selection of the Mn-Mn distances in both phases from Rietveld refinements of the high-resolution data. Though the unit cell expands to accommodate the larger Ba$^{2+}$ cation, there are not clear changes evident in these distances which can be easily assigned as the key reason for the different magnetic structures. The most obvious change is in the Mn(1)-O(5)-Mn(2) angle, which is closer to linear in Ba$_7$Mn$_4$O$_{15}$ than in Sr$_7$Mn$_4$O$_{15}$ and may therefore promote superexchange, promoting stronger AFM coupling.

Table 3.6 Selected Mn-Mn distances in Sr$_7$Mn$_4$O$_{15}$ and Ba$_7$Mn$_4$O$_{15}$ from Rietveld refinements.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sr$_7$Mn$<em>4$O$</em>{15}$</th>
<th>Ba$_7$Mn$<em>4$O$</em>{15}$</th>
<th>Ba$_7$Mn$<em>4$O$</em>{15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K</td>
<td>3.719(2)</td>
<td>3.881(7)</td>
<td>3.897(12)</td>
</tr>
<tr>
<td>Mn(1)-O(6)-Mn(1) distance (Å)</td>
<td>2.564(2)</td>
<td>2.640(11)</td>
<td>2.638(11)</td>
</tr>
<tr>
<td>Mn(1)-Mn(2) intradimer distance (Å)</td>
<td>3.697(2)</td>
<td>3.814(5)</td>
<td>3.836(11)</td>
</tr>
<tr>
<td>Mn(1)-O(5)-Mn(2) angle (°)</td>
<td>164.8(2)</td>
<td>171.5(5)</td>
<td>170.9(5)</td>
</tr>
</tbody>
</table>

3.4 Conclusions

The binary metal oxide Ba$_7$Mn$_4$O$_{15}$ was successfully synthesised and characterised for the first time by powder synchrotron X-ray diffraction and PND. Variable-temperature analysis indicates that no phase transition from the $P2_1/c$ space group occurs in the 100-300 K temperature range, though DC SQmID magnetisation versus temperature and magnetisation versus field data, as well as low-temperature neutron diffraction data show an AFM ground state with a weak FM component below 50 K. Careful analysis of this ground state reveals that a pair of magnetic modes which transform like the $m\Gamma_1^+$ and $m\Gamma_2^-$ irreps act simultaneously and, in doing so, couple to a polar distortion mode transforming as $\Gamma_2^-$. Though the proposed structural distortion mode was not observed in the available data, a trilinear coupling between these modes is possible, and future work might focus on investigating this ground state to corroborate these results. The discovery of a novel magnetoelectric material is exciting and demonstrating switchability should be a major focus of any future study.
Chapter 4. Pressure-Dependent Phase Transitions in Hybrid Improper Ferroelectric Ruddlesden-Popper Oxides

4.1 Introduction

The Ruddlesden-Popper (RP) phases are a family of compounds which are related to the perovskite structure. They exhibit great compositional variety, generating properties such as magnetism and ferroelectricity and applications such as catalysis\textsuperscript{149}, superconductivity\textsuperscript{150}, negative thermal expansion\textsuperscript{151-154} and colossal magnetoresistance\textsuperscript{155}, with new variations on the structure being envisaged for solar cell applications\textsuperscript{156,157}.

Among the earliest RP phases to be synthesised were Sr\textsubscript{2}TiO\textsubscript{4}, Ca\textsubscript{2}MnO\textsubscript{4} and SrLaAlO\textsubscript{4} in 1957\textsuperscript{158}, followed by Sr\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7} and Sr\textsubscript{4}Ti\textsubscript{3}O\textsubscript{10} in 1958\textsuperscript{159}; they consist of a number of layers of perovskite-like slabs which are interspersed with rock salt-like layers. The number of perovskite-like slabs in the structure is usually cited when referring to the RP phase and is also calculable from the formula. The general formula for RP phases is A\textsubscript{n+1}B\textsubscript{n}X\textsubscript{3n+1}, where A and B are cations, X is an anion such as O\textsuperscript{2-} or S\textsuperscript{2-} and n is the number of perovskite-like slabs. Indeed, the formula may be rearranged to (ABX\textsubscript{3})\textsubscript{n}AX to highlight the number of slabs. As shown in Figure 4.1, a perovskite may be considered to be an RP phase with infinitely many perovskite-like layers.

![Figure 4.1 Relationship between perovskites and Ruddlesden-Popper phases.](image)
Chapter 4. Pressure-Dependent Phase Transitions in Hybrid Improper Ferroelectric Ruddlesden-Popper Oxides

A variety of RP phases are well-known to crystallise in the tetragonal $I4/mmm$ space group, which is the highest possible symmetry (or ‘aristotype’) for this structural class\textsuperscript{160-168}. However, in certain $n = 2$ compositions such as $(Ca/Sr)\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7}\textsuperscript{169}$, $Ca\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7}\textsuperscript{170}$, $(Ca/Sr)\textsubscript{3}SnO\textsubscript{7}\textsuperscript{171,172}$, $Sr\textsubscript{3}HfO\textsubscript{7}\textsuperscript{173}$ and $Sr\textsubscript{3}ZrO\textsubscript{7}\textsuperscript{174}$ the structure is orthorhombic with the polar $A2\textsubscript{1}am$ space group. This space group is a subgroup of $I4/mmm$, related by a series of distortion modes that transform as irreps $\Gamma^+_4$, $X^+_2$ and $X^-_5$. The first of these distortions is a mode which transforms like the irrep $\Gamma^+_4$ and describes orthorhombic strain, changing the space group from the body-centred aristotype to the face-centred $Fmmm$ (basis $= \{(1,1,0),(1,1,0),(0,0,1)\}$ and origin shift $= (0,0,0)$ with respect to the $I4/mmm$ structure) with $a$ and $b$ unit cell parameters larger by $\sqrt{2}$. The remaining irreps (with propagation vector $k = (0.5, 0.5, 0)$) correspond to in-phase rotation about the [001] axis (transforming like the irrep $X^+_2$) and out-of-phase tilt about the [110] axis (transforming like the irrep $X^-_5$) of the $BO_6$ octahedra in the perovskite-like layers (Figure 4.2). Applying these individually distortions to an RP phase in $I4/mmm$ produce structures of $Acam$ and $Amam$ symmetry, respectively, and the $A2\textsubscript{1}am$ structure (basis $= \{(-1,1,0),(1,1,0),(0,0,1)\}$ and origin shift $= (-0.25, 0.25, 0.5)$ with respect to the $I4/mmm$ structure) corresponds to the direct sum of the symmetry spaces spanned by these space groups. It is valuable to note at this point that $A2\textsubscript{1}am$ is an alternative setting of $Cmc2\textsubscript{1}$ in which the longest axis is the $c$ direction. This is done to aid comparisons with the tetragonal $I4/mmm$ aristotype structure, which also has $c$ as its longest axis. As with the $Fmmm$ structure, this unit cell is $\sqrt{2}$ larger in the $ab$ plane.

The distortions which occur in $Ca\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7}$ and $Ca\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7}$ are significant because they break inversion symmetry, resulting in a form of improper ferroelectricity referred to as hybrid improper ferroelectricity\textsuperscript{175}. First observed in a superlattice of $PbTiO\textsubscript{3}$ and $SrTiO\textsubscript{3}\textsuperscript{176-178}$, this type of improper ferroelectricity occurs as a result of coupling between the pair of non-polar rotational modes\textsuperscript{179}, and is particularly interesting for its potential to produce novel type-II multiferroics in which both magnetic and FE orderings are induced through the same set of distortions\textsuperscript{179}. In $n = 2$ RP phases, $A2\textsubscript{1}am$ symmetry is established by the simultaneous condensation of the $X^+_2$ and $X^-_5$ modes. A polar distortion with irrep $\Gamma^-_5$ is induced as a secondary order parameter (OP) of the HIF phase transition because its OP — labelled $Q\textsubscript{r}^-_5$, where $Q$ is the distortion amplitude — and the ‘hybrid’ OP $Q\textsubscript{x}^+_2 Q\textsubscript{x}^-_3$ transform in the same way under the symmetry operations of the aristotype $I4/mmm$ space group. The polar

\textsuperscript{1}In the context of $n = 2$ RP phases, the word ‘rotation’ here also refers to the out-of-phase tilting ($X^-_5$) of the $BO_6$ octahedra as there is a distinct axis in which the tilts occur relative to the in-phase rotation ($X^+_2$) mode.
mode is described as a 'two-against-one' displacement of the Ca\(^{2+}\) cations in each perovskite-like slab, where the displacements in a pair of neighbouring slabs are in the same direction, resulting in a net polarisation\(^{26}\).

Equation 4.1 shows a truncated Landau expansion of the free energy about the high symmetry phase\(^{180}\):

\[
\mathcal{F} = \mathcal{F}_0 + \frac{1}{2} \alpha (T - T_c) \left( Q_{X_2^+}^2 + Q_{X_3^+}^2 \right) + \frac{1}{4} \beta \left( Q_{X_2^+}^2 + Q_{X_3^+}^2 \right)^2 \\
+ \frac{1}{6} \kappa \left( Q_{X_2^+}^2 + Q_{X_3^+}^2 \right)^3 + \gamma Q_{X_2^+} Q_{X_3^+} Q_{\Gamma_5^-} + \cdots
\]

4.1

Where \(T_c\) represents the temperature of the FE phase transition. The key part of Equation 4.1 is the third-order term, which directly relates the amplitude of the rotation and tilt modes to produces an equation to describe the mechanism of hybrid improper ferroelectricity referred to as trilinear coupling:

\[
\mathcal{F}_{\text{tri}} = \gamma Q_{X_2^+} Q_{X_3^+} Q_{\Gamma_5^-}
\]

4.2

Where \(\gamma\) is a coefficient that describes the strength of the coupling. It can be deduced from Equation 4.2 that the sign of \(\gamma\) is irrelevant to the stabilisation of the free energy as the polarisation \((Q_{\Gamma_5^-})\) may adopt either a positive or negative sign. Further, switching the
polarisation state in a HIF material requires that the amplitude of only one of the octahedral distortions must be reversed.

The temperature-dependent phase transitions of \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) and \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) are well-documented\textsuperscript{154,181}. \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) exhibits a phase coexistence in the temperature range 150-400 K between the \( A2_1\text{am} \) space group and phase which exhibits negative thermal expansion (NTE) behaviour with \( Acaa \) symmetry. As with the \( A2_1\text{am} \) structure, the \( Acaa \) structure can once again be considered as a distorted form of the \( I4/mmm \) structure which contains only an out-of-plane rotation of the \( \text{MnO}_6 \) octahedra which transforms like the irrep \( X_1^- \) (Figure 4.2). With increasing temperature \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) exhibits a first-order phase transition around 1100 K, also to \( Acaa \) symmetry. Due to the greater difficulty associated with performing high-resolution diffraction experiments under high pressure, relatively few investigations have been performed to investigate the pressure-dependence of the phase transitions in these structures. Zhu \textit{et al.}\textsuperscript{182,183} described a pair of irreversible phase transitions around 1-1.3 GPa (tetragonal to orthorhombic) and 9.5 GPa\textsuperscript{184} (orthorhombic to tetragonal) for \( \text{Ca}_3\text{Mn}_2\text{O}_7 \), but the specific symmetries of the structures have not been demonstrated and the effect of higher pressures is unknown.

In this chapter, \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) and \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) will be investigated by high-pressure powder synchrotron X-ray diffraction experiments. The experimental results will be complemented by first-principles calculations in an attempt to elucidate the mechanisms associated with the phase transitions in these structures.

\subsection*{4.2 Experimental}

Polycrystalline samples of \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) and \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) were synthesised using standard solid-state methods. Stoichiometric quantities of \( \text{CaCO}_3 \), \( \text{TiO}_2 \) and \( \text{MnO}_2 \) were ground together in an agate mortar until homogeneous and sintered at 1300-1500 °C. The samples were loaded into LeToullec-style membrane diamond anvil cells (DACs) equipped with Boehler-Almax anvils with 400 \( \mu \text{m} \) culets. The gasket material was Re, pre-indentented to approximately 50 \( \mu \text{m} \), with a 200 \( \mu \text{m} \) EDM ‘drilled’ hole to form the sample chamber. The pressure-transmitting medium was Ne, and small ruby chips and Cu were added to act as pressure gauges. The X-ray beam size was 70 \( \mu \text{m} \) round diameter. Powder X-ray diffraction measurements were performed at Beamline I15 at Diamond Light Source. The beam energy was approximately 29 keV (\( \lambda = 0.42448(1) \)), refined using a LaB\textsubscript{6} standard. Diffraction patterns were recorded at intervals as the pressure was increased up to a maximum of 39.8 GPa for \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) and 38.48 GPa for \( \text{Ca}_3\text{Ti}_2\text{O}_7 \). Pawley refinements were performed using TOPAS Academic v6\textsuperscript{143}. Compressibility calculations for both phases were performed.
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using PASCa1142. Symmetry-adapted refinements were performed in TOPAS using the parameterisation provided by ISODISTORT24,25.

Ab initio calculations were performed for Ca$_3$Ti$_2$O$_7$ by Dr Nicholas Bristowe (Durham University). The calculations were performed using the Vienna Ab Initio Simulation Package (VASP) v5.4.4 with the PBEsol exchange correlation potential and projector augmented-wave (PAW) pseudopotentials185–190. A plane wave basis set with a 700 eV energy cutoff and a 6x6x1 Monkhorst-Pack k-point mesh with respect to the parent tetragonal primitive cell (scaled accordingly for other supercells) were found to be appropriate. DFT calculations were not performed for Ca$_3$Mn$_2$O$_7$, as the properties of the magnetic spin states as a function of pressure are very complex to model.

4.3 Results and Discussion

4.3.1 Ca$_3$Mn$_2$O$_7$ Experimental Results

A selection of diffraction patterns for Ca$_3$Mn$_2$O$_7$ under varying pressure are shown in Figure 4.3. Diffraction artifacts arising due to the DAC are marked with black star symbols. It is difficult to differentiate the HIF A2$_1$am and NTE Acaa phases by Pawley refinements alone, but previous work154 under variable temperatures has shown that the $c$ parameter of the Acaa phase is consistently longer than that of the A2$_1$am phase and the contributions of each phase to the diffraction pattern are thus assigned. Rietveld refinements were not found to be suitable for the data acquired in the experiment due to several factors. The intensities of the diffraction peaks were heavily attenuated by the application of pressure, and despite attempts to model this through preferred orientation macros within TOPAS, no suitable solution was found. The 2θ range was also very limited as a result of the DACs, which restrict the available angular range in the diffraction experiment.

In contrast to previous work182,184, there is no evidence for a tetragonal-orthorhombic phase transition at 1.3 GPa, nor an orthorhombic-tetragonal phase transition around 9.5 GPa. Instead, a phase coexistence is evident in the lower-pressure diffraction patterns: the (0 0 10) reflection for the A2$_1$am phase appears as a small peak to the right-hand side of the same reflection for the Acaa phase at 0.2 GPa and decreases in intensity before disappearing at approximately 2.3 GPa. This is highlighted in Figure 4.3 with a dotted red rectangle. Figure 4.4 shows the results of single-phase (Acaa-only) and dual-phase (Acaa and A2$_1$am) Pawley refinements at 0.2 and 2.3 GPa. At the lower of the two pressures, the dual-phase model is clearly superior, while a single-phase model is more appropriate for the 2.3 GPa data. The assignment of a 'split peak profile' by Zhu and co-workers may actually
be due to the phase coexistence, an error arising from the relatively low resolution of the white-beam experiment.

Figure 4.3 I15 powder synchrotron X-ray diffraction data measured at I15 (λ = 0.42448(1) Å) of Ca₃Mn₂O₇ at various pressures using a DAC. Diffraction artifacts resulting from the DAC fulfilling the diffraction condition are marked using stars. The dotted red box indicates the disappearance of the (0 0 10) reflection for the A₂1am phase of Ca₃Mn₂O₇ with increasing pressure.
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Figure 4.4 Pawley refinements of I15 powder synchrotron X-ray diffraction data ($\lambda = 0.42448(1)$ Å) of Ca$_3$Mn$_2$O$_7$ at (a) 0.2 and (d) 2.3 GPa. Observed data are marked with crosses, calculated data are shown with a red line and the difference is plotted as a grey line below the data. Blue (upper) ticks indicate reflections for the A2$_1$am phase, green (lower) ticks indicate reflections for the Acaa phase. Insets (b) and (e) show the result of a two-phase refinement including both an A2$_1$am phase and an Acaa phase, showing an improved fit for the (0 0 10) peaks against insets (c) and (f), which show the result of a refinement including only an Acaa phase.

The lattice parameters of Ca$_3$Mn$_2$O$_7$ with increasing pressure are shown in Figure 4.5, with insets showing the two-phase behaviour up to 1 GPa in greater detail. The lattice parameters decrease smoothly and, as with the tetragonal-to-orthorhombic phase transition at 1.3 GPa, there is no evidence of a tetragonal-to-orthorhombic phase transition around 9.5 GPa. Single-phase refinements in A2$_1$am and Acaa (not pictured) exhibit significant instability below 2 GPa, providing further evidence for the phase coexistence model. It is notable that Ca$_3$Mn$_2$O$_7$ is already partway through a first-order phase transition at room temperature and standard pressure$^{154}$. The conventional wisdom that high pressure has a similar effect to low temperature is not obeyed, as the low-temperature phase is A2$_1$am, whereas the high-pressure phase is Acaa.

As stated above, there is no strong evidence of a further phase transition up to 40 GPa in this dataset. However, since the Acaa $\rightarrow$ I4/mmm phase transition is expected to be second-order, with a continuous evolution of the OPs and strain and no phase coexistence, it is possible that the phase transition is present but is missed since the refinements do not find a significant orthorhombic strain.
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Figure 4.5 Lattice parameters extracted from Pawley refinements of I15 powder synchrotron X-ray diffraction data of Ca$_3$Mn$_2$O$_7$ with increasing pressure. Blue symbols indicate the $a$ parameter, green symbols indicate the $b$ parameter and red symbols indicate the $c$ parameter. Insets (a) and (b) show the 0-2 GPa regions of each part of the plot, showing details of the two-phase system over the pressure range. Over the pressure range studied, the $a$ and $b$ lattice parameters of the $A_{21}am$ phase refine to within experimental error of one another.

4.3.2 Ca$_3$Ti$_2$O$_7$ Experimental Results

As with Ca$_3$Mn$_2$O$_7$, Figure 4.6 shows selected diffraction patterns for Ca$_3$Ti$_2$O$_7$ with increasing pressure. Diffraction artifacts arising from the DAC are indicated by black star symbols. The majority of the diffraction patterns were fitted using a single-phase $A_{21}am$ model — this being the only phase present between ambient pressure and 23.87 GPa, in contrast to Ca$_3$Mn$_2$O$_7$ — with the only exceptions being the data at 30.65 and 38.48 GPa. Figure 4.7 shows the Pawley refinement of the diffraction pattern for Ca$_3$Ti$_2$O$_7$ at nominally zero pressure as it was loaded into the DAC. Additional reflections appear in the diffraction patterns at 30.65 and 38.48 GPa; these were well-fit using an additional phase that was inferred to have $Aca$ symmetry by analogy to Ca$_3$Mn$_2$O$_7$. The most obvious new peak resulting from the $Aca$ phase is indicated in Figure 4.6 with a red dotted rectangle, appearing to the right hand side of a pair of reflections due to the $A_{21}am$ phase. This reflection was identified as the (0 2 0) reflection of the $Aca$ phase, highlighted in greater detail in Figure 4.8 for both single-phase and two-phase refinements.

Inset (a) in Figure 4.8 shows how the refinement fails to model all of the intensity using only the $A_{21}am$ phase. Inset (b) shows the improvement achieved by the addition of the $Aca$ phase. Further support for the two-phase refinement comes from the observable peak broadening present in the $hhl$ reflections of the $A_{21}am$ phase, which are not subject to peak splitting for

---

*The (0 0 10) reflection which was used for Ca$_3$Mn$_2$O$_7$ is not suitable for monitoring the structural evolution of Ca$_3$Ti$_2$O$_7$ because it is overlapped with an artifact resulting from the DAC fulfilling the diffraction condition.*
structures with orthorhombic symmetry. The most likely origin of the broadening is therefore a two-phase coexistence.

![Figure 4.6](image1.png)

**Figure 4.6** I15 powder synchrotron X-ray diffraction data measured at I15 ($\lambda = 0.42448(1)$ Å) of Ca$_3$Ti$_2$O$_7$ at various pressures using a DAC. Diffraction artifacts resulting from the DAC fulfilling the diffraction condition are marked using stars. The dotted red box indicates the appearance of the (0 2 0) reflection for the $A_2$ $a_{1}$ am phase of Ca$_3$Ti$_2$O$_7$ with increasing pressure.

![Figure 4.7](image2.png)

**Figure 4.7** Pawley refinement of I15 powder synchrotron X-ray diffraction data ($\lambda = 0.42448(1)$ Å) of Ca$_3$Ti$_2$O$_7$ as-loaded (i.e. at nominally zero applied pressure). Observed data are marked with crosses, calculated data are shown with a red line and the difference is plotted as a grey line below the data. Blue ticks indicate reflections for the $A_2$ $a_{1}$ am phase. The small feature at $2\theta = 12^\circ$ is a result of the DAC fulfilling the diffraction condition.
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Figure 4.8 Pawley refinement of I15 powder synchrotron X-ray diffraction data ($\lambda = 0.42448(1) \text{ Å}$) of Ca$_3$Ti$_2$O$_7$ at 38.48 GPa. Observed data are marked with crosses, calculated data are shown with a red line and the difference is plotted as a grey line below the data. Blue ticks indicate reflections for the A2$_1$am phase, green ticks indicate reflections for the Acaa phase. The excluded data around $2\theta = 13^\circ$ is a result of the DAC fulfilling the diffraction condition. Insets (a) and (b) show the result of a single-phase and a two-phase refinement including both an A2$_1$am phase and an Acaa phase on the fit of the peak assigned as the (0 2 0) reflection of the Acaa phase.

The evolution of the lattice parameters of Ca$_3$Ti$_2$O$_7$ with increasing pressure is shown in Figure 4.9. The lattice parameters decrease smoothly with pressure until the final pressure point measured in the experiment at 38.48 GPa, where the secondary Acaa phase appears. At this point the $a$ and $b$ parameters of the model, which have been close to metrically tetragonal for much of the pressure rise, deviate to a significant degree as a result of the phase transition; this is an artifact of the refinement attempting to fit two phases with only an A2$_1$am phase. Also shown in Figure 4.9 are the results of the DFT calculations on Ca$_3$Ti$_2$O$_7$ in the Acaa and A2$_1$am space groups. The calculated A2$_1$am $a$ and $b$ lattice parameters match well with the experimental values up to 30.65 GPa, while the $c$ parameter is qualitatively similar to the experimental result but shorter by approximately 0.1 Å. This could indicate that the ground-state DFT calculations overestimate the magnitude of the $X^7_3$ octahedral tilting mode, as this mode causes a slight decrease in the $c$ parameter as the octahedra tilt off the axis. Additionally, the DFT calculations model the structure at an effective temperature 0 K and any possible effects of thermal expansion has been ignored. The calculated Acaa lattice parameters clearly disagree with the experimental data up to 30.65 GPa, supporting the single-phase A2$_1$am assignment of the structure over this pressure range. However, these parameters also do not fit with the experimentally-observed lattice parameters for the Acaa phase above 30 GPa. While the $a$ and $b$ parameters are calculated to be metrically tetragonal (consistent with experimental observations at
high pressure), they are slightly underestimated compared to observations, and the \( c \) parameter is overestimated compared to the observed value. There is a qualitative agreement, with the \( c \) parameter becoming longer than in the \( A2_1 \text{am} \) phase and the \( a \) and \( b \) parameters becoming shorter, but a quantitative agreement is lacking. Later in this chapter, analysis of the DFT ground-state energies of the various phases will support this assignment. The disagreement may also be due to strong strain coupling arising from the intergrowth of coexisting \( A2_1 \text{am} \) and \( Acaa \) domains. Figure 4.10 shows the Lorentzian strain extracted from the Pawley refinements on \( \text{Ca}_3\text{Ti}_2\text{O}_7 \). The strain rises steadily as a function of the applied pressure and appears to be relieved by the first-order phase transition. It was not possible to increase the pressure beyond 38.48 GPa, so further measurements of the lattice parameters and strain in a single-phase \( Acaa \) regime were not acquired, but it is expected that the calculated and the experimental lattice parameters would converge at higher pressures.

Figure 4.9 Lattice parameters extracted from Pawley refinements of I15 powder synchrotron X-ray diffraction data of \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) with increasing pressure.
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Figure 4.10 Lorentzian strain extracted from Pawley refinements of I15 powder synchrotron X-ray diffraction data of Ca$_3$Ti$_2$O$_7$ with increasing pressure.

Compressibility parameters and Birch-Murnagahan coefficients were calculated using PASCaL$^{142}$. Only the single-phase data for each composition was used in these calculations: all data at pressures greater than 2.3 GPa for Ca$_3$Mn$_2$O$_7$ (i.e. the Acaa data) and all data at pressures lower than 30.65 GPa for Ca$_3$Ti$_2$O$_7$ (i.e. the $A_{21}am$ data). Table 4.1 contains the calculated second-order Birch-Murnagahan coefficients for the experimental Ca$_3$Mn$_2$O$_7$ and Ca$_3$Ti$_2$O$_7$ phases and the DFT-calculated $A_{21}am$, Acaa and I4/mmm phases. The calculated results for the Ca$_3$Ti$_2$O$_7$ $A_{21}am$ phase show an excellent agreement with the experimental results (especially the value of $B_0$), though with somewhat greater standard deviations due to the smaller number of input data points.
Table 4.1. Second-order Birch-Murnaghan coefficients calculated using PASCal. For the experimental results, the same data were used as for Table 4.2. $B_0$ and $V_0$ represent values of the bulk modulus and unit cell volume at zero pressure (extrapolated backwards from the input data), $B'$ is the dimensionless pressure derivative of the bulk modulus and $P_c$ represents an estimate of the critical pressure to induce a phase transition (zero in all cases because single-phase data were used as the input).

<table>
<thead>
<tr>
<th>Material</th>
<th>$B_0$ (GPa)</th>
<th>$\sigma B_0$ (GPa)</th>
<th>$V_0$ (Å$^3$)</th>
<th>$\sigma V_0$ (Å$^3$)</th>
<th>$B'$</th>
<th>$\sigma B'$</th>
<th>$P_c$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_3$Mn$_2$O$_7$</td>
<td>177.4223</td>
<td>2.0277</td>
<td>531.4008</td>
<td>0.4401</td>
<td>4</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>Exp. Aca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$_3$Ti$_2$O$_7$</td>
<td>161.7441</td>
<td>0.5437</td>
<td>572.1454</td>
<td>0.1043</td>
<td>4</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>Exp. A2$_1$am</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$_3$Ti$_2$O$_7$</td>
<td>161.4027</td>
<td>1.7490</td>
<td>566.1091</td>
<td>0.7090</td>
<td>4</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>DFT A2$_1$am</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$_3$Ti$_2$O$_7$</td>
<td>162.5499</td>
<td>0.8882</td>
<td>563.0012</td>
<td>0.3540</td>
<td>4</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>DFT Aca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$_3$Ti$_2$O$_7$</td>
<td>167.9115</td>
<td>0.3207</td>
<td>284.9060</td>
<td>0.0614</td>
<td>4</td>
<td>N/A</td>
<td>0</td>
</tr>
<tr>
<td>DFT I4/mmm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2 and Table 4.3 summarise the compressibility parameters for the experimental Ca$_3$Ti$_2$O$_7$ and Ca$_3$Mn$_2$O$_7$ data and DFT-calculated Ca$_3$Ti$_2$O$_7$ data, respectively. For both sets of calculations on the experimental data, the principal axes are mapped directly onto the crystallographic axes as the orthorhombic structures have orthogonal lattice vectors by definition, so the ‘direction’ heading is omitted. Ca$_3$Ti$_2$O$_7$ is more compressible than Ca$_3$Mn$_2$O$_7$ on all axes, possibly as a result of the $X_3^-$ octahedral tilting mode present in the A2$_1$am structure, which may permit greater compressibility by increasing in magnitude to some extent. Comparing the results of the compressibility calculations for the experimental data with the results for the DFT-calculated structures, the DFT compressibilities are found to be lower in all three of the calculated structures. With each phase transition to a lower-symmetry phase, the compressibility increases. This can be rationalised by the greater degrees of freedom available at each step down in symmetry. The DFT A2$_1$am phase has the closest results to the compressibilities calculated using the experimental data, supporting the assignment of this phase for the majority of the pressure range studied.
4.3.3 Ca₃Ti₂O₇ DFT Calculation Results

Figure 4.11(a) shows the calculated ground-state energies of the $A2_{1}am$ and $Acaa$ phases of Ca₃Ti₂O₇ relative to the I₄/mmm aristotype phase. With increasing pressure up to 50 GPa, both the polar $A2_{1}am$ and non-polar $Acaa$ phase become more stable relative to the aristotype. However, the $Acaa$ phase is stabilised at a greater rate than the $A2_{1}am$ phase. At a pressure of approximately 30 GPa, the $Acaa$ phase becomes more stable, in good agreement with the experimental observation of the phase transition in the 30.65-
38.48 GPa range. This validates our speculative assignment of the phases in Section 4.3.1 that was based on the experimentally-observed lattice parameters only. This simultaneous stabilisation of the FE and PE phases is unexpected: in proper FE perovskites, an increase in hydrostatic pressure generally favours the more ordered PE phase and causes the FE phase to increase in energy.\(^{191-196}\)

![Figure 4.11](a): DFT-calculated ground state energies for the $A_2\text{I}_{4\text{am}}$ and Acaa phases of Ca$_3$Ti$_2$O$_7$ with increasing pressure; (b,c): DFT-calculated mode amplitudes for the $A_2\text{I}_{4\text{am}}$ and Acaa structures of Ca$_3$Ti$_2$O$_7$; (d): calculated degree of rumpling for each phase of Ca$_3$Ti$_2$O$_7$ with increasing pressure.
To better understand the pressure-induced phase transitions in Ca$_3$Ti$_2$O$_7$, the DFT-relaxed $A_2\alpha m$ and $Aca$ phases were decomposed in terms of symmetry-adapted displacements using ISODISTORT with respect to the I4/mmm aristotype. The results of these decompositions are shown in Figure 4.11(b) and (c), which plot the amplitude of the assorted distortion modes against pressure. The modes are described using the ISODISTORT parent cell-normalised amplitude, $A_p$, which is defined according to:

$$A_p = A_s \sqrt{\frac{V_p}{V_s}}$$  \hspace{1cm} (4.3)

Where $A_s$ is defined as the square root of the sum of the squares of the displacements in the primitive supercell, $V_p$ is the volume of the primitive parent cell and $V_s$ is the volume of the supercell resulting from the distortion.

For the $Aca$ phase — which exhibits only an out-of-phase rotation of the oxide octahedra with irrep $X_1^-$ in addition to the always-allowed $\Gamma_1^+$ mode — a slow increase in the amplitude of the $X_1^-$ mode is evident (Figure 4.11(b)). The calculations of the behaviours of the modes in the $A2\alpha am$ phase were performed up to 70 GPa (Figure 4.11(c)) and can be divided into two regimes: below 40 GPa and above 40 GPa. The $X_2^+$ in-phase octahedral rotation mode amplitude increases with increasing pressure up to 40 GPa, while the $X_3^-$ octahedral tilt mode remains almost constant, only slightly decreasing at the upper end of the regime. The $\Gamma_5^-$ polar mode coupled to the two octahedral distortions increases slightly in this regime.

While it was not directly measured in the experiment, the associated FE polarisation is expected to increase over this pressure range as a result of these mode amplitude variations, in contrast to the expected trend with pressure for phases which display proper ferroelectricity. Above 40 GPa the $X_2^+$ mode continues to increase in amplitude, with an initial small increase in gradient which begins to plateau at 70 GPa. The $X_3^-$ and $\Gamma_5^-$ mode amplitudes begin to rapidly decrease above 40 GPa and vanish at 70 GPa. To investigate the extent to which the unexpected increase in the amplitude of the $\Gamma_5^-$ polar mode with increasing pressure is driven by the trilinear coupling mechanism, the $\Gamma_5^-$ mode amplitude was plotted against the product of the rotation and tilt modes ($|X_2^+| \times |X_3^-|$) as shown in Figure 4.12. According to the trilinear coupling mechanism, a linear correlation should be expected between the polar mode and the product of the octahedral distortions. At higher pressures (45-70 GPa, marked in red in Figure 4.12) this relationship is observed, but at lower pressures (0-45 GPa, marked in black in Figure 4.12) the amplitude of the polar mode is in excess of what would be expected. This implies that there is a small proper FE component present in Ca$_3$Ti$_2$O$_7$ at low pressures in addition to the improper FE. Figure 4.13
shows the calculated individual atomic displacements resulting from an isolated condensed $\Gamma_5^-$ mode in a $\text{Ca}_3\text{Ti}_2\text{O}_7$ phase. Without the octahedral distortions, this phase has $F2mm$ symmetry (basis = $\{(-1,-1,0),(0,0,1),(-1,1,0)\}$ and origin shift = $(0,0,0)$ with respect to the $I4/mmm$ parent) and the polar mode vanishes with increasing pressure around 40 GPa. Thus the additional proper component of the FE polarisation is shown to have the same trend with pressure as is observed in proper FEs, and it is only the improper component that contradicts the conventional expectation as a result of the varied coupling of the rotations and tilts with hydrostatic pressure.

![Figure 4.12](image)

*Figure 4.12 The DFT-calculated amplitude of the $\Gamma_5^-$ polar mode in $\text{Ca}_3\text{Ti}_2\text{O}_7$ plotted against the product of the rotation and tilt mode amplitudes ($|X_2^+| \times |X_3^-|$), showing deviations of the trilinear coupling mechanism (red line) below approximately 30-45 GPa.*

The final key degree of freedom not yet discussed in $\text{Ca}_3\text{Ti}_2\text{O}_7$ and $\text{Ca}_3\text{Mn}_2\text{O}_7$ is referred to as ‘rumpling’. This distortion transforms like the irrep $\Gamma_1^+$ (and is thus allowed in the $I4/mmm$ phase in addition to the $\text{Acam}$, $\text{Acaa}$ and $\text{A2}_1\text{am}$ phases) and consists of the B-site cations and $\text{O}^{2-}$ anions moving in opposite directions at the interface between the perovskite-like slab and the rock salt-like layer. Ghosez and co-workers\(^\text{197}\) tabulated rumpling amplitudes for a variety of RP phases, including $\text{Ca}_3\text{B}_2\text{O}_7$ (B: Mn, Ti, Sn, Zr), $\text{Sr}_2\text{B}_2\text{O}_7$ (B: Sn, Zr) and $\text{SrR}_2^{3+}\text{Fe}_2\text{O}_7$ ($\text{R}^{3+}$: Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm). Their work found that the rumpling mode competes with the $X_2^+$ rotation mode as the latter shortens bonds lengths between A-site cations and $\text{O}^{2-}$ anions. In the $\text{SrR}_2\text{Fe}_2\text{O}_7$ phases, the rotation mode is suppressed by the rumpling and a decreasing value of the Goldschmidt tolerance factor indicates a greater degree of rumpling, while in $\text{Ca}_3\text{B}_2\text{O}_7$ and $\text{Sr}_3\text{B}_2\text{O}_7$ phases the rotation mode is retained and there is no significant correlation with tolerance factor.
Chapter 4. Pressure-Dependent Phase Transitions in Hybrid Improper Ferroelectric Ruddlesden-Popper Oxides

Figure 4.11(d) shows the degree of rumpling in the calculated I4/mmm, Acaa, A21 am and Acam phases of Ca3Ti2O7. In this context, ‘degree of rumpling’ refers to a metric relating the z-coordinate difference arising from the rumpling with the amplitude of the modes and allows comparison between different symmetries of Ca3Ti2O7. The derivation of the method is shown in Appendix 2. At zero pressure, the rumpling is greatest in the I4/mmm phase and increasing pressure favours an increase in the rumpling. The X2+ rotation-only Acam phase behaves similarly, demonstrating the weak competition between the tilt mode and rumpling. In contrast, the X1− out-of-phase rotation mode in the Acaa structure and the X2+ in-phase rotation mode in the A21 am structure both increase with pressure and, as a result, the rumpling mode is suppressed. A rationalisation for this suppression has been proposed by Ablitt et al., referred to as the ‘corkscrew mechanism’ (Figure 4.14). By assuming that the four shortest A-O bonds are rigid (in a similar way as intra-octahedral B-O bonds are treated in a rigid unit model) and that all other A-O interactions are weak, the action of a rotation mode on the oxide octahedra results in pushing the A-site cation into a plane with the axial O2− anions, decreasing the rumpling. This mechanism has also been used to explain how compressive lattice strain in the Ca2+ plane can effectively couple via the octahedral rotation to expansion in the c lattice parameter, and hence explain why this phase exhibits pronounced uniaxial negative thermal expansion.

![Graph showing individual atomic displacements resulting from a Γ5− mode for a theoretical Ca3Ti2O7 phase with F2mm symmetry and no octahedral rotation or tilt modes.](image)

*Figure 4.13 Individual atomic displacements resulting from a Γ5− mode for a theoretical Ca3Ti2O7 phase with F2mm symmetry and no octahedral rotation or tilt modes.*
Chapter 4. Pressure-Dependent Phase Transitions in Hybrid Improper Ferroelectric Ruddlesden-Popper Oxides

Compared to proper FE phases, relatively little work has been published on the high-pressure behaviours of improper FE phases\textsuperscript{30,40,200–204}, though with the recent description of the hybrid improper mechanism there appears to be more interest. Very recent \textit{ab initio} calculations by Ramkumar and Nowadnick\textsuperscript{205} investigated the effect of pressures up to 20 GPa on Ca\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7}, Sr\textsubscript{3}Zr\textsubscript{2}O\textsubscript{7} and Sr\textsubscript{3}Sn\textsubscript{2}O\textsubscript{7}. At 0 GPa, all three phases adopt the same HIF ground state with $A2_1 am$ symmetry, but upon compression display different properties. The results for Ca\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7} are qualitatively very similar to the results presented here, with a very small decrease in the $X_3^-$ and $\Gamma_5^-$ mode amplitudes and a small increase in the $X_2^+$ mode amplitude with increasing pressure. In Sr\textsubscript{3}Zr\textsubscript{2}O\textsubscript{7}, the $X_3^-$ tilt mode and $X_2^+$ rotation mode amplitudes increase with pressure and the $\Gamma_5^-$ mode amplitude decreases. For Sr\textsubscript{3}Sn\textsubscript{2}O\textsubscript{7} all three of the $X_2^+$, $X_3^-$ and $\Gamma_5^-$ mode amplitudes decrease as the pressure increases up to 20 GPa. High-pressure synchrotron spectroscopy experiments on Sr\textsubscript{3}Sn\textsubscript{2}O\textsubscript{7} agree with the calculations\textsuperscript{206}, showing a series of phase transitions $A2_1 am \rightarrow Pnab \rightarrow Acaa \rightarrow I4/mmm$. The $Pnab$ phase contains a combination of the $X_3^-$ octahedral tilt and $X_1^+$ out-of-phase octahedral rotation modes, which induce a further distortion which transforms like the $M_5^+$ irrep and consists of displacements of the Sr\textsuperscript{2+} cations which cancel one another to produce non-polar behaviour.

The differences in the pressure responses of each phase were explained as being due to differing coupling between distortions and strain, with the $X_2^+$ and $X_3^-$ being stabilised by strains of opposing sign and the amount of strain being related to the tolerance factor and hence to the composition. The calculations were supported by a Landau expansion of the free energy. This picture of strain coupling is in agreement with the description of

\textit{Figure 4.14 Schematic representation of the corkscrew mechanism described by Ablitt et al.\textsuperscript{190,199}}
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competition with the $\Gamma_1^+$ rumpling mode described above. However, as the maximum pressure in the calculations was 20 GPa, Ramkumar and Nowadnick stop short of the observed first-order phase transition described in this work.

4.4 Conclusions

The effects of high hydrostatic pressure on the $n=2$ RP phases $\text{Ca}_3\text{Mn}_2\text{O}_7$ and $\text{Ca}_3\text{Ti}_2\text{O}_7$ have been investigated by a powder synchrotron X-ray diffraction experiment. In both structures, a phase transition is observed from HIF $A2_1\text{am}$ symmetry to the non-polar $A\text{ca}\text{a}$ symmetry, corresponding to a suppression of the $X_3^-$ out-of-phase octahedral tilting mode. There is a significant difference in the pressure at which the phase transition occurs: for $\text{Ca}_3\text{Mn}_2\text{O}_7$ the transition takes place at approximately 1-1.3 GPa and for $\text{Ca}_3\text{Ti}_2\text{O}_7$ it occurs between 30-38 GPa. Ab initio calculations on $\text{Ca}_3\text{Ti}_2\text{O}_7$ agree with the experimental observations and indicate that the $\Gamma_1^+$ rumpling mode is also partially suppressed by increasing pressure. The effect of increasing pressure on the energies of the $A2_1\text{am}$ and $A\text{ca}\text{a}$ phase is different to that expected for proper FEs. Instead of destabilising the polar phase and stabilising the non-polar phase, both phases become more stable with increasing pressure, but the non-polar phase is stabilised more rapidly. Strikingly, up to the phase transition pressure, the calculations predict that increasing pressure causes an enhancement of the polarisation. This property appears to have been overlooked in the literature to date. Provided that at least one of the OP amplitudes present in the trilinear coupling of a HIF is stabilised at high hydrostatic pressures, this trend is anticipated to appear in other phases.
Chapter 5. An *in situ* Experiment to Investigate Switching in a Hybrid Improper Ferroelectric Ruddlesden-Popper Oxide

5.1 Introduction

As discussed in Chapter 1, ferroelectric materials are those which display a spontaneous electric polarisation which is switchable through the application of an external electric field. This chapter is concerned with switching the FE polarisation in an \( n = 2 \) RP phase. As the structure and properties of these phases and the HIF mechanism have already been described in Chapter 4, they will only be briefly recapped here. The \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) and \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) RP compositions crystallise in the orthorhombic \( A2_1 \ am \) space group, which is related to the tetragonal \( I4/mmm \) space group by the simultaneous occurrence of two distortion modes — a rotation and a tilt of the \( \text{BO}_6 \) octahedra — which transform like the irreps \( X_2^+ \) and \( X_3^- \).

The \( A2_1 \ am \) structure has a basis = \{(-1,-1,0),(1,-1,0),(0,0,1)\} and origin shift = (-0.25, 0.25, 0.5) with respect to the \( I4/mmm \) structure. A polar distortion mode which transforms like the \( \Gamma_5^- \) irrep is induced as a secondary OP of the \( I4/mmm \)-to-\( A2_1 \ am \) phase transition, resulting in hybrid improper ferroelectricity. The Landau expansion of the free energy in these phases produces Equation 4.2 (recreated below), which demonstrates the trilinear coupling of the polar mode and the two octahedral distortion modes.

\[
F_{trt} = \gamma Q_{X_2^+} Q_{X_3^-} Q_{\Gamma_5^-}
\]

The essence of Equation 4.2 is that, in order to switch the sense of the polarisation, the sense of either the \( X_2^+ \) rotation mode or the \( X_3^- \) tilt mode must be switched. If both modes were to be switched, the polarisation would return to its initial state. On the scale of FE domains, switching mechanisms are highly dependent on the form of the FE phase (powder, single-crystal and thin-film forms may all behave differently under the same experimental conditions) and vary with defect structure, applied field frequency and the nature of the electrical probe\textsuperscript{207-211}, though recent work\textsuperscript{212} has proposed a general model to be applied to both thin films and bulk ceramics based on the motion of domain walls under an applied field. As this work is focused on studying a unit-cell-scale mechanistic understanding of switching in HIF RP compounds, the domain-scale mechanism will not be considered further.

The energy barrier to switching \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) and \( \text{Ca}_3\text{Mn}_2\text{O}_7 \) has been shown\textsuperscript{213} to be much greater than the barrier to switch proper FE materials such as \( \text{BaTiO}_3 \), and transmission
electron microscopy measurements by Gao et al.\textsuperscript{179} suggested that true switching is not achievable in Ca\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7} due to stacking of 90° domains along the [001] direction. However, switchable polarisation has been observed in Ca\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7}\textsuperscript{214,215}, and both enhancement of the polarisation magnitude and reduction of the energy barrier to switching has been shown to be possible in RP phases by chemical substitution\textsuperscript{215–218}, with a proposed mechanism being described loosely as strain coupling mediated by the tolerance factor\textsuperscript{219}. For the Sr-substituted phase Ca\textsubscript{2.15}Sr\textsubscript{0.85}Ti\textsubscript{2}O\textsubscript{7}, increasing Sr\textsuperscript{2+} content results in a decrease to the polarisation and a change in the nature of the high-temperature phase transition from first-order between \textit{A}\textsubscript{2}1\textit{a}m and \textit{A}c\textsubscript{2}a to second-order between \textit{A}\textsubscript{2}1\textit{a}m and \textit{P}4\textsubscript{2}2/mnm\textsuperscript{181}. The reduction in the polarisation magnitude is the reason for the choice of Ca\textsubscript{2.15}Sr\textsubscript{0.85}Ti\textsubscript{2}O\textsubscript{7} in this study in place of the non-substituted Ca\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7}; it was hoped that the smaller magnitudes of the octahedral distortion OPs would make the switching process more achievable using smaller applied fields.

Nowadnick and Fennie\textsuperscript{26,175} used \textit{ab initio} calculations to propose several possible pathways by which switching may occur in Ca\textsubscript{3}Ti\textsubscript{2}O\textsubscript{7}. They described the pathways using two two-dimensional distortion OPs with amplitude, \(Q\), and phase, \(\theta\), which describe the overall OP, \(\eta\), as follows:

\[
\eta^X_3 = Q X_3 e^{-i\theta} X_3^-
\]

\[
\eta^X_2 = Q X_2 e^{-i\theta} X_2^+
\]

Equivalently, the OPs may also be described with a direction, for which the symmetry-unique options are \((a, 0)\), \((a, a)\) and \((a, b)\), where \(Q = \sqrt{a^2 + b^2}\) and \(\theta = \tan^{-1}(b/a)\). The calculations performed by Nowadnick and Fennie are used as a framework for simulations later in this chapter and will be discussed in more detail in later sections. This chapter presents the results of the first \textit{in situ} synchrotron X-ray diffraction experiment to attempt to elucidate the pathway by which FE switching occurs in Ca\textsubscript{2.15}Sr\textsubscript{0.85}Ti\textsubscript{2}O\textsubscript{7}.

### 5.2 Experimental

#### 5.2.1 Sample Preparation

Samples of Ca\textsubscript{2.15}Sr\textsubscript{0.85}Ti\textsubscript{2}O\textsubscript{7} were prepared via standard solid-state methods. CaCO\textsubscript{3}, SrCO\textsubscript{3} and TiO\textsubscript{2} were ground in stoichiometric proportions in an agate mortar before being pressed into 13 mm-diameter disc-shaped pellets around 1 mm in thickness and heated to 900 °C for 20 hours. The pellets were then reground, re-pressed and heated to 1200 °C for a total of 72 hours with several additional intermediate regrindings. Sample purity was confirmed by powder X-ray diffraction at I11 at Diamond Light Source (\(\lambda = 0.82454(1)\) Å
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refined using a Si standard). An example of the refined lattice parameters of the samples is $a = 5.4605(3)$ Å, $b = 5.4828(3)$ Å and $c = 19.7340(16)$ Å. The sintered pellets were cut into wafers around 2 mm long, 1.5 mm wide and 1 mm thick with a diamond-edged saw before being coated on both of the largest faces with conductive silver paste. Care was taken to avoid coating the narrow faces with silver paste to avoid conduction across the surface of the wafers.

### 5.2.2 Apparatus

The *in situ* experiment was performed at Beamline ID15A at the ESRF using a Pilatus3X CdTe 2M detector. The beam energy was 71.5 keV, equivalent to an X-ray wavelength of 0.17341(1) Å (refined against a CeO$_2$ standard). The prepared sample wafers were placed into a specialised experimental cell developed by Critus Pty. Ltd. The key components of the cell were a silicone oil bath into which the sample was placed to mitigate any effect of heating due to the X-ray beam. The oil bath was fixed atop a conductive plate connected to an oscilloscope which was programmed to control the applied electric field. Placing a sample wafer into the oil bath allowed the circuit to be closed, with the upper electrode holding the sample in place. A schematic diagram of the sample cell is shown in Figure 5.1, and Figure 5.2 shows the placement of the cell on the beamline.

![Schematic diagram of sample cell](image)

*Figure 5.1 Schematic representation of sample cell; inset: photograph of sample cell.*
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![Photograph of experimental cell placed on Beamline ID15A with key components highlighted.](image)

Figure 5.2 Photograph of experimental cell placed on Beamline ID15A with key components highlighted.

The cell was mounted on the beamline using a mobile table, which allowed pristine parts of each wafer to be exposed to the beam for different experiments, thus sampling a wide variety of crystallite grains from within the wafer. A voltage was then applied across the sample wafers which followed a triangular waveform between 0 kV and 4 kV. This voltage was cycled ten times per experiment for a total of 20, 40 or 80 seconds (0.5, 0.25 and 0.125 Hz, respectively). Simultaneous to the initiation of the applied field, the beamline shutter was opened and detector acquisition was triggered. For twelve of the sixteen experimental runs, one hundred diffraction patterns were recorded across each set of voltage cycles. For the remaining four runs, three hundred diffraction patterns were recorded, providing greater time resolution of reflection intensities at the expense of overall intensity. The output of the *in situ* experiment comprised datasets collected using six different Ca$_{2.15}$Sr$_{0.85}$Ti$_2$O$_7$ wafers. Several these samples were collected to calibrate the parameters of experiment, identifying variables such as the maximum field which could be applied before the sample underwent dielectric breakdown, sample positioning within the beam and appropriate scan lengths. Diffraction patterns were first radially integrated using Fit2d$^*$ and powder X-ray diffraction refinements were performed using TOPAS Academic v6$^{143}$. In

$^*$https://www.esrf.fr/computing/scientific/FIT2D/, accessed April 2018
order to expedite the refinements, a batch script was written using Python 2.7.12. All of the data and figures displayed in this chapter are taken from a specific experimental run and a single wafer sample.

### 5.3 Data Analysis

#### 5.3.1 Initial Rietveld Refinement

In order to begin analysing the large volume of output data from the *in situ* experiment, an initial Rietveld refinement was performed on the I11 *ex situ* data, both to identify sample purity and to act as a basis for a seed file for a Python script which would automate the process of running Pawley refinements. The result of the Rietveld refinement is shown in Figure 5.3. A small (0.5%) impurity phase was identified as CaO, but this was deemed to be sufficiently low for the sample to be suitable for the *in situ* experiment.

![Rietveld refinement](image)

*Figure 5.3 Rietveld refinement for I11 powder X-ray diffraction data for Ca$_{2.15}$Sr$_{0.85}$Ti$_2$O$_7$ ($\lambda = 0.82454(1)$ Å). Blue ticks indicate reflections for the desired phase, green ticks indicate reflections for a small (~0.5%) CaO impurity.*

#### 5.3.2 Pawley Refinements

The lattice parameters calculated in the Rietveld refinement were used to produce a Pawley refinement for the *in situ* ID15A data, shown in Figure 5.4. It is clear that some combination of preferred orientation and texturing significantly affect the peak intensities compared to the powder diffraction pattern in Figure 5.3. Artifacts arising due to the conductive silver paste also affect the diffraction pattern. Despite significant efforts, it was not possible to fully resolve these discrepancies with a preferred orientation model using Rietveld refinements and Figure 5.4 shows the fit that was achieved using Pawley refinements. The Pawley refinement was used along with a script written in Python to refine the large batches of data collected during each run.
Figure 5.4 Example Pawley refinement of Ca$_{2.15}$Sr$_{0.85}$Ti$_2$O$_7$ wafer X-ray diffraction pattern measured at ID15A (0.17341(1) Å) with several superstructure peaks indicated by green stars in insets. Blue ticks indicate reflections for the desired phase, green ticks indicate reflections for a small (~0.5%) CaO impurity.

The intensities of a total of 349 reflections were tabulated in the Pawley refinement. In order to reduce the volume of data to be analysed, only the peaks arising in the $A2_1$$_{am}$ supercell that are forbidden in the $I4/mmm$ aristotype were considered: additional superstructure reflections arise with Miller indices $h + k \neq 2n$; that is, the sum of the $h$ and $k$ values is an odd number. Since these reflections only arise for the octahedral rotation and tilt that couple to the polar distortion, they are intrinsically related to the switching pathway; by monitoring the evolution of their intensities we may identify structural behaviours to help elucidate the switching process.

### 5.3.3 Time-Resolved Intensity Plots

As synchrotron X-ray intensities are extremely high, it is possible to record diffraction patterns with an equal or greater number of measured counts as a laboratory diffractometer may measure in several hours in only a fraction of a second. By taking advantage of this property, diffraction patterns were recorded frequently enough that the intensities of each reflection (extracted from the Pawley refinements) can be plotted as a function of time and hence the applied electric field. Two examples of such a plot are shown in Figure 5.5 for the (5 2 4) and (2 1 3) reflections (all indexation is with respect to the $A2_1$$_{am}$ supercell). The measured intensities are marked with green crosses and the percentage change in the
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Intensity from the value at the start of the voltage cycle is marked with a blue line. The applied electric field that was varied from 0 to 4 kV is indicated with a black dashed line. It can be seen that the intensity of both of the reflections varies in accordance with the applied field. However, true switching is likely not achieved as the intensity modulations are very small, on the order of only a few percent.

Superstructure reflections are not the only peaks which exhibit a response to the applied field. For completeness, the time-resolved intensity of a non-superstructure reflection, (3 1 13), is shown in Figure 5.6. Also depicted is the Fourier amplitude of the reflection (an explanation of this metric can be found in Section 5.3.4. The reflection shows a strong response to the applied field. However, since it does not obey the reflection condition for superstructure peaks, it is not considered further. To demonstrate the appearance of reflections which do not show a strong response to the applied field, the time-resolved and frequency-resolved responses of the (1 2 2) and (0 0 8) reflections are shown in Figure 5.7. Since the responses to the applied electric field are not identical across all reflections, the changes observed in the superstructure reflections are likely to be intrinsic to the switching process in nature.
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Figure 5.5 Time-resolved intensities of (5 2 4) and (2 1 3) reflections; green crosses indicate individual intensities extracted from Pawley refinements, blue line indicates percentage change from initial intensity and black dashed line indicates waveform of applied voltage.

Figure 5.6 Time-resolved intensity and Fourier amplitude of non-superstructure (3 1 13) reflection
In order to quantify and compare the responses of different reflections to the applied field, several methods to normalise the results were scrutinised. The first of these was to simply examine the intensity shifts of each reflection. However, the very small values of intensity and the differences in their variation between reflections (and between runs) rendered this impractical. The next option was comparison of root-mean-squared average intensity shifts. However, while the oscillations for many reflections had little variation in their intensity minima and maxima, many others exhibited a slow increase or decrease in their intensity as a run progressed, which could be the result of ring current decay at the synchrotron. For an example of this, see the experimental results for the (3 2 6) and (4 1 5) reflections in Figure 5.9; a tendency for the baseline intensity to increase over time is evident, and results in the root-mean-squared intensity shifts also being incomparable between reflections. Eventually, a method was devised which converts the time-resolved data into the frequency domain using a Fourier transform. This bypasses the issues caused by intensity shifts and
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means that the response of a given reflection to the field is dependent only on the frequency of the intensity oscillations.

5.3.4 Fourier Transform of Time-Resolved Data

To perform the Fourier transform the data were first normalised according to:

\[
I_{i,\text{norm}} = \frac{I_i - \bar{I}}{\sigma_i}
\]

where \(I_i\) is the intensity associated with a given reflection \(i\) at a specific point in time (and therefore at a specific applied voltage), \(\bar{I}\) is the average intensity across the entire experimental run, and \(\sigma_i\) is the standard deviation of the reflection intensity across the experimental run. The reason for performing the normalisation prior to the Fourier transform is due to the variation in the intensities of different reflections; by standardising the data by the relationship between the mean and the standard deviation, all the Fourier amplitudes will fall within a fixed range of values, making comparisons between different reflections and different runs possible. The same normalisation and Fourier transform was then performed for the waveform of the applied electric field. Examples of the Fourier-transformed intensities of the (524) and (213) are shown in Figure 5.8. The y-axis of each plot is the transformed intensity and will be referred to as the Fourier amplitude of the reflection, and the x-axis is the frequency in units of hertz. A single main peak is visible at the frequency of the applied voltage with some small lower-frequency harmonics also visible; these harmonics are believed to arise due to subtle evolutions of the synchrotron X-ray beam characteristics associated with beam current decay. The dotted line in the transformed plots is the Fourier transform of the normalised voltage. When the peak of the Fourier amplitude of the reflection is close to the peak of the transformed voltage, the oscillation in the time domain of the intensity matches closely with the oscillation of the applied voltage and the reflection is selected for further investigation. Reflections with a poor agreement between the time-resolved intensity and the applied voltage have a lower Fourier amplitude. The degree to which these quantities match is quantified using the following equation:

\[
\text{Relative Fourier amplitude} = \frac{\text{Fourier amplitude}(hkl)}{\text{Fourier amplitude}(\text{field})}
\]

The value of the relative Fourier amplitude of each reflection allows each reflection to be ranked both within a dataset and across different experimental runs.
Performing a normalisation and Fourier transform on peaks which satisfy the superstructure reflection condition and ranking the results by their relative Fourier amplitude generates a shortlist of reflections which most consistently display intensity variations aligned with frequency of the applied voltage. By considering only those superstructure reflections which appear consistently in the top ten rankings across all datasets, this shortlist is further reduced to six reflections: (1 2 4), (2 1 3), (3 2 6), (3 4 0), (4 1 5) and (5 2 4). This shortlist is contained in Table 5.1, which also includes details on the 2\(\theta\) values, initial intensities, maximum percentage change in the intensity over a run, Fourier amplitude and a calculated value referred to as \(\cos \phi\), which will be described in detail in Section 5.4.3.

The time-resolved and frequency-resolved results for the remaining reflections not shown in Figure 5.5 are shown in Figure 5.9. On initial inspection, the (3 2 6) and (4 1 5) reflections may initially appear to be poorly related to the frequency of the applied voltage; this is due to the figures presented in this chapter all being drawn from a single experimental run. In other runs these reflections consistently displayed a closer relationship with the voltage. With a shortlist of superstructure reflections identified as consistently displaying a response to the applied field generated, the relationship between the responses and the mechanism must be investigated.

Figure 5.8 Results of normalised Fourier transform applied to (5 2 4) and (2 1 3) reflections; red line indicates the Fourier amplitude of the reflection and the dashed black line indicates the normalised Fourier transform of the applied field.
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Table 5.1 Shortlist of superstructure reflections used for comparisons with simulations, 2θ values, initial intensities (I₀), maximum percentage change in intensities (ΔI), relative Fourier amplitudes and the calculated values of cos φ from Ewald sphere calculations (See Section 5.4.3). 2θ and I values are extracted from a single run of the experiment and are representative of values from different runs in the experiment.

<table>
<thead>
<tr>
<th>hkl</th>
<th>2θ (°)</th>
<th>I₀ (× 10⁻³)</th>
<th>ΔI (%)</th>
<th>Fourier amplitude</th>
<th>cos φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 2 4)</td>
<td>4.53</td>
<td>23.8</td>
<td>0.67</td>
<td>0.90</td>
<td>0.44</td>
</tr>
<tr>
<td>(2 1 3)</td>
<td>4.34</td>
<td>19.8</td>
<td>0.57</td>
<td>0.73</td>
<td>0.86</td>
</tr>
<tr>
<td>(3 2 6)</td>
<td>7.22</td>
<td>8.14</td>
<td>2.40</td>
<td>0.69</td>
<td>0.80</td>
</tr>
<tr>
<td>(3 4 0)</td>
<td>9.09</td>
<td>7.91</td>
<td>4.18</td>
<td>0.89</td>
<td>0.66</td>
</tr>
<tr>
<td>(4 1 5)</td>
<td>7.92</td>
<td>14.2</td>
<td>1.72</td>
<td>0.57</td>
<td>0.94</td>
</tr>
<tr>
<td>(5 2 4)</td>
<td>10.02</td>
<td>9.29</td>
<td>10.8</td>
<td>0.86</td>
<td>0.94</td>
</tr>
</tbody>
</table>
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Figure 5.9 Experimental results and Fourier amplitude plots for remaining shortlisted superstructure reflections (1 2 4), (3 2 6), (3 4 0) and (4 1 5).
5.4 Simulations

5.4.1 Description of Switching Pathways

To begin to understand the switching mechanism or mechanisms in action in Ca$_{2.15}$Sr$_{0.85}$Ti$_2$O$_7$, the starting point is to examine all possible pathways from a theoretical perspective. For the sake of simplicity, only the three switching pathways proposed by Nowadnick and Fennie$^{26}$ for Ca$_3$Ti$_2$O$_7$ will be examined here: a one-step pathway, a two-step pathway proceeding via an antipolar intermediate and another two-step pathway proceeding via an orthorhombic twin intermediate. Each of the switching pathways involves the complete reversal of either of the $X_2^+$ and $X_3^-$ OPs, leading to a total of six possibilities (three pathways multiplied by two distortions). On closer examination, the two-step mechanism proceeding via an orthorhombic twin structure is independent of the choice of OP. Both of these possible routes are investigated here due to the known differences in the temperature-induced phase transition behaviours of Ca$_3$Ti$_2$O$_7$ and Ca$_{2.15}$Sr$_{0.85}$Ti$_2$O$_7$.

Table 5.2 shows a summary of the switching pathways proposed by Nowadnick and Fennie, illustrating how the choice of the reversed OP for the $X_2^+$ or $X_3^-$ irrep affects the symmetries of intermediate structures. The ‘space group at energy barrier’ column describes the symmetry of the structure at the halfway point in a one-step pathway (and is therefore equivalent to the intermediate in these cases) and at one-quarter and three-quarters of complete switching in a two-step pathway. The intermediate space group is the symmetry of the structure at the halfway point of complete switching. In the one-step pathway, the OP is reversed by simply reducing in amplitude from some value ($Q$) through an amplitude of zero to the initial amplitude but with opposite sign ($-Q$). The phase of the OP remains constant through the switching pathway. Where the amplitude of the OP is zero, the polarisation is also zero due to the trilinear coupling of the OPs with the polarisation.

The two-step pathways are slightly more complex: in the antipolar pathway one of the OPs reverses by rotating in OP space (i.e. changing its phase, $\theta$, by $\pi$) while its amplitude remains finite. The polarisation never fully vanishes as the amplitudes of both the reversing and non-reversing OPs are always greater than zero. In the orthorhombic twin pathway, both OPs begin to rotate in OP space, but when the phase reaches $\pi/2$, only one OP continues to change phase while the other reverts back to its initial value. Once again, the polarisation never vanishes throughout the switching process as the amplitudes of both OPs remain non-zero. The inclusion of $\theta$ means that the two-step switching pathways may be considered using a pair of neighbouring perovskite-like slabs stacked along the $c$ direction, where the choice of direction of the OP determines the symmetry of the structure. For example, in the
antipolar pathway, the combination \( \{ \eta^{X_3} = (a, 0), \eta^{X_2} = (0, b) \} \) (i.e. both distortions in different directions with different magnitudes) reverses the rotation mode and produces an intermediate structure with the \( Pnam \) space group, in which the sense of the in-phase rotation mode in one of a pair of neighbouring perovskite-like slabs has been reversed. By contrast, the combination \( \{ \eta^{X_2} = (0, a), \eta^{X_2} = (b, 0) \} \) (swapping the directions of the distortions but maintaining the magnitudes) and produces a \( Pbnm \) structure with the tilt direction rotated and the in-phase rotation mode unchanged. According to the calculations by Nowadnick and Fennie, these routes have the lowest calculated energy barriers, with the pathway reversing the octahedral rotation mode having a slightly lower energy barrier (Table 5.2).

Table 5.2 Summary of one- and two-step switching pathways proposed by Nowadnick and Fennie\(^{26}\).

<table>
<thead>
<tr>
<th>Switching pathway</th>
<th>OP reversed</th>
<th>Space group at energy barrier</th>
<th>Intermediate space group</th>
<th>Calculated energy barrier (meV per Ti(^{4+}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-step</td>
<td>( X^+_2 )</td>
<td>( Amam )</td>
<td>N/A</td>
<td>56</td>
</tr>
<tr>
<td>One-step</td>
<td>( X^-_3 )</td>
<td>( Acam )</td>
<td>N/A</td>
<td>90</td>
</tr>
<tr>
<td>Two-step via antipolar structure</td>
<td>( X^+_2 )</td>
<td>( P2_{1}am )</td>
<td>( Pnam )</td>
<td>32</td>
</tr>
<tr>
<td>Two-step via antipolar structure</td>
<td>( X^-_3 )</td>
<td>( P2_{1}nm )</td>
<td>( Pbnm )</td>
<td>35</td>
</tr>
<tr>
<td>Two-step via orthorhombic twin structure</td>
<td>( X^+_2 )</td>
<td>( C2mm )</td>
<td>( Bb2_{1}m )</td>
<td>41</td>
</tr>
<tr>
<td>Two-step via orthorhombic twin structure</td>
<td>( X^-_3 )</td>
<td>( C2mm )</td>
<td>( Bb2_{1}m )</td>
<td>41</td>
</tr>
</tbody>
</table>

With an overall understanding of several possible switching pathways, the next step is to simulate the effect of these pathways on the observed intensities of the superstructure peaks and compare with the experimental results.

5.4.2 Simulation Procedure

The simulations of the different switching pathways were performed using ISODISTORT\(^{24,25}\). First, a .cif for \( \text{Ca}_{2.15}\text{Sr}_{0.85}\text{Ti}_2\text{O}_7 \) (produced using the initial Rietveld
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refinement described in Section 5.3.1) in the $A2_1am$ space group was edited to remove the partial A-site occupancy. This step was required as ISODISTORT would otherwise produce multiple copies of the modes at each site which were not constrained together by symmetry. The structure was then converted into the $Pm$ space group with basis = $\{(-1,0,0),(0,0,1),(0,1,0)\}$ and origin = $(0,0,0)$ with respect to the input structure. This was chosen as it spans the lowest-symmetry OP direction associated with the $X_2^+$ and $X_3^-$ OPs. A .cif of the related Sr$_3$Ti$_2$O$_7$ — which exists in the $I4/mmm$ space group — was used as a new input for ISODISTORT to decompose the $A2_1am$ structure into a collection of OPs related to the $I4/mmm$ aristotype. These include the rotation and tilt OPs ($X_2^+$ and $X_3^-$), the polar mode ($\Gamma_5^+$) and the degrees of freedom available to the high-symmetry structure ($\Gamma_1^+$), as well as several other degrees of freedom with zero amplitude ($\Gamma_2^+, M_1^+, M_2^+, M_3^-, X_4^+$ and $X_4^-$). By choosing amplitudes and directions for the $X_2^+$ and $X_3^-$ OPs, isotropy subgroups of a variety of symmetries could be generated. For example when the $X_2^+$ and $X_3^-$ OP directions are $\{\eta^{X_2} = (a,0), \eta^{X_3} = (b,0)\}$, the resultant space group is $A2_1am$ with basis = $\{(0,0,1),(-1,0,1),(-1,0,0)\}$ and origin shift = $(0.25, 0.25, -0.5)$. When both OPs are along general directions $\{\eta^{X_2} = (a,b), \eta^{X_3} = (c,d)\}$, the space group is $Pm$ (basis = $\{(1,1,0),(-1,1,0),(0,0,1)\}$ and origin shift = $(0,0,0)$), as described above.

With the reduced-symmetry model prepared, symmetry-adapted simulations were performed using TOPAS Academic v6, manually varying the amplitudes and directions of the $X_2^+$ and $X_3^-$ OPs to model a complete switching process within the Ca$_{2.15}$Sr$_{0.85}$Ti$_2$O$_7$ structure. The intensities of the assorted reflections were then calculated according to a Rietveld model of the structure. The initial results of this simulation process for the $(5\ 2\ 4)$ and $(2\ 1\ 3)$ reflections are shown in Figure 5.10. The y-axis shows the modulus of the percentage change in intensity and the x-axis shows a quantity referred to as the ‘switching coordinate’, calculated as a fraction of the degree to which the amplitude or phase has varied. For example, for the one-step mechanisms the switching coordinate represents the progress towards reversing the amplitude of the OP; at a switching coordinate of 0.5 the amplitude of the reversing OP is zero. For the two-step mechanisms, the switching coordinate represents the degree to which the phase of the OP (or OPs) has shifted; a switching coordinate of 0.5 represents a phase shift of $\pi / 2$.

The mechanisms with the greatest calculated impact on the intensity of the $(5\ 2\ 4)$ reflection include the one-step and antipolar mechanisms acting on the $X_2^+$ rotation mode as well as both of the mechanisms proceeding via an orthorhombic twin structure, while the one-step and antipolar mechanisms acting on the $X_3^-$ tilt mode cause the intensity to change by less than 20% at a switching coordinate of 0.5. In contrast, the one-step and antipolar tilt
mechanisms and orthorhombic twin mechanisms result in the greatest change to the (2 1 3) reflection, while the other switching pathways have little to no effect.

Figure 5.10 Simulated effects of switching mechanisms on the intensities of the (5 2 4) and (2 1 3) reflections; 1S stands for one-step mechanism, AP for mechanism via antipolar structure and OT for mechanism via an orthorhombic twin structure.

The results of the simulations for the remaining shortlisted superstructure reflections are shown in Figure 5.11. The amount to which each intensity varies in intensity is different for each mechanism and each reflection, and it can be seen that the simulated intensity changes for each reflection for most mechanisms far exceeds the observed intensity changes from the experimental data (see Figure 5.5). A simple conclusion to draw from this is that complete ferroelectric switching is not observed in the experiment; instead, a subtle perturbation of the structure is achieved which may be used to infer how switching may proceed by indicating the softest pathway through which the structure is deformed under the application of an electric field.

Since it is clear that not all reflections will be simultaneously able to fulfil the reflection conditions of the experiment while having their polar axes aligned with the applied electric field, the next step is to consider the geometric constraints of the experiment.
Chapter 5. An in situ Experiment to Investigate Switching in a Hybrid Improper Ferroelectric Ruddlesden-Popper Oxide

Figure 5.11 Simulated effects of switching mechanisms on the intensities of the (1 2 4), (3 2 6), (3 4 0) and (4 1 5) reflections; 1S stands for one-step mechanism, AP for mechanism via antipolar structure and OT for mechanism via an orthorhombic twin structure.

5.4.3 Geometric Constraints

The polar axis of the $A2_{1}am$ space group is parallel to the crystallographic $a$ direction. Each wafer sample of Ca$_{2.15}$Sr$_{0.85}$Ti$_{2}$O$_{7}$ was composed of a compressed, sintered powder, which could otherwise be considered a collection of randomly-oriented crystallite grains. The law of powder averaging results in only one-third of the available FE domains having their polar axis aligned with directions which are favourable for interaction with the applied electric field. Of this reduced set of reflections, only one-half of the domains will be anti-aligned favourably with the applied field such that they will exhibit any form of signal associated with a switching process.

Due to the high field required to achieve full switching in the samples and their tendency to undergo dielectric breakdown when excessive voltage was applied, it was not possible to
pre-treat the samples with a negative field in order to improve the switching response (as would be performed in a PUND-type ferroelectric measurement experiment\textsuperscript{220}). Hence, the observed intensity for each reflection is reduced to a maximum of one-sixth of the intensity which would be expected if all grains were properly aligned. The resultant component of the electric field experienced by a grain along its polar $a$ axis for a given reflection condition may be estimated by considering a modified Ewald sphere construction.

\textbf{5.4.3.1 Modified Ewald Construction}

In the standard usage of the Ewald construction, the Ewald sphere is held motionless as the crystal (and hence the reciprocal lattice) is rotated about the (0 0 0) point. By using appropriate values for the wavelength of the incident beam and the $d$-spacing in the lattice, the planes which satisfy the Bragg condition and the relevant angles are identified according to their intersection with the surface of the sphere. Only those reflections which lie within a sphere of radius $2/\lambda$ (where $\lambda$ is the X-ray wavelength) centred on the (0 0 0) point (known as the limiting sphere), are able to intersect the reflection sphere and are thus observable. The key modification used here is that, instead of rotating the reciprocal lattice, the Ewald sphere is rotated about a line tangent which is parallel to the polar $a^*$ reciprocal space direction. This produces a horn torus (i.e. a ring with an infinitesimally small inner diameter) with a tube radius $r_T = 1/\lambda$. The torus is centred on the (0 0 0) reciprocal lattice point and describes the limiting reflection conditions with the constraint that the polar axis must align with the applied field. Figure 5.12 shows the Ewald torus for the switching experiment with $\lambda = 0.17341$ Å. Within the torus, several of the shortlisted superstructure reflections are marked with blue circles.

Since a vanishingly small number of reflections will precisely fulfil the requirement that the polar axis aligns with the applied field, the misalignment of each reflection with the applied field must be quantified. Rather than attempting to tilt the torus, however, it is conceptually and geometrically simpler to now consider a fixed torus and tilt the reciprocal lattice about the origin (similar to the more traditional application of the Ewald construction).

For a given reflection, the associated reciprocal lattice point generates its own sphere with radius $r_s = \sqrt{(ha^*)^2 + (kb^*)^2 + (lc^*)^2}$, where $h, k, l$ are the Miller indices and $a^*, b^*$ and $c^*$ are the reciprocal lattice parameters of the reflection. It is then the angle between the intersection point of the torus and sphere and the initial position of the reciprocal lattice point that permits calculation of the resultant electric field on the polar axis of a given grain (by multiplication of the cosine of this tilt angle by the applied field). An example of the sphere carved out by the (3 4 0) reciprocal lattice point is shown in Figure 5.12, where the lattice point is marked in yellow and other points from the shortlist are marked in blue.
Figure 5.12 Modified Ewald construction showing the torus generated by rotation of the Ewald sphere, the (3 4 0) reciprocal lattice point and its associated tilt sphere (yellow point, green wireframe) in addition to the (1 2 4), (2 1 3), (3 2 6) (4 1 5) and (5 2 4) reciprocal lattice points (blue points).

In a similar way as with the standard Ewald construction, it is conceptually rather simpler to visualise a lower-dimensional representation of the sphere. As such, a 2-dimensional projection of the torus construction was used to derive the required angles in the 3-dimensional construction.

5.4.3.2 2-Dimensional Projection

Figure 5.13(a) shows a 2-dimensional projection of the modified Ewald construction, viewed such that the $a^*$ direction is the vertical axis and the circles projected by the Ewald torus and reflection sphere are perpendicular to the viewer (half of the torus is omitted for clarity). By drawing lines from the origin of the Ewald circle (a slice from one half of the Ewald torus described in section 5.4.3.1 with radius $r_T$) to the intersection of the Ewald circle with the reciprocal lattice circle (with radius $r_S$), a kite figure is described: this kite is isolated in Figure 5.13(b). The kite has sides of length $r_S$ and $r_T$ and contains internal angles $\phi_1$, $\phi_2$ and $\phi_3$. By bisecting this kite along its axis of symmetry, a triangle is generated (Figure 5.13(c)) which permits the calculation of the internal angles.
According to the law of cosines, each of the angles may be calculated according to:

\[
\phi_1 = 2 \cos^{-1} \left( \frac{2r_T^2 - r_S^2}{2r_T^2} \right) \tag{5.5}
\]

\[
\phi_2 = \cos^{-1} \left( \frac{r_S^2}{2r_T^2} \right) \tag{5.6}
\]

\[
\phi_3 = 2 \cos^{-1} \left( \frac{r_S^2}{2r_T r_T} \right) \tag{5.7}
\]
Converting this back to the 3-dimensional reciprocal space construction with a coordinate system \( x_{hkl} = ha^\ast \), \( y_{hkl} = kb^\ast \), \( z_{hkl} = lc^\ast \), the intersection coordinates for the Ewald circle and reciprocal lattice point circle are calculated according to:

\[
x_{\text{intersect}} = r \cos \left( \frac{\phi}{2} \right)
\]

\[
y_{\text{intersect}} = r \sin \left( \frac{\phi}{2} \right)
\]

The \( \phi \) angle reported in Table 5.1 (Section 5.3) is therefore the angle between the vector from the reciprocal space origin point to any given reflection’s reciprocal space point and the vector from the origin to the nearest intersection of the Ewald torus with the reflection sphere, as illustrated in Figure 5.14.

Figure 5.14 2-dimensional representation of the intersection between the sphere described by tilting the \((3 \, 4 \, 0)\) reciprocal lattice point and the Ewald torus. The initial position of the reciprocal lattice point (filled orange circle), intersection position (hollow orange circle) and \( \phi \) angle are highlighted.

Small values of \( \phi \) indicate that, for a given reciprocal lattice point to be brought into the diffraction condition, a relatively small misalignment of the \( a^\ast \) polar axis with the external electric field will occur. Such grains in the powder diffraction experiment will experience distortions that represent the bulk of the applied electric field. For reflections with \( \phi \) values approaching \( \pi/2 \) the experimental geometry renders diminishing sensitivity. It follows from this analysis that the experiment is most sensitive to those reflections with large \( h \) and small \( k \) and \( l \) values.
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5.5 Discussion

It is now possible to apply the correction factors to the simulated intensity shift calculations. The first correction factor to account for is the maximum achievable switching coordinate being $1/6$ of complete switching due to the powder averaging. This maximum is then multiplied by the cosine of $\phi$ to yield a maximum switching coordinate observable for each reflection:

$$\text{Maximum Switching Coordinate} = \frac{\cos \phi}{6}$$

These maximum switching coordinates are summarised in Table 5.3.

Table 5.3 Calculated maximum switching coordinates for shortlisted reflections.

<table>
<thead>
<tr>
<th>$hkl$</th>
<th>Maximum switching coordinate ($\frac{\cos \phi}{6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 2 4)</td>
<td>0.073</td>
</tr>
<tr>
<td>(2 1 3)</td>
<td>0.143</td>
</tr>
<tr>
<td>(3 2 6)</td>
<td>0.133</td>
</tr>
<tr>
<td>(3 4 0)</td>
<td>0.110</td>
</tr>
<tr>
<td>(4 1 5)</td>
<td>0.156</td>
</tr>
<tr>
<td>(5 2 4)</td>
<td>0.156</td>
</tr>
</tbody>
</table>

Figure 5.15 shows the simulated intensity changes for the (5 2 4) and (2 1 3) reflections with the x-axis limited to the maximum switching coordinate calculated using the correction factors. The calculated intensity shifts within these limits are much closer to the experimental results. For the (5 2 4) reflection, the one-step $X^+_2$ mechanism shows the greatest change in intensity across the smallest switching coordinate, reaching a $\Delta I$ value of 10% (the maximum intensity shift observed in the experimental data) at a switching coordinate of 0.04. The orthorhombic twin mechanisms and the antipolar $X^+_2$ mechanism are the next-closest, with switching coordinates of approximately 0.08. The remaining one-step $X^-_3$ and antipolar $X^-_3$ mechanisms do not reach the same maximum inside the predicted switching coordinate upper limit of 0.156, reaching only around 7% across this range. Recalling the 10% maximum intensity shift for the (5 2 4) reflection (Table 5.1), the latter pair of mechanisms described above may be discarded as plausible options. Of the remaining mechanisms, the most plausible option is that which reaches the experimental intensity shift with the smallest amount of distortion (and therefore smallest switching
Chapter 5. An *in situ* Experiment to Investigate Switching in a Hybrid Improper Ferroelectric Ruddlesden-Popper Oxide coordinate, leaving the one-step $X^+_2$ mechanism as the most plausible option for this reflection.

Also noted on Figure 5.15 and the other corrected simulated intensity plots is an estimate of the switching coordinate achieved in the experiment, marked with a black vertical line. This value was estimated by comparing the simulated results with the experimental data and is fixed at 20% of the maximum switching coordinate calculated for each reflection. For the (5 2 4) reflection, this value is approximately 0.03.

![Figure 5.15 Corrected simulated intensity changes for the (5 2 4) and (2 1 3) reflections. The black vertical line indicates the estimated switching coordinate achieved in the experiment (fixed at 20% of the maximum switching coordinate calculated for each reflection) and the simulations of complete switching are displayed as insets.](image)

For the (2 1 3) reflection, we see that the one-step $X^-_3$ mechanism now results in the greatest intensity change over the shortest switching coordinate, reaching a $\Delta I$ of 10% at a switching coordinate of approximately 0.03. The least effect is calculated for the one-step $X^+_2$ and antipolar $X^+_3$ mechanisms, which result in a maximum intensity shift of 1% or less across the range of switching coordinates. An intermediate result is observed for the antipolar $X^-_3$ and orthorhombic twin mechanisms, which display an initially small intensity shift which smoothly begins to increase as the switching coordinate exceeds 0.05. Comparing these simulations with the experimental observations, we see that the maximum observed intensity shift is approximately 0.5%, so the only mechanism which can initially be eliminated is the one-step $X^-_3$ due to its large predicted impact on the intensity. By comparing this result against the (5 2 4) reflection, one may deduce that the one-step $X^+_2$ mechanism is once again the most plausible, as its intensity shift is non-zero, but less than...
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1\% around the 0.03-0.04 switching coordinate range. The remaining mechanisms result in either too great or too little intensity change at this switching coordinate.

\begin{center}
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure516}
\caption{Corrected simulated intensity changes for the (1 2 4), (3 2 6), (3 4 0) and (4 1 5) reflections. The black vertical line indicates the estimated switching coordinate achieved in the experiment (fixed at 20\% of the maximum switching calculated for each reflection) and the simulations of complete switching are displayed as insets.}
\end{figure}
\end{center}

Continuing to analyse the remaining superstructure reflections, some variation in the most likely mechanism is evident. For the (1 2 4) reflection, the experimental observation is a relatively small intensity shift of less than 1\%, which matches poorly to the simulated result for the one-step $X_2^+$ mechanism, but very well with each of the others. This may be due to the lower sensitivity of this analysis to reflections with small $h$ and large $k$ and $l$ values, or possibly due to the very small resultant field for this reflection. The (3 2 6) reflection has an observed maximum intensity change of approximately 2.5\%, which corresponds well to the simulated results for both the one-step $X_2^+$ and one-step $X_3^-$ mechanisms. The (3 4 0) reflection behaves similarly, albeit with a slightly larger maximum intensity change of
Chapter 5. An *in situ* Experiment to Investigate Switching in a Hybrid Improper Ferroelectric Ruddlesden-Popper Oxide

approximately 4%, with each of the other mechanisms underpredicting the intensity shift. For the (4 1 5) reflection, the one-step $X_2^+$ mechanism predicts a much larger intensity shift than is observed. Over the permitted switching coordinate range, all the other mechanisms underestimate the intensity shift, though the orthorhombic twin mechanisms are closest to the observed result.

Examining all of the experimental and simulated shortlisted reflections, the $X_2^+$ rotation distortion appears to dominate the plausible switching pathways. This is consistent with it being the softest distortion pathway as observed in the VT study by Pomiro *et al.*

### 5.6 Conclusions

In this chapter, a substituted $n=2$ RP phase, $\text{Ca}_{2.15}\text{Sr}_{0.85}\text{Ti}_2\text{O}_7$, has been synthesised and its behaviour under an applied electric field has been investigated in an *in situ* synchrotron X-ray diffraction experiment. Simulations of the key superstructure reflections have been performed using ISODISTORT, with several correction factors calculated to bring the simulations closer in line with experimental observations.

The results are subtle and do not allow for a quantitative assignment of the switching pathway. Since both of the antipolar pathways have very similar calculated energy barriers it is possible that several switching pathways are active simultaneously, particularly at low degrees of switching. The difficulty in fully identifying the pathway may be attributed to several factors. The experimentally-observed structural perturbation under the applied field is very small and not necessarily representative of a full switching event. Indeed, upon removal of the electric field, the reflection intensities appeared to return to their initial values, suggesting that a complete switching of significantly-sized domains was not achieved.

In spite of these limitations, upon collation of the results of the analysis across the shortlist of six superstructure reflections, there is evidence for a subtle tendency for pathways involving the $X_2^+$ rotation mode to agree with the experimental data. This implies that the rotation mode is the softer of the two octahedral distortions involved in hybrid improper ferroelectricity in $\text{Ca}_{2.15}\text{Sr}_{0.85}\text{Ti}_2\text{O}_7$, in agreement with the phase transitions observed in both $\text{Ca}_3\text{Ti}_2\text{O}_7$ and $\text{Ca}_{2.15}\text{Sr}_{0.85}\text{Ti}_2\text{O}_7$ with temperature.
Chapter 6. Perspectives

The work presented in this thesis represents advancements in magnetic and ferroelectric materials research. In particular, a common theme of improper ferroelectricity runs through all of the chapters, from attempts to produce magnetoelectrically-coupled materials in Chapters 1 and 2 to the phase transitions observed in Chapter 3 and attempting to elucidate the switching of an improper ferroelectric in Chapter 4. This section aims to summarise the general findings and reflect on possible future directions which could be taken by future workers in related fields.

6.1 Synthesis and Characterisation of Sr\(_{7-x}A_x\)Mn\(_4\)O\(_{15}\)

The expansion of the solid solution Sr\(_{7-x}A_x\)Mn\(_4\)O\(_{15}\) (A: Ca, Ba; 0 ≤ x ≤ 7) was achieved using standard solid-state synthetic methods. The main challenge associated with these syntheses was the elimination of impurity phases such as 4H-SrMnO\(_3\); minimisation of impurities was achieved using relatively low temperatures of 900-1000 °C, though this results in very slow formation of the desired products. Despite repeated attempts, synthesis of the highly-substituted SrCa\(_6\)Mn\(_4\)O\(_{15}\), Ca\(_7\)Mn\(_4\)O\(_{15}\) and SrBa\(_6\)Mn\(_4\)O\(_{15}\) phases was not achieved. Future work on these phases may benefit from computational analysis of the stability of these phases compared with the common impurity phases.

If the impurity phases can be further minimised by optimisation of the reaction conditions, there is an assortment of further work which could be performed on this family of compounds. A small amount of simultaneous substitution by both Ca\(^{2+}\) and Ba\(^{2+}\) cations has been described in the literature; the structural flexibility exhibited by this phase suggests that this may also be extended. Indeed, substitution by alternative cations with similar radii at the A-site may be possible — Pb\(^{2+}\) and Eu\(^{2+}\) are possible candidates for this application. Substitution at the B-site has not yet been explored but holds a strong possibility for novel magnetic orderings by either partially or completely replacing the Mn\(^{4+}\) on this position. Candidate cations for this could include Cr\(^{5+}\), Fe\(^{3+}\) or Co\(^{4+}\). The latter of these is possibly the most likely to substitute on to the B-site due to its similar ionic radius and oxidation state, but Cr\(^{5+}\) and Fe\(^{3+}\) could produce a phase containing Mn in multiple oxidation states. No assumptions about the feasibility of finding appropriate reagents containing these cations are made here. Beyond synthesising further substituted compositions, the temperature- and pressure-dependent phase transitions of the entire family of compounds could be investigated. A greater understanding of the phase behaviour of the phases may benefit future work to tune a magnetoelectric response.
6.2 Synthesis and Characterisation of $\text{Ba}_7\text{Mn}_4\text{O}_{15}$

A successful synthetic procedure for $\text{Ba}_7\text{Mn}_4\text{O}_{15}$ was discovered by an iterative trial-and-error approach, leaving only a small amount of slightly amorphous $\text{BaCO}_3$ starting material as an impurity phase in the final samples. Fine-tuning the synthesis to mitigate this impurity should be a straightforward process of reducing the amount of excess $\text{BaCO}_3$ in the reaction, though it is likely that this will need to be balanced with the formation of the $\text{Ba}_4\text{Mn}_3\text{O}_{10}$ impurity.

$\text{Ba}_7\text{Mn}_4\text{O}_{15}$ represents the first magnetoelectric compound in its structural class. As with the rest of the $\text{Sr}_7\text{A}_x\text{Mn}_4\text{O}_{15}$ solid solution, future works investigating this material could use variable-temperature and -pressure studies to gain an understanding of any phase transitions or may choose to attempt substitution at the B-site. Future work specific to $\text{Ba}_7\text{Mn}_4\text{O}_{15}$ should include further direct characterisation of the nature of the polar displacement, and could include demonstrating its existence and switchability, as well as performing additional synthetic work to enhance the magnetoelectric order temperature and the magnitude of the displacement. First-principles calculations on the magnetoelectric ground state could also prove useful in gaining an understanding of the structural and magnetic irreps which are active at low temperatures.

6.3 Pressure-Dependent Phase Transitions in Hybrid Improper Ferroelectric Ruddlesden-Popper Oxides

The HIF materials $\text{Ca}_3\text{Ti}_2\text{O}_7$ and $\text{Ca}_3\text{Mn}_2\text{O}_7$ were investigated by variable-pressure synchrotron X-ray diffraction experiment, with a phase transition from a polar $A2_1\text{am}$ phase to a non-polar $A\text{ca}_a$ phase observed in both materials at different pressures. A supporting computational study into $\text{Ca}_3\text{Ti}_2\text{O}_7$ was in good agreement with the experimental observations. The findings that both the polar and non-polar phases are stabilised with increasing pressure and that the polar mode increases in magnitude up to a certain pressure are surprising as they oppose the results that would be expected for a proper FE phase. Hopefully this discovery may increase interest in HIF materials, stimulating further experimental and computational investigations to find if this phenomenon is exclusive to the $n=2$ Ruddlesden-Popper phases. In particular, phases such as the mixed ($\text{Ca/ Sr})_3\text{Ti}_2\text{O}_7$ could be of interest as the temperature-based phase transitions in this substituted material are known to follow a different set of symmetries.

The results of this study are of particular interest as they may have applications in devices for piezoelectric power generation based on HIF materials. One could envisage a wind- or
wave-based system in which the pressure-based polarisation is repeatably harvested as a potential difference.

6.4 An in situ Experiment to Investigate Switching in a Hybrid Improper Ferroelectric Ruddlesden-Popper Oxide

This first-of-its-kind experiment on a HIF material aimed to discern the mechanism by which FE switching occurs in an \( n = 2 \) Ruddlesden-Popper oxide. While this goal was not fully achieved, steps were made towards elucidating a mechanism through the identification of the \( X_2^+ \) rotation mode as the softer of the two octahedral distortions. As a novel experiment, there are a number of ways in which any following work could improve on the methodology. For example, the use of a compressed powder sample is mandated by the need to pass an electric current but causes significant preferred orientation effects in the diffraction pattern, confounding the analysis and limiting the applicability of symmetry-adapted Rietveld refinements. To combat this issue, a single-crystal experiment could be envisioned, though this brings a new set of experimental considerations such as how the crystal may be oriented while under an applied field in such a way as to collect sufficient diffraction measurements.

Additionally, no consideration has been given to the azimuthal angle of the 2d diffraction patterns. It is possible that the intensities of various reflections may depend on the azimuthal angle at which the reflections are recorded, and further analysis could be performed to identify any relationship therein, to the benefit of future experiments of this type.

The concept that a mechanism may be identified in the first instance assumes that a singular mechanism is at play. It is entirely plausible that several different mechanisms act simultaneously, with one or more being dominant as the switching proceeds. The analysis presented in this thesis does not allow for multiple mechanisms to act simultaneously as this would be extremely complex to model, but future work may need to take this factor into account.

In spite of these limitations, this experiment shows \textit{in situ} measurements of HIF materials can capture crystallographic information and there is a good possibility that future experiments may elucidate greater detail. Investigating HIFs under different state variables such as temperature or pressure may reveal additional information which is valuable to understanding the phenomena as a whole. More generally, the experimental technique and analytical approach developed in this work is likely to be applicable to a wide variety of polar systems.
References

References

References

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References


References

References


References

Appendices

Appendix 1: Crystallographic information for Chapter 2

Table A1.1 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 (λ = 0.82451(1) Å) for Sr$_6$CaMn$_4$O$_{15}$ at 300 K.

<table>
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<th>Composition</th>
<th>Sr$_6$CaMn$<em>4$O$</em>{15}$</th>
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</thead>
<tbody>
<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
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</tr>
<tr>
<td>$b$ (Å)</td>
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<tr>
<td>$c$ (Å)</td>
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<td>$\beta$ (°)</td>
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</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>90</td>
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</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$B_{iso}$ (Å$^2$)</th>
</tr>
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<tbody>
<tr>
<td>Sr1</td>
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<td>0.46488</td>
<td>Sr 0.661(5) Ca 0.339(5)</td>
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<tr>
<td>Sr2</td>
<td>0.351306</td>
<td>0.15167</td>
<td>0.19500</td>
<td>Sr 0.903(5) Ca 0.097(5)</td>
<td>0.626</td>
</tr>
<tr>
<td>Sr3</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
<td>Sr 1.000(6) Ca 0.000(6)</td>
<td>0.626</td>
</tr>
<tr>
<td>Sr4</td>
<td>0.17532</td>
<td>0.00200</td>
<td>0.83179</td>
<td>Sr 1.000(4) Ca 0.000(4)</td>
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<td>0.24415</td>
<td>0.71022</td>
<td>1</td>
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</tr>
</tbody>
</table>
Table A1.2 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at 111 ($\lambda = 0.82451(1)$ Å) for Sr$_5$Ca$_2$Mn$_4$O$_{15}$ at 300 K.

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>B$_{iso}$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.998422</td>
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<td>0.464038</td>
<td>Sr 0.450(5) Ca 0.550(5)</td>
<td>0.620</td>
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<tr>
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<td>Sr 0.800(6) Ca 0.200(6)</td>
<td>0.620</td>
</tr>
<tr>
<td>Sr3</td>
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<td>0</td>
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Table A1.3 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82451(1) \, \text{Å}$) for Sr$_4$Ca$_3$Mn$_4$O$_{15}$ at 300 K.

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<td>$\beta$ (°)</td>
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Table A1.4 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 (\( \lambda = 0.82638(3) \) Å) for Sr₃Ca₄Mn₄O₁₅ at 300 K.

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Table A1.5 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82634(1) \, \text{Å}$) for Sr$_2$Ca$_5$Mn$_4$O$_{15}$ at 300 K.

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<td>0.0012(2)</td>
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Composition: Sr$_2$Ca$_5$Mn$_4$O$_{15}$

Space group: $P2_1/c$

$\lambda = 0.82634(1) \, \text{Å}$

Sr$_2$Ca$_5$Mn$_4$O$_{15}$ at 300 K.
Table A1.6 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82453(5)$ Å) for Sr$_6$BaMn$_4$O$_{15}$ at 300 K.

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Appendices

Table A1.7 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82453(5)$ Å) for Sr$_5$Ba$_2$Mn$_4$O$_{15}$ at 300 K.

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Table A1.8 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at II1 (λ = 0.82453(5) Å) for Sr₄Ba₃Mn₄O₁₅ at 300 K.

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<th>Occupancy</th>
<th>Bᵦₒ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr1</td>
<td>0.99409</td>
<td>0.181686</td>
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<td>Sr 0.957(6)</td>
<td>0.967</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>Ba 0.043(6)</td>
<td></td>
</tr>
<tr>
<td>Sr2</td>
<td>0.34709</td>
<td>0.152812</td>
<td>0.194498</td>
<td>Sr 0.738(6)</td>
<td>0.967</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ba 0.262(6)</td>
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</tr>
<tr>
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<td>0</td>
<td>0.5</td>
<td>Sr 0.205(9)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ba 0.795(9)</td>
<td></td>
</tr>
<tr>
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<td>0.834522</td>
<td>Sr 0.245(6)</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td>Ba 0.755(6)</td>
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</tr>
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<tr>
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<td>1</td>
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</tr>
<tr>
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<td>0.187398</td>
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<td>O3</td>
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<tr>
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<td>0.233554</td>
<td>0.077502</td>
<td>1</td>
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</tr>
<tr>
<td>O6</td>
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<td>0</td>
<td>0</td>
<td>1</td>
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</tr>
<tr>
<td>O7</td>
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<td>0.631626</td>
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<td>0.437</td>
</tr>
<tr>
<td>O8</td>
<td>0.022172</td>
<td>0.251108</td>
<td>0.715598</td>
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### Table A1.9 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82495(1)$ Å) for Sr$_3$Ba$_4$Mn$_4$O$_{15}$ at 300 K.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Space group</th>
<th>( P2_1/c )</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>( a ) (Å)</td>
<td>7.0101(2)</td>
</tr>
<tr>
<td></td>
<td>( b ) (Å)</td>
<td>9.9183(3)</td>
</tr>
<tr>
<td></td>
<td>( c ) (Å)</td>
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<tr>
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<td>( \alpha ) (°)</td>
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<tr>
<td></td>
<td>( \beta ) (°)</td>
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<tr>
<td></td>
<td>( \gamma ) (°)</td>
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</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>Occupancy</th>
<th>( B_{\text{ISO}} ) (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr1</td>
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<td>0.180788</td>
<td>0.464834</td>
<td>Sr 0.8286(14)&lt;br&gt;&lt;br&gt;Ba 0.1714(14)</td>
<td>1.078</td>
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<tr>
<td>Sr2</td>
<td>0.34594</td>
<td>0.153266</td>
<td>0.194114</td>
<td>Sr 0.608(1)&lt;br&gt;&lt;br&gt;Ba 0.392(1)</td>
<td>1.078</td>
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<td>0</td>
<td>0.5</td>
<td>Sr 0.1000(17)&lt;br&gt;&lt;br&gt;Ba 0.9000(17)</td>
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</tr>
<tr>
<td>Sr4</td>
<td>0.173224</td>
<td>0.000568</td>
<td>0.835246</td>
<td>Sr 0.054(11)&lt;br&gt;&lt;br&gt;Ba 0.946(11)</td>
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<tr>
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<tr>
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<td>0.401</td>
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<tr>
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<tr>
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<tr>
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</table>
Table A1.10 Lattice parameters and atomic coordinates extracted from powder synchrotron X-ray diffraction at I11 ($\lambda = 0.82495(1)$ Å) for Sr$_2$Ba$_5$Mn$_4$O$_{15}$ at 300 K.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sr$_2$Ba$_5$Mn$<em>4$O$</em>{15}$</th>
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</thead>
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<tr>
<td>Space group</td>
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</tr>
<tr>
<td>$b$ (Å)</td>
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</tr>
<tr>
<td>$c$ (Å)</td>
<td>10.56867(11)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
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</tr>
<tr>
<td>$\beta$ (°)</td>
<td>91.6523(6)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>90</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$B_{iso}$ (Å$^2$)</th>
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</thead>
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<tr>
<td>Sr1</td>
<td>0.9925(3)</td>
<td>0.1799(2)</td>
<td>0.46461(19)</td>
<td>Sr 0.646(9) Ba 0.351(9)</td>
<td>1.19(3)</td>
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<tr>
<td>Sr2</td>
<td>0.3447(3)</td>
<td>0.1536(2)</td>
<td>0.19375(20)</td>
<td>Sr 0.443(9) Ba 0.557(9)</td>
<td>1.19(3)</td>
</tr>
<tr>
<td>Sr3</td>
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<td>0</td>
<td>0.5</td>
<td>Sr 0.056(14) Ba 0.944(14)</td>
<td>1.19(3)</td>
</tr>
<tr>
<td>Sr4</td>
<td>0.1727(3)</td>
<td>0.00018(18)</td>
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<td>Sr 0.000(9) Ba 1.000(9)</td>
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<tr>
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<tr>
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<td>0.37(6)</td>
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</table>
Appendices

**Appendix 2: Method for Calculating ‘Degree of Rumpling’ in n = 2 Ruddlesden-Popper phases**

In Chapter 4, the rumpling mode (which transforms as the $\Gamma_1^+$ irrep) present in $n = 2$ Ruddlesden-Popper phases is in competition with the octahedral rotation modes present in the $A_2 am$ and $Aca a$ phases (an in-phase rotation transforming as $X_2^+$ and an out-of-phase rotation transforming as $X_1^-$, respectively). In order to compare the effect of the rumpling mode between different DFT-calculated phases of $\text{Ca}_3\text{Ti}_2\text{O}_7$, we define a metric referred to as the ‘degree of rumpling’. To calibrate this metric, we begin by calculating the amplitude of the $\Gamma_1^+$ mode for two neighbouring sites in the $I4/mmm$ phase. The sites selected in this instance were the Ca(2) and O(2) sites, indicated in Figure A2.1.

*Table A2.1 Lattice parameters and atomic coordinates of parent $I4/mmm$ structure of $\text{Ca}_3\text{Ti}_2\text{O}_7$ used for calculating degree of rumpling.*

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ca$_3$Ti$_2$O$_7$</th>
<th>$I4/mmm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.83281</td>
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</tr>
<tr>
<td>$b$ (Å)</td>
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<tr>
<td>$c$ (Å)</td>
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<td>$\alpha$ (°)</td>
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<tr>
<td>$\beta$ (°)</td>
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<td></td>
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<tr>
<td>$\gamma$ (°)</td>
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</tr>
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</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>$B_{iso}$ (Å$^2$)</th>
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<tbody>
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<td>0.4</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>1</td>
<td>0.4</td>
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<tr>
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<td>0</td>
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<td>1</td>
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<tr>
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<td>0.09871</td>
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<td>0.4</td>
</tr>
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</table>
Using ISODISTORT, the mode amplitudes are decomposed and the amplitudes on each site are tabulated as a function of pressure as shown in columns 3 and 4 of Table A2.1. Also tabulated are the z-coordinates of these sites. The sums of the $\Gamma_1^+$ mode amplitudes and the differences between the z-coordinates at each pressure are calculated.

**Table A2.1 Mode amplitudes and z-coordinate differences for Ca(2) and O(2) sites of theoretical $I4/mmm$ structure of Ca$_3$Ti$_2$O$_7$.**

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$\Gamma_1^+$ (Ca(2)) (Å)</th>
<th>$\Gamma_1^+$ (O(2)) (Å)</th>
<th>$\sum \Gamma_1^+$ (Å)</th>
<th>Ca(2) z-coordinate</th>
<th>O(2) z-coordinate</th>
<th>z-coordinate difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.31503</td>
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<td>0.0343</td>
<td>0.31523</td>
<td>0.29892</td>
<td>0.01631</td>
</tr>
<tr>
<td>20</td>
<td>0.01427</td>
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<tr>
<td>30</td>
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<td>0.09521</td>
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<tr>
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<td>0.0205</td>
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</table>
The z-coordinate difference is then plotted against the sum of the $\Gamma_1^+$ modes as shown in Figure A2.2. A straight-line fit of this graph produces the calibration equation:

\[
z\text{-coordinate difference} = (0.0364 \times \sum \Gamma_1^+) + 0.0151 \tag{A2.1}
\]

The degree of rumpling may then be calculated for a Ca$_3$Ti$_2$O$_7$ phase of any symmetry according to:

\[
\text{degree of rumpling} = z\text{-coordinate difference} \times c \tag{A2.2}
\]

Where $c$ is the lattice parameter of the Ca$_3$Ti$_2$O$_7$ phase.