

A Study of Y_2NiMnO_6 and ErCrO_3 : Unveiling the Properties of (Double) Perovskite Oxides

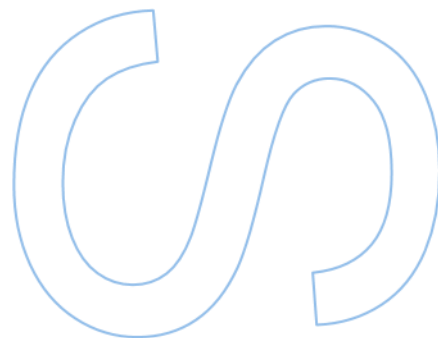
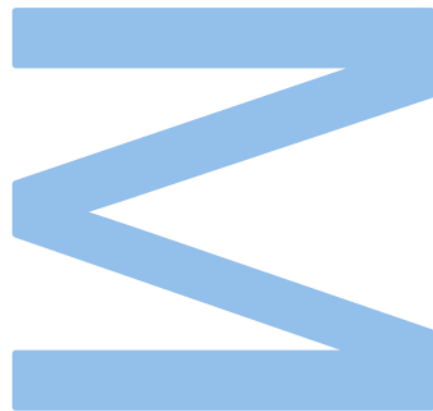
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Masters Thesis

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Unveiling the Properties of (Double)
Perovskite Oxides**

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“It does not matter how slowly you go as long as you do not stop.”

Confucius

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Resumo

O campo dos multiferroicos, materiais que exibem duas ou mais ordens ferroicas, como o ferromagnetismo, a ferroeletricidade ou a ferroelasticidade (ou seus anti contrapostos), numa única fase, têm atraído considerável atenção na comunidade científica devido ao seu imenso potencial para o desenvolvimento de dispositivos multifuncionais avançados, como células solares de terceira geração, dispositivos spintrônicos, baterias, catálise e dispositivos de conversão de energia. Neste contexto, as perovskites têm-se mostrado uma classe promissora de materiais devido à sua estrutura cristalina altamente ajustável, potencialmente induzindo notáveis propriedades como o ferromagnetismo, ferroeletricidade e até mesmo supercondutividade. No entanto, é raro observar ao mesmo tempo ferroeletricidade e ferromagnetismo numa única perovskite. Assim, uma profunda investigação tem sido realizada nesta área para encontrar formas de combinar ambas as propriedades em materiais do tipo perovskite.

Com base nestes conceitos, esta tese visa expandir o conhecimento sobre as propriedades deste tipo de material, com particular ênfase no óxido de perovskite duplo Y_2NiMnO_6 e no óxido de perovskite simples ErCrO_3 , incluindo a análise das propriedades estruturais (macroscópicas e locais), magnéticas, elétricas e térmicas. No caso do Y_2NiMnO_6 , foi investigada a influência do método de síntese na pureza final da amostra e no impacto subsequente nas suas propriedades, comparando-se dois métodos: sol-gel e reação em estado sólido. Ambas as amostras cristalizaram no grupo espacial esperado $P2_1/n$, mas a amostra obtida por reação em estado sólido apresentou maior pureza, com apenas uma fase secundária residual de NiO , enquanto a amostra sol-gel revelou maior desvio composicional, como confirmado por espectroscopia de raios-X por dispersão de energia. Magneticamente, ambas as amostras exibiram transições magnéticas duplas, indicativas de interações magnéticas concorrentes. A amostra de estado sólido apresentou a temperatura de transição de Curie mais elevada (64 K) e um momento magnético efetivo de $4.89 \mu_B$, próximo do valor teórico. Em contraste, a amostra sol-gel apresentou um momento magnético mais elevado, sugerindo a presença de estados de valência mistos para Ni e Mn. A amostra de estado sólido demonstrou também melhor desempenho magnetocalórico, com uma variação máxima de entropia de $2.46 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ e uma potência de refrigeração relativa de $207 \text{ J} \cdot \text{kg}^{-1}$ sob um campo magnético de 70 kOe. As medições elétricas na amostra sol-gel revelaram um comportamento semicondutor, com uma resistência à temperatura ambiente de 2435Ω e uma energia de ativação de 0.227 eV,

obtida a partir da análise de Arrhenius.

Finalmente, para obter uma compreensão mais profunda dos aspetos fundamentais subjacentes aos óxidos de perovskite dupla, voltamos à estrutura simples estudando o material ErCrO_3 . Aqui, realizamos um estudo tanto macroscópico (difração de raios-X) como em escala local (Função de Distribuição de Pares) numa faixa de temperaturas entre 5 K e 500 K. O objetivo foi investigar a possível existência de distorções estruturais locais que pudessem contribuir para propriedades físicas anómalas — como o surgimento de ferroeletricidade — numa estrutura cristalina centrosimétrica. A difração de raios-X confirmou a persistência do grupo espacial centrosimétrico $Pbnm$ em toda a gama de temperaturas. No entanto, a análise da Função de Distribuição de Pares revelou distorções locais confinadas a intervalos específicos de temperatura. Estas distorções, caracterizadas por um comprimento de correlação de aproximadamente 5 Å (comparável ao tamanho da célula unitária), manifestaram-se como deformações dos octaedros e um deslocamento do ião Cr ao longo do eixo z de cerca de 0.1 Å. Nessas gamas de temperatura, a estrutura local foi melhor descrita pelo grupo espacial de simetria inferior $P2_1$. O refinamento mostrou que o ambiente octaédrico se divide em dois conjuntos distintos: um consistente com a estrutura média obtida por raios-X ($Pbnm$), e outro com distorções locais evidentes, correspondendo a colunas adjacentes dentro da célula unitária.

Palavras-chave: Óxidos do tipo perovskite, Multiferroicos, Função de Distribuição de Pares, Distorções locais

Abstract

The field of multiferroics, materials that exhibit two or more ferroic orders, for example, ferromagnetism, ferroelectricity, or ferroelasticity (or their anti-counterparts), in a single phase, has attracted considerable attention in the scientific community due to its immense potential for the development of advanced multifunctional devices, such as third-generation solar cells, spintronic devices, batteries, catalysis and energy conversion devices. In this context, perovskites are a promising class of materials due to their highly adjustable crystal structure, potentially inducing remarkable properties like ferromagnetism, ferroelectricity, and even superconductivity. Nevertheless, simultaneously observing ferroelectricity and ferromagnetism in a single perovskite structure is rare. Thus, extensive research has been done in this area to find ways to combine both of these properties in perovskite-type materials.

Building on these concepts, this thesis aims to expand the knowledge on the bulk properties of some of these perovskite-type materials, in particular focusing on the double perovskite oxide Y_2NiMnO_6 and the simple perovskite oxide ErCrO_3 , including structural (macroscopic and local), magnetic, electrical, and thermal property analysis. In detail, for the case of Y_2NiMnO_6 , we investigate the influence of the synthesis method on the final purity of the sample and its subsequent impact on the bulk properties by dividing into two synthesis routes, sol-gel and solid-state reaction methods. Both samples crystallized in the expected $P2_1/n$ space group, but the solid-state sample showed higher purity, with only a minor NiO secondary phase, while the sol-gel sample exhibited greater compositional deviation, as confirmed by energy-dispersive X-ray spectroscopy. Magnetically, both samples displayed dual-phase transitions indicative of competing magnetic interactions. The solid-state sample had the highest Curie temperature (64 K) and an effective magnetic moment of $4.89 \mu_B$, matching theoretical predictions. In contrast, the sol-gel sample showed a higher effective magnetic moment, suggesting mixed Ni/Mn valence states. The solid-state sample also exhibited superior magnetocaloric performance, with a maximum entropy change of $2.46 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ and a relative cooling power of $207 \text{ J}\cdot\text{kg}^{-1}$ at 70 kOe. Electrical measurements on the sol-gel sample revealed semiconducting behaviour, with a room-temperature resistance of 2435Ω and an activation energy of 0.227 eV derived from an Arrhenius analysis.

Finally, to better understand the fundamental aspects underlying perovskite oxides, we return to the simple perovskite structure by studying the material ErCrO_3 . Here, we perform

a macroscopic (X-Ray diffraction) and local scale (Pair Distribution Function) study within a temperature range of 5 K to 500 K. The aim was to investigate the possible existence of local structural distortions that could contribute to anomalous physical properties—such as the emergence of ferroelectricity—in this centrosymmetric crystal structure. While X-Ray diffraction confirmed the persistence of the centrosymmetric $Pbnm$ space group throughout the entire temperature range, the Pair Distribution Function analysis revealed the presence of local distortions confined to specific temperature intervals. These distortions, characterised by a correlation length of approximately 5 Å (comparable to the unit cell size), manifested as octahedral deformations and an off-centering of the Cr ion along the z -axis by about 0.1 Å. Furthermore, in these temperature ranges, the local structure was best described by the lower-symmetry $P2_1$ space group. The refinement showed that the octahedral environment splits into two distinct sets: one consistent with the average structure obtained by X-Ray ($Pbnm$), and another exhibiting clear local distortions, corresponding to adjacent columns within the unit cell.

Keywords: Perovskite oxides, Multiferroic, Pair Distribution Function, Local distortions

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List of Abbreviations

ADP	Atomic Displacement Parameter
AFM	Antiferromagnetic
μ_B	Bohr Magneton
C	Curie Constant
CIF	Crystallographic Information File
T_C	Curie Temperature
Θ_{CW}	Curie-Weiss Temperature
D	Crystalline Size
DC	Direct Current
DFT	Density Functional Theory
μ_{eff}	Effective Paramagnetic Moment
EDS	Energy Dispersive X-Ray Spectroscopy
EFG	Electric Field Gradient
E	Einstein Constant
Θ_E	Effective Einstein Temperature
FMR	Ferromagnetic Resonance
FM	Ferromagnetic
FC	Field Cooling
FWHM	Full Width at Half Maximum
C_p	Heat Capacity
IRREP	Irreducible representation
M	Magnetization
H	Magnetic Field
χ	Magnetic Susceptibility
MCE	Magnetocaloric Effect
ΔS_m	Magnetic Entropy Variation
MPMS	Magnetic Property Measurement System
T_N	Néel Temperature
PAC	Perturbed Angular Correlation
PDF	Pair Distribution Function
PVA	Polyvinyl Alcohol
PPMS	Physical Properties Measurement System
PDF	Pair Distribution Function
PC	Personal Computer
RF	Radio Frequency
RT	Room Temperature
RCP	Relative Cooling Power
RDF	Radial Distribution Function
SEM	Scanning Electron Microscopy
SSR	Solid-State Reaction
SG	Sol-Gel
SQUID	Superconducting Quantum Interference Device

ϵ	Strain
T_{SR}	Spin Reorientation Temperature
λ	Wavelength
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy
ZFC	Zero Field Cooling

Thesis Outline

The present thesis explores the structural, magnetic, electrical, and thermal properties of two promising perovskite oxides with multiferroic behaviour. Multiferroics exhibit two or more ferroic orders within a single phase, such as ferromagnetism, ferroelectricity, ferroelasticity, and ferrotoroidicity (or their antiferroic counterparts). We start with the double perovskite (Y_2NiMnO_6) and study its physical properties with the help of numerous characterization techniques, such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) for structural characterization, a Magnetic Property Measurement System (MPMS) with a Superconducting Quantum Interference Device (SQUID) magnetometer for the magnetic measurements, and a Physical Properties Measurement System (PPMS) for the electrical and thermal properties. Afterwards, we take a step back to the single perovskite oxide (ErCrO_3) to unveil the underlying basics of this type of material by coupling a macroscopic study (XRD) with a local scale one (Pair Distribution Function (PDF)).

The primary aim of this thesis was to produce solid-state and sol-gel samples of the double perovskite oxide and characterize its structural, magnetic, electrical, and thermal properties to illustrate its potential usage in advanced technological devices due to its multiferroic properties. Furthermore, a local scale study, in pair with a macro scale, was performed in the single perovskite oxide to uncover the potential existence, and also origin, of local distortions that could be responsible for the appearance of several physical properties, like ferroelectricity, in this material, and others alike (rare-earth orthochromites).

This thesis comprises five chapters: an introduction, a chapter detailing the experimental techniques, two on the main results and discussion, and a chapter with conclusions and future perspectives. A brief summary of each chapter is presented below.

Chapter 1 introduces key concepts relevant to this thesis, such as multiferroics, ferroelectricity, the influence of spin configurations on magnetic properties, and transition metal oxides with perovskite structure. We present an overview of the basic principles that define a perovskite structure and also, in particular, we review the physical properties of the studied perovskite oxides in this thesis, Y_2NiMnO_6 and ErCrO_3 .

In Chapter 2 we present a summary of the experimental techniques used in this work. This incorporates the synthesis method of the solid-state reaction and sol-gel synthesis, both

used in producing the sample Y_2NiMnO_6 . As for the sample ErCrO_3 , also prepared from a solid-state reaction, was produced from a different work [1]. Additionally, we perform a detailed description of the used characterization techniques, such as XRD (Rietveld refinement and Pair Distribution Function methods), SEM, EDS, MPMS, and PPMS.

Chapter 3 presents a study of the double perovskite Y_2NiMnO_6 . The chapter is composed of two sections. Section 3.1 reports the synthesis methods used to produce the bulk samples, along with the corresponding X-Ray evolution after each step during the synthesis process. In Section 3.2 we present the sample characterization of the studied material. The structural characterization was conducted by refining the X-Ray powder diffraction data. Morphological and chemical analyses were performed with Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy. For the magnetic measurements, DC magnetization and the magnetocaloric effect, we used a Superconducting Quantum Interference Device magnetometer. We used the Physical Property Measurement System for the thermal and electrical properties.

Chapter 4 is divided into four main sections, in the first two, section 4.1 and section 4.2, we present, respectively, an overview and detail the experimental conditions of the studied sample ErCrO_3 . In the last two sections, we perform a macroscopic and local study of ErCrO_3 . In section 4.3, we present the results from the Rietveld refinement of the sequential synchrotron X-Ray diffraction data. And in section 4.4, we conduct an atomic scale analysis using the Pair Distribution Function method on sequential synchrotron X-Ray diffraction data and compare our findings with other local studies of rare-earth orthochromites.

Finally, Chapter 5 summarises the main conclusions drawn from this study and an outline of future perspectives.

1. Introduction

Materials science has been a crucial driver of human progress, from creating essential survival tools that set us apart from other species to developing cutting-edge technologies that define our modern way of living. The pursuit of materials with new and improved properties has been guided throughout history by humanity's desire for functionality, comfort, and sustainability. In today's world, the role of materials extends far beyond simple utility. They are an integral part of systems that power a sustainable and interconnected world, a reality only made possible thanks to understanding and refining their fundamental properties, enabling breakthroughs across industries and addressing challenges in energy and environmental sustainability [2].

In this context, perovskites have emerged as a particularly intriguing and versatile material amongst the wide range of materials available to mankind. This is due to their remarkable structural adaptability, which makes them exhibit highly desirable properties for today's cutting-edge applications. For example, they show immense potential in fields such as renewable energy, particularly solar cells, and in other domains like optoelectronics and magnetoelectric devices [3–5].

Therefore, this thesis intends to explore and study perovskite materials, focusing on single and double oxide perovskites, more specifically ErCrO_3 and Y_2NiMnO_6 . To achieve this, we investigate their structural and magnetic properties, in addition to the electrical and thermal properties for the double perovskite case, and how the chosen synthesis method might influence these properties. Thus, this contributes to understanding how these materials can be optimized for advanced applications, such as renewable energy sources (e.g., solar cells), optoelectronics, and potential multiferroic devices. In particular, we also aim to bridge the gap in the current literature regarding rare-earth orthochromites, as some doubts still persist about the possible existence of a ferroelectric phase transition, whose origin might be from local distortions, by employing, in parallel, a macroscopic (X-Ray diffraction) and local (Pair Distribution Function) study.

1.1. Fundamentals

This section will focus on the fundamental principles of transition metal oxides with perovskite structure, both single and double. We will introduce some key concepts that define the unique characteristics of these materials and discuss the various classifications they

belong to based on their properties and behaviour. Transition metal oxides with perovskite structures have been primarily studied for electron correlations since their physical properties, such as electrical transport, magnetism, optical response, thermal conductivity and superconductivity, are determined by the strongly correlated d -electrons that remained from the transition metal s -electrons that were transferred to the oxygen ions [6].

1.1.1 Multiferroics

In this regard, an exciting class of materials are the multiferroics, which exhibit more than one primary ferroic order in a single-phase material, such as ferromagnetism, ferroelectricity, ferroelasticity, and ferrotoroidicity. Even though this term was first used for materials that exhibit ferroelectricity and ferromagnetism, as shown in Fig. 1.1, the current trend is to extend to their corresponding antiferroic properties, like antiferroelectricity and antiferromagnetism [7].

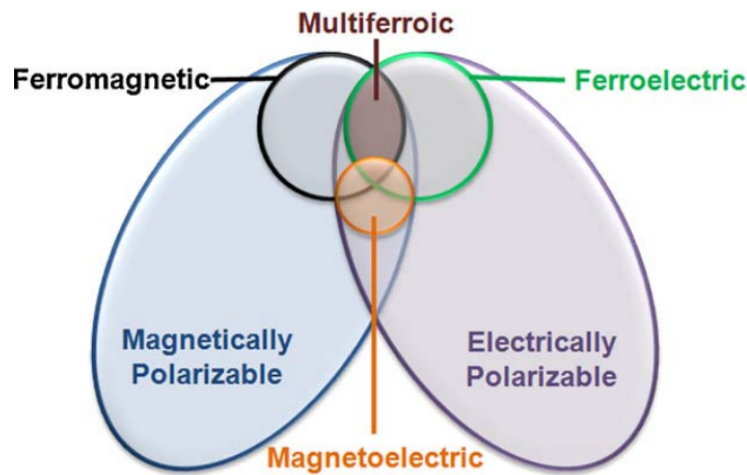


Figure 1.1: Relationship between multiferroic and magnetoelectric materials. Adapted from Ref. 7.

These materials, as proposed by Khomskii [8], can be divided into two classes: type-I multiferroic, which has different origins of magnetism and ferroelectricity, with usually high values of polarizations and critical temperatures [9], and type-II multiferroics, where ferroelectricity is strongly coupled with the magnetic ordering, typically referred to as magnetism-driven multiferroics. Unlike the first type, these materials have a low critical temperature and polarization value, two significant drawbacks for practical applications [9]. As an example, the studied double perovskite Y_2NiMnO_6 in this thesis is defined as a multiferroic material of the type-II [9, 10]; put into other words, it exhibits more than one ferroic property in the same phase [11], in this case, ferromagnetism and ferroelectricity.

1.1.2 Spin configurations

Magnetism is a quantum mechanical phenomenon closely tied to electrons' spin and orbital motion. Within materials, electrons can have either paired or unpaired spins, where only materials with unpaired electrons exhibit ordered magnetic behaviours. In contrast, materials with paired electrons have diamagnetic properties due to spin cancellation [12].

A visual representation of the different types of magnetic materials under an applied magnetic field is demonstrated in Fig. 1.2. In particular, paramagnetic materials, in the absence of an applied magnetic field, the spins are randomly oriented, meaning that there is no preferred direction for the unpaired electrons' magnetic moments, resulting in zero net magnetization. However, when a magnetic field is applied, their unpaired electrons are oriented in the same direction as the magnetic field, as seen in Fig. 1.2.

Similarly, in ferromagnetic materials, the magnetic domains (spins of unpaired electrons) align with the direction of the applied magnetic field. It is worth mentioning that these types of materials show spontaneous magnetic moments even without an external magnetic field (below T_C).

As for ferrimagnetic materials, which arise from the unequal distribution of magnetic moments between two or more magnetic sublattices [12], they have magnetic moments that are not aligned in the same direction. Instead, they align in such a way that a non-zero net magnetic moment is produced. In contrast, antiferromagnetic materials have their magnetic moments completely cancel out.

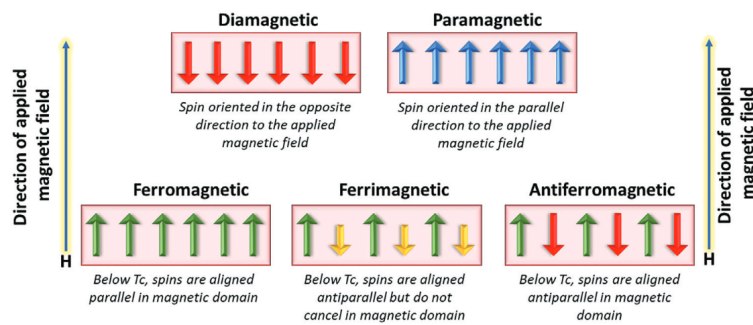


Figure 1.2: Visual representation of spin configurations of different types of magnetism under an applied magnetic field. Taken from Ref. 12.

Furthermore, there are different types of antiferromagnetic configurations, each defined by the specific arrangement of spins within the material. In Fig. 1.3, a schematic view of the A , C , G and E type antiferromagnetic structures are shown. In A -type, the intra-plane coupling is ferromagnetic while the inter-plane coupling is antiferromagnetic; meanwhile,

in a C-type, the intra and inter-plane are reversed. Furthermore, a G-type, which is the one assigned to ErCrO_3 , has both intra-plane and inter-plane coupling antiferromagnetic, and a E-type follows the cube's edge (Y_2NiMnO_6 case), in other words, two spins point in one direction and the next two in the other

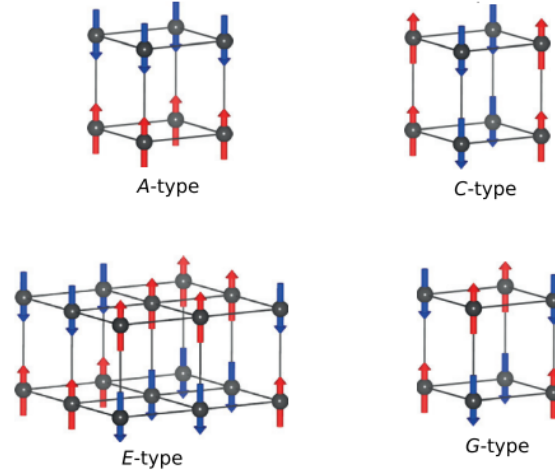


Figure 1.3: Schematic view of the A, C, E and G type antiferromagnetic structures. Adapted from Ref. 13.

In addition, Fig. 1.4 presents a schematic representation of possible spin configurations in the G-type antiferromagnetic structure, corresponding to the perovskite ErCrO_3 , which has a $Pbnm$ structure. The figure illustrates different magnetic arrangements labelled as $\Gamma_1(A_x, G_y, C_z)$, $\Gamma_2(F_x, C_y, G_z)$, $\Gamma_4(G_x, A_y, F_z)$, each defining distinct orientations of the Cr spins (blue arrows) within the lattice.

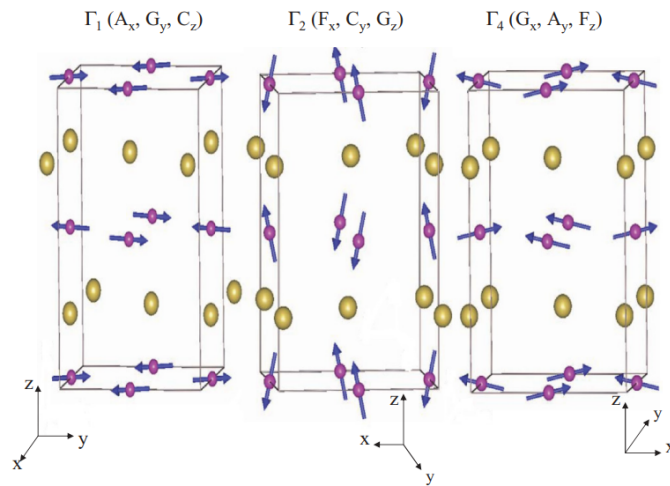


Figure 1.4: Schematic view of Γ_1 , Γ_2 , Γ_4 spin configurations types. Taken from Ref. 14.

1.1.3 Ferroelectricity

Another important concept to discuss is ferroelectricity. Materials exhibiting this property belong to a class of crystalline dielectrics that show spontaneous polarization within a specific temperature range. The orientation of this polarization can be reversed by an electric field, which can vary significantly under the influence of external factors [15]. In many ways, ferroelectric materials' electrical behaviour is similar to ferromagnetic materials' magnetic properties.

As previously mentioned, these materials undergo a phase transition from the paraelectric phase to the ferroelectric phase at a given temperature. Additionally, in the higher temperature phase (paraelectric), the material typically has a non-polar crystalline structure [16]. This transition induces significant changes in the crystal structure as well as in key thermodynamic properties, such as dielectric, elastic, and thermal characteristics. Moreover, these materials are characterized by a non-linear relationship between polarization and the applied electric field [16], showcased by a hysteresis loop. Figure 1.5 illustrates the typical polarization response (P , Y -axis) to an applied electric field (E , X -axis) in a ferroelectric material.

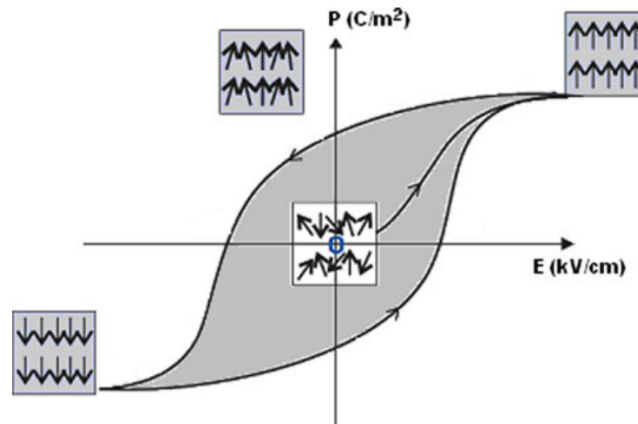


Figure 1.5: Illustration of the hysteresis loop (P - E) of ferroelectric materials. Adapted from Ref. 15.

1.2. Overview of Perovskites

The first perovskite dates back to 1839, when the German scientist Gustav Rose discovered CaTiO_3 in the Russian Ural Mountains. However, it was named after Alekseyevich von Perovski, who later characterized these materials [17]. Since then, much development and research have been done on this material, focusing on solar cell research in the 21st century [18]. Although silicon solar cells run the market, due to their relatively high efficiency and long-lasting guarantee of at least 25 years, they are expensive to mass

produce [19], as it is required to have high levels of uniformity. The perovskite solar cells show the advantage of still functioning despite imperfections, reducing production costs. They have come a long way in terms of efficiency, starting at only 3 % as of 2009 [20], to a record value of 26.7 % and 30.1 % as a tandem solar cell [21].

Perovskites have a general structure of ABX_3 , where the A is the central cation (electron donor) surrounded by 8 ligands. Here, a ligand is the B cation surrounded by 6 X anions in an octahedral shape, forming a 3-dimensional structure. In Fig. 1.6, the left side illustrates the cubic framework, where the A cations occupy the corners, and the B cation is positioned at the center of the octahedron formed by the X anions. Meanwhile, the right side provides the 3-dimensional perovskite structure, highlighting the arrangement of A, B, and X ions.

One of the many advantages of these materials is their versatility, having different possibilities in each atom site. For example, in the A-site, which has a larger ionic radius, it consists typically of rare-earth metals, like, for instance, Erbium (Er), alkaline-earth and divalent base alkaline elements, while in the smaller ionic radii B-site, it is made from transition metal elements, like Chromium (Cr). Finally, in the X-site, the most common atom is oxygen (O), so oxide perovskites, or other larger ions like halides, sulfides, and nitrides [22].

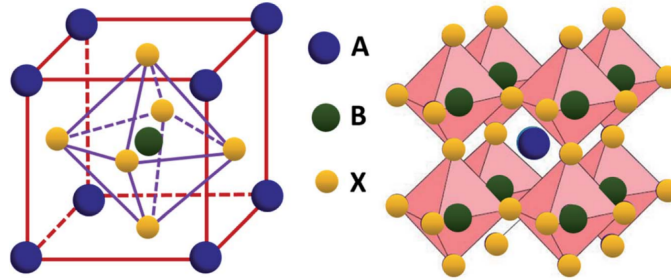


Figure 1.6: Structure of a ABX_3 perovskite. Taken from Ref. 23.

To determine which combinations are probable in terms of stability and predict their structural arrangement, Victor Goldschmidt made a concept named tolerance factor in 1926 [24]. In perovskites, the stability is mainly dependent on the ionic size of the atoms A, B and X [25], which can be calculated using this tolerance factor given by equation. 1.1 [25], where r_A is the ionic radii of the cation A, r_B is the ionic radii of the cation B, and r_X is the ionic radii of the anion X.

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1.1)$$

Based on their structure, perovskites can be classified into different types. If the element sitting on the X-site is O, we refer to them as perovskite oxides. In this thesis, we will be focusing on these types of perovskites: single (ErCrO_3) and double (Y_2NiMnO_6). Furthermore, the arrangement of the atoms in the crystal lattice leads to variations in symmetry and distortions of the BO_6 octahedra, resulting in different physical, electrical and chemical properties. The ideal structure is cubic, with the A cations sitting in the corners of the unit cell and a repeating interconnected pattern of the BO_6 octahedral throughout the structure, which plays an essential role in the appearance of ferromagnetism and ferroelectricity [22].

Depending on the type of distortion in the octahedral, the perovskite can have several symmetry reduction phases, going from the ideal cubic structure to other crystal systems such as tetragonal, orthorhombic, or rhombohedral. These distortions can have several reasons, and one is if there is a big difference between the radii of the A and B cations, making it difficult to fit within the octahedral voids of the lattice. Another example that can lead to these imperfections is, for instance, at higher temperatures, changes in the oxidation states of the cations, which results in distortions to maintain charge balance, in other words, charge compensation effects [22].

In addition, the perovskite structure offers remarkable versatility, allowing for multiple cation configurations at the A and/or B sites, evolving from a single to a double perovskite structure. Single perovskites, such as ErCrO_3 , contain only one type of cation at the B site, resulting in a relatively simpler structure. In contrast, double perovskites, such as Y_2NiMnO_6 , incorporate two distinct cations at either the A or B sites (in this case, at the B site). For example, a double A-site perovskite, with the formula $\text{AA}'\text{B}_2\text{O}_6$, typically features +1 or +2 valence atoms from the first or second group of the periodic table. Meanwhile, in a double B-site perovskite, with the formula $\text{A}_2\text{BB}'\text{O}_6$, the B and B' cations exhibit a combination of oxidation states (+3, +4, +5, or +6) [26]. This dual arrangement of cations, either at the A or B sites, introduces additional complexity and flexibility to the system, enabling the appearance of new and important properties. In the following subsections, we will describe each of these perovskite structures, single and double, in greater detail.

1.2.1 Single Perovskite Oxide - ErCrO_3 case study

An example of a single oxide perovskite that shall be studied in this thesis is the case of ErCrO_3 . In this material, the element in the A-site is Er with an oxidation state of +3, Cr

in the B-site with an oxidation state as well as +3, and O as the anion with an oxidation state of -2. Knowing that the ionic radii of Er, Cr and O are 1.004 Å, 0.615 Å and 1.35 Å [27], respectively, we can determine, from equation. 1.1, it has a tolerance factor of 0.847 [28], which means it can be classified as having an orthorhombic structure [22].

A visual representation of the unit cell (space group $Pbnm$) of this structure can be seen in Fig. 1.7, where the Er atoms are depicted in green, the Cr atoms and their corresponding octahedra are shown in blue, the O atoms appear in red, and the black line represents the orthorhombic unit cell. Additionally, Fig. 1.7 highlights the evident tilt along the $[110]$ -axis of the octahedrons and their rotation around the $[001]$ axis.

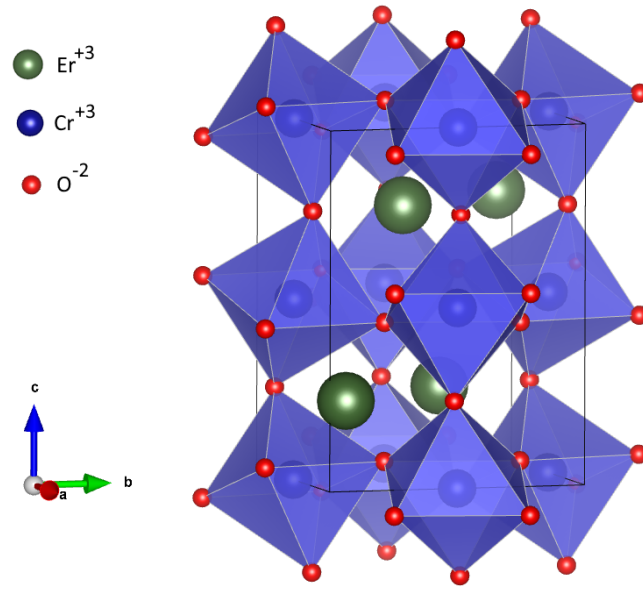


Figure 1.7: Structure representation of ErCrO_3 perovskite, produced in VESTA [29].

This material presents an antiferromagnetic G -type spin arrangement, with a T_N of 133 K, a T_N^{Er} of [6-13] K, and a T_{SR} of 22 K. These parameters are summarized in Table 1.1, where T^* is the supposed ferroelectric phase transition temperature [25] and T_N corresponds to the antiferromagnetic ordering (Néel temperature) due to the $\text{Cr}^{3+}-\text{Cr}^{3+}$. Additionally, T_{SR} symbolizes the magnetic arrangement of spins of the Cr ions in the lattice due to the Er spins, following Bertaut's notation ($\Gamma 4 \rightarrow \Gamma 1$) [30] and T_N^{Er} is the ordering temperature of the Er sub-lattice.

Space Group	T_N^{Er} (K)	T_{SR} (K)	T_N^{Cr} (K)	T^* (K)
$Pbnm$	6–13	22 ($\Gamma 4 \rightarrow \Gamma 1$)	133	460

Table 1.1: Summary of the magnetic ordering properties. Data taken from Ref. 25, 30, 31.

As previously mentioned, since ErCrO_3 has a $Pbnm$ structure, the following three types of G-type antiferromagnetic configurations can be observed: $\Gamma_1(A_x, G_y, C_z)$, $\Gamma_2(F_x, C_y, G_z)$, $\Gamma_4(G_x, A_y, F_z)$. As seen in Fig. 1.4, only the first configurations do not have a spin canting and thus do not exhibit a weak ferromagnetic component. In contrast, Γ_2 and Γ_4 exhibit one along the x and z directions, respectively. It should be noted that there are three possible kinds of exchange interactions in this material, which are $\text{Cr}^{3+}-\text{Cr}^{3+}$, $\text{Cr}^{3+}-\text{Er}^{3+}$, and $\text{Er}^{3+}-\text{Er}^{3+}$, corresponding to isotropic, symmetric, and antisymmetric anisotropic interactions respectively [32].

Due to this spin canting, at temperatures above the spin reorientation and below the Néel temperature, ErCrO_3 is weakly ferromagnetic. Moreover, the $\text{Cr}^{3+}-\text{Cr}^{3+}$ exchange interaction slightly deviates the Cr-O-Cr bond angle from the ideal value of 180° due to the Dzialoshinski–Moriya interaction, resulting in the mentioned residual spin [14].

As previously noted, ErCrO_3 , like other rare-earth chromites, belongs to a centrosymmetric orthorhombic system. Therefore, it would be surprising that this material exhibits a ferroelectric phase transition, T_{FE} (here denoted as T^*). A similar perovskite, YCrO_3 , also a canted antiferromagnet below 140 K, undergoes a ferroelectric transition around 473 K [25]. To understand the origin of the ferroelectricity in this material, a detailed study of the PDF was performed with neutron diffraction data of YCrO_3 [33]. It was shown that in a local distance range (1-6 Å), the data best fitted to a non-centrosymmetric $P2_1$ space group at the low-temperature ferroelectric phase, while in the high temperature, the PDF data was assigned to a centrosymmetric structure, as expected, in the same distance range. In other words, this type of ferroelectric materials could be locally non-centrosymmetric even though they are globally centrosymmetric.

In another work, the Direct Current (DC) magnetization and Perturbed Angular Correlation (PAC) were measured for a polycrystalline ErCrO_3 , with the intent to understand the multiferroic and magnetoelectric properties further. PAC results, showed two clear signs of local environment changes by analysing the Electric Field Gradient (EFG) parameter's evolution with temperature, one below 250 K and the other at the supposed ferroelectric phase transition ($T^* = 460$ K) [1]. So, similar to the analysis done in the YCrO_3 perovskite, it is of great interest to further analyse this local distortions and its origin with the help of the PDF method. (See section 4.4).

1.2.2 Double Perovskite Oxide - Y_2NiMnO_6 case study

Another type of perovskite that shall be studied is the double perovskite Y_2NiMnO_6 , in other words with the general formula $\text{A}_2\text{BB}'\text{O}_6$. In the A-site sits the element Yttrium (Y) with oxidation state +3, in the B-site Nickel (Ni) and B'-site sits Manganese (Mn) with the oxidation state +2 and +4, respectively. Finally, the anion is O with an oxidation state -2. This double perovskite is indexed to the monoclinic crystal structure (space group $P2_1/n$) [34]. In Fig. 1.8, a visual representation of this structure is shown, where the Y atoms are depicted in green, the Ni and Mn atoms are shown in blue and orange, respectively, as well as their corresponding octahedra, the O atoms appear in red, and the black line represents the monoclinic unit cell. Additionally, just like in the previous perovskite mentioned, we can see a tilt of the octahedral with the A-site element sitting in the corners of the cubic cell.

Since it is a double perovskite with the B-site divided, the element inside the octahedral is alternated between Ni and Mn, with the change occurring both intra-plane and inter-plane. In the first one, the octahedral with Ni at their center are directly adjacent to the ones with Mn at their center, while as we stack up the layers, the position of the Ni and Mn atoms are reversed, so there is not an adjacent same BO_6 in the [001] direction. This layered arrangement helps stabilize the crystal structure and allows to manipulate and tune the material's physical properties, such as electronic conductivity and magnetism [35], in order to satisfy the industrial and technological demands [36].

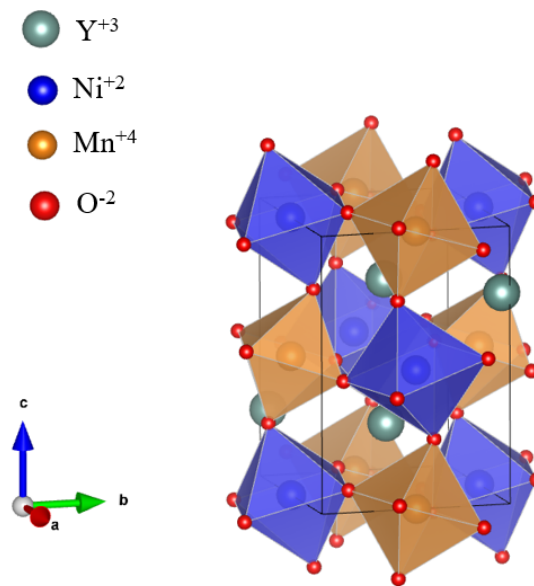


Figure 1.8: Structure of a Y_2NiMnO_6 , produced in VESTA.

In terms of magnetic properties, Kumar et al. [37] showed based on *ab initio* density-functional theory (DFT) calculations that in double perovskites with the formula R_2NiMnO_6 , where R is a rare-earth element, changes from ferromagnetic (R = Sm, La) to the antiferromagnetic E^* -type, see Fig. 1.3 e), for R = Y with magnetic frustrated Ising spin chains with $\uparrow\uparrow\downarrow\downarrow$ spin patterns [10]. Moreover, this spin configuration breaks inversion symmetry and generates a ferroelectric polarization (few microcoulomb per square centimeter) [37].

Nevertheless, the magnetic behaviour of double perovskites is of complex form due to the various exchange interactions between ions with different valencies facilitated by the connecting oxygen atoms. In these types of materials, the valencies are stabilized due to the presence of "antisite" disorder where the B and B' cations, in this case Ni^{2+} and Mn^{4+} , interchange their respective crystallographic positions [38], with the ground state magnetic properties determined by their degree of cationic ordering [39]. Y_2NiMnO_6 has been described to be ferromagnetic due to the $\text{Mn}^{4+}-\text{O}^{2-}-\text{Ni}^{2+}$ 180° superexchange interaction conforming to Goodenough-Kanamori rules [39, 40]. In addition, the "antisite" disorder can introduce antiferromagnetic interactions ($\text{Mn}^{4+}-\text{O}-\text{Mn}^{4+}$ and $\text{Ni}^{2+}-\text{O}-\text{Ni}^{2+}$) across the exchange pathways, reducing the long-range ferromagnetic ordering [39, 40]. In other words, the material can be described as having ferromagnetic clusters separated by an antiferromagnetic matrix phase, as evidenced by the bifurcation in the FC and ZFC data [9] (see Fig. 3.9 and Fig. 3.10).

2. Experimental Techniques

The following chapter is divided into two main parts. The first one briefly describes the synthesis methods used to produce the studied materials in this thesis (solid-state and sol-gel synthesis process used to produce the bulk samples of the Y_2NiMnO_6 double perovskite) and the second part will review some techniques used to characterize the structure and morphology of the samples, like XRD and SEM, their magnetic, thermodynamic, and electrical properties, using both the MPMS and the PPMS. In addition, on the topic of XRD, we will delve into the techniques of Rietveld refinement and also the PDF method, used to study the local atomic structure of perovskite-like ErCrO_3 .

2.1. Sample Preparation

In developing new materials, the synthesized samples must have the desired properties to be studied and/or to discover new physical phenomena. So, before producing the sample, it is essential to choose the proper synthesis process since the chosen method can impact some of its final properties, like, for example, phase purity. One should always be on alert to the existence of a second phase due to possible non-reactions, grain size, and crystallinity that can compromise our results. In the following section, we will describe the synthesis process and highlight some advantages and limitations of each synthesis method.

2.1.1 Solid-State Reaction

One of the most reliable and versatile sample preparations in materials science is the Solid-State Reaction (SSR), a diffusion-controlled reaction with a simple producing process of four stages. First, we mix the required reactants (in powder form) until a homogeneous mixture is obtained. Then, this mixture is ground, pressed into pellets, and heated to elevated temperatures. In each of these four stages, the material may undergo significant changes in the lattice structure, particle size, or crystallinity before becoming the reactant in the next phase of the process. Thus, several cycles of grinding and pelletizing may be necessary until a homogeneous uniform composition is obtained, usually confirmed by XRD of a small amount of the material (in this work, a powder form sample was always used).

As mentioned before, several factors play a crucial role in the success of solid-state synthesis, including heating conditions, the atmosphere it is developed in, ensuring a correct stoichiometry is obtained, or avoiding unwanted phases, the microstructure of the reactants, and their grain size and porosity. In addition, the method used to prepare the solid precursors, such as the degree of grinding or other mechanical pretreatments, can profoundly affect the reactants' reactivity and the reaction's kinetics. Thus, having a well-prepared sample with optimal particle size will increase the surface area available for the reaction, contributing to a faster diffusion or, in other words, sample formation.

Therefore, although this sample preparation method offers several advantages, such as producing thermodynamically stable phases [41] while being highly versatile, it also comes with some inherent challenges. In some situations, achieving a final homogeneous product is challenging due to the solid nature of the reactants. This can lead to incomplete reactions, resulting in secondary phases. Moreover, it often requires long exposures to elevated temperatures and several cycle repetitions to ensure the complete reaction of the materials, which can be both costly and time-consuming.

2.1.2 Sol-Gel Process

Another preparation method used to synthesize bulk materials (e.g. Y_2NiMnO_6 double perovskite samples), and in this way, perform a comparison with the previously discussed method, is the Sol-Gel (SG) synthesis. This low-cost, well-established, and flexible synthetic route typically focuses on production in the micro- and nano-range [42] particle sizes.

As previously indicated, one of the drawbacks of solid-state reactions is the inhomogeneity of the starting materials. This results in mass transport limitations, often resulting in incomplete reactions, such as second phases, as diffusion barriers block further conversion. In contrast, sol-gel synthesis allows for better atomic-level mixing at lower time and temperature synthesis, with greater control over particle size [43].

For the synthesis of perovskites, the most used sol-gel technique is the Pechini method [42]. This technique stands out for its simplicity, low temperature, and excellent control over the composition of the final product. In contrast to the previous method, it uses chelating agents to prevent metal segregation and polyhydroxy alcohols to improve uniformity further. This can significantly impact thermal decomposition and phase formation, leading to a well-ordered perovskite structure with minimal unwanted phases.

In summary, unlike in the SSR method, which usually relies on oxides as precursors, such as the approach used in this thesis, the SG process typically employs carbonates or nitrates. These precursors are dissolved in a homogeneous solution, displaying better reactivity due to atomic-level mixing [44], thus requiring lower temperatures for phase formation [45]. Additionally, the incorporation of polymeric agents, such as polyvinyl alcohol (PVA), restricts cation mobility, ensuring local stoichiometry is maintained and minimizing the precipitation of unwanted phases [46, 47].

2.2. Sample Characterization Techniques

Understanding a material's properties is of significant importance in the scientific community, either in the academic field for research purposes or in the engineering world, to ensure that we are in the presence of a material with the desired properties. As a result, a wide range of characterization techniques is available, which can be divided into microscopic and macroscopic ranges. The following section will delve into the fundamental principles of the characterization techniques used in this thesis.

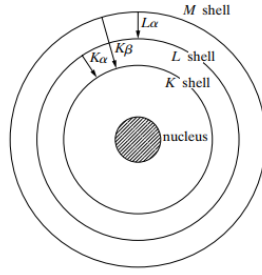
2.2.1 X-Ray Diffraction

XRD is a non-destructive characterization technique used to determine the crystalline structure of materials. In particular, it allows us to define several structural properties of the studied material, such as, if the data collected is of sufficiently high quality, the lattice parameter, atomic positions, atomic displacement factor, strain, or even the grain size. In addition, since the diffraction pattern produced is an intrinsic property of the material, like a “fingerprint”, this can be used for phase identification, determining if the sample is pure or if a second phase may also be present.

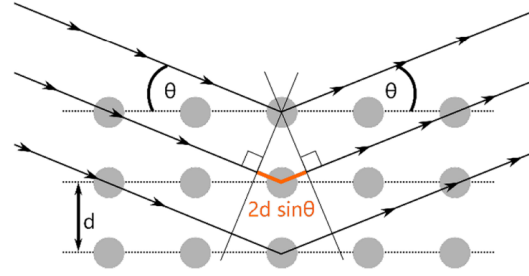
A typical XRD experimental setup consists of four major components: an X-Ray source, a sample holder, a detector, which records the intensity of the diffracted X-Rays as a function of the diffraction angle (2θ), and a connected Personal Computer (PC) equipped with suitable data acquisition software.

X-Rays are generated at the source, which comprises a tube with a Tungsten (W) filament at one end and a target, typically Copper (Cu), at the other. When the filament is heated, electrons are extracted and accelerated by an electric field toward the Cu target. These electrons create vacancies in the inner K-shell of the copper atoms, which are subsequently filled by electrons from the L-shell, resulting in K_α radiation, or the M-shell,

producing K_β radiation. Fig. 2.1 a) presents a schematic representation of the previously described electronic transitions in the atom.



(a) Schematic of electronic transitions in an atom. Taken from Ref. 48.



(b) Illustration of Bragg's radiation reflection. Taken from Ref. 49.

Figure 2.1: Working Principle of X-Ray diffraction technique.

The X-Rays interact with the crystalline structure of the sample, scattering according to the periodic arrangement of atoms, resulting in either constructive or destructive interference. This interference depends on the spacing between the atomic planes, creating a diffraction pattern. To ensure that the X-Rays interacting with the sample are monochromatic ($\lambda_{K_\alpha} = 1.5418 \text{ \AA}$), a Nickel (Ni) filter is employed to remove K_β radiation, with minimal loss of K_α . The K_α radiation is ideally suited for examining crystalline materials because its wavelength matches the scale of the interplanar distances within most crystals, allowing for precise diffraction analysis.

The fundamental principle underlying X-Ray diffraction is Bragg's Law, which relates the angle of incidence of the X-Rays to the spacing between the atomic planes in a crystal. A visual representation of the Bragg's radiation reflection is demonstrated in Fig. 2.1 b). Moreover, Bragg's Law is mathematically expressed as:

$$n\lambda = 2d_{hkl} \sin(\theta) , \quad (2.1)$$

here, λ is the X-Ray wavelength, d_{hkl} is the interplanar spacing of the crystal planes, θ is the angle of incidence, and n is the order of reflection. This law dictates that diffraction occurs when the path difference between X-Rays scattered by adjacent planes is an integer multiple of the X-Ray wavelength, resulting in constructive interference and the appearance of a diffraction peak that is indexed using Miller indices (hkl), which describes the orientation of the atomic planes. Since the diffraction pattern is a direct representation of

the crystal's reciprocal lattice, by analyzing them, it is possible to determine several properties, such as the lattice parameter, the Atomic Displacement Parameter (ADP), and the space group (symmetry of the crystal).

2.2.1.1 Peak Broadening

Furthermore, peak broadening can provide further information about the crystallite size and microstrain. These are estimated from the Full Width at Half Maximum (FWHM) of the diffraction peaks by the Scherrer equation, expressed as:

$$D = \frac{K\lambda}{\beta \cos(\theta)} , \quad (2.2)$$

where D is the crystallite size, K is the shape factor (~ 0.94 for spherical crystallites), λ is the incident X-Ray wavelength, and β is the FWHM. To separate the contributions of crystallite size and microstrain, the Williamson–Hall method can be used. Assuming a uniform and isotropic strain distribution (Uniform Deformation Model), the broadening is given by:

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\epsilon \sin \theta , \quad (2.3)$$

where ϵ represents the average microstrain.

2.2.1.2 Rietveld Refinement

When the data obtained from the XRD is of sufficiently high quality, we can perform a refinement to obtain valuable information, such as microstructural details, atomic occupancy, grain size, and strain. Several refinement analysis methods and tools are available to perform this. The FullProf software suite, developed by Rodriguez-Carvajal et al. [50], uses the Le Bail and Rietveld methods for any X-Ray or neutron diffraction pattern. This software was used to analyze the diffraction patterns presented in this thesis.

The principle of the Rietveld method is described as minimizing the difference between the calculated and observed intensities of the fitted powder diffraction profiles using the least squares criteria. We start by employing the Le Bail method, which does not account for peak intensities. Instead, we focus on the peak position and lattice constants to index the Bragg positions within our chosen hypothetical crystallographic space group.

After reaching a good fit with this method, we advance to the Rietveld refinement, which analyses the peak shapes, positions, and intensities.

Since we are dealing with statistical analysis to find the best fit, it is important to have a numerical "figure of merit" to quantify the quality of the fit. Some of these "figures of merit" are as follows [51]:

$$\chi^2 = \frac{\sum_{i=1}^n (Y_i^{\text{obs}} - Y_i^{\text{calc}})^2}{n - p} = \left(\frac{R_{wp}}{R_{\text{exp}}} \right)^2 \quad \text{and} \quad (2.4)$$

$$R_B = \frac{\sum_{j=1}^m |I_j^{\text{obs}} - I_j^{\text{calc}}|}{\sum_{j=1}^m I_j^{\text{obs}}}, \quad (2.5)$$

where in equation 2.4, also known as the goodness of fit, Y_i^{obs} and Y_i^{calc} are, respectively, the observed and calculated intensity values, n is the number of points, and p is the number of varied parameters. In addition, equation 2.5 (Bragg R factor), unlike the previous one, has no statistical basis since it is a reflection intensity-based (I) R factor.

There is no consensus on the complete reliability of these figures since no acceptance value determines when a good fit has been achieved. Therefore, the most used "figure of merit" is equation 2.4, which should approach the unity value for a perfect fit to the available data, although it rarely happens.

2.2.2 Pair Distribution Function

The crystallographic routines described until now only reveal the average structure of the samples. So, a different approach is needed to understand more complex materials on an atomic scale and predict their properties. The PDF, a total scattering analysis method, which was initially applied to the study of liquids and amorphous materials [52], is obtained from the diffraction pattern of a sample. It gives an expression for a probability of finding pairs of atoms separated by a real space distance, in other words, a bond length distribution, given by the following expression [53]:

$$G(r) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} Q[S(Q) - 1] \sin(Qr) dQ. \quad (2.6)$$

This equation can be seen as a sine Fourier transform from a $Q_{\min}$ to a $Q_{\max}$ of a total coherent scattering function $S(Q)$. This latter function is obtained by normalizing the

experimental data to the sample's total cross-section (square of the average atomic scattering factor). Moreover, $Q[S(Q) - 1]$, when rescaled by Q and averaged over all angles, is written as $F(Q)$, and $Q = 4\pi \sin(\theta)/\lambda$ is the magnitude of the scattering vector.

Another way to see this function, in a statistical sense, is by examining a similar function, the Radial Distribution Function (RDF), defined as:

$$R(r) = 4\pi r^2 \rho(r) , \quad (2.7)$$

where $\rho(r)$ is the local atom pair density. This function can be seen as the number of atoms inside a shell of thickness dr at a distance r from the origin, $R(r)dr$, and to relate it to the $G(r)$ function, we have to divide it by r . To better illustrate the process of this analysis, Fig 2.2 demonstrates how the $G(r)$ function is obtained from a spherical shell of thickness dr at a distance r from the origin.

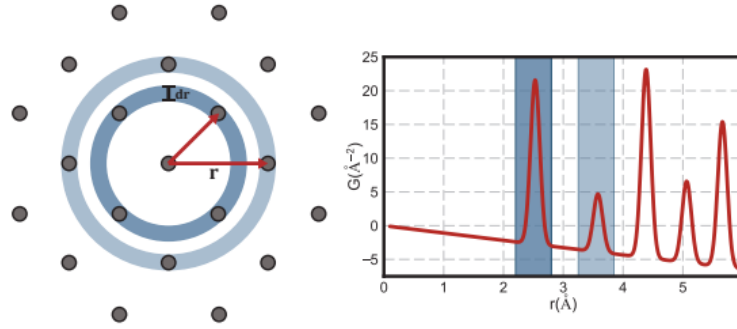


Figure 2.2: Illustration on how a $G(r)$ graph is constructed from a spherical shell of thickness dr , distance r from the origin. Taken from Ref. 52.

In an ideal world, the range of the integral goes from $Q_{\min}$ of zero to infinity $Q_{\max}$, but this is impossible to reciprocate. The usage of higher angles is needed since, at these values, the atomic form factors reduce the coherent scattering intensity and counting statistics rapidly deteriorate [53]. So, the resolution of the PDF is given by $\delta r \approx \pi/Q_{\max}$, with $Q_{\max}$ values, typically being sufficient for most experiments, around 25 $\text{\AA}$.

Compared with other conventional crystallographic analyses, the advantages of using PDF analysis are shown when studying a material with some disorder in its structure. Here, the former assumes periodicity, only considering the Bragg peaks, and ignores the diffuse scattering, which significantly impacts the results because it only gives an average picture of the structure and does not show local variations. The real-space PDF method considers both diffuse scattering and Bragg scattering, allowing us to see and describe

the disorder of the said material. These materials have attracted a lot of interest due to their technological potential. Some examples that will be useful in this thesis are rare earth orthochromites perovskites, like YCrO_3 [33], or even ferroelectrics [54], whose local structure has been studied with PDF analysis.

To convert and analyze the PDF data, adequate software is needed. In this thesis, we used xPDFsuite [55], a powerful PDF analysis software with many features, including raw data visualization and modulation (creation of the $S(Q)$, $F(Q)$ and $G(r)$ data). Also, PDFgui [56], where we can use the transformed $G(r)$ data and refine structural parameters, like, for example, lattice parameters, site occupancies, isotropic/anisotropic atomic displacement parameters, scale parameters and also the atomic position. Although this may seem the same as a Rietveld refinement, in PDF analysis, the structural model obtained comes from only length scales corresponding to the r range defined, allowing for the study of the local structure.

Therefore, to obtain the correct $G(r)$ data, the data reduction process is crucial to ensure the accuracy and quality of the resulting PDF data, eliminating possible artefacts and minimizing noise in the experimental raw data. Below is an outline of the methodology and reasoning behind each step, following a proposed approach by Simon Billinge, one of the responsible for the software used here [57]:

1. **Dataset Selection:** A representative dataset is chosen from the available data collection to perform the preliminary analysis and parameter adjustments, which will be later used for all the datasets.
2. **Visual Inspection in xPDFsuite:** The dataset is loaded into xPDFsuite, then we set $Q_{\text{max_inst}}$ and Q_{max} to their maximum values, allowing for a complete view of the dataset. Then, we select the 2D plot option but display, for now, $I(Q)$ and $F(Q)$, where the latter one is the most important to check.
3. **Identification of Data Quality:** In $F(Q)$, we want to see how bad/good the data is by looking for "glitches" that often happen at the edges of the data in the high- Q range. Then, we identify the Q value point on this plot to the left of the biggest seen "glitch"; for now, the minor "glitches" are unimportant.
4. **Setting $Q_{\text{max_inst}}$:** Once identified this Q value, we set the $Q_{\text{max_inst}}$ to it. This is because we want the polynomial to fit over as wide a Q range as possible, but we

do not want it to try and fit signals that are not real ("glitches"). For now, the statistical noise does not matter, we are just caring about these artefacts.

5. **Optimization of $Q_{\max}$:** With $Q_{\max_inst}$ fixed, we move the $Q_{\max}$ value around from lower to higher and see how it affects the PDF. It is also useful now to plot as well $G(r)$ and interchange what we are looking at between this and $F(Q)$. Then, without changing $Q_{\max_inst}$, we move $Q_{\max}$ around to get the right balance between resolution in the PDF (which wants a higher $Q_{\max}$) and reduction of noise (which wants lower $Q_{\max}$), where the real measure is what $G(r)$ looks like. In $F(Q)$, we are looking for signal-noise ratio, so we identify what we think is a signal and want it to be comparable to, or higher than, what we recognise as noise. Nevertheless, since the appearance of noise depends on the binning, the better measure is how small the ripples look in $G(r)$.
6. **Finalization of $Q_{\max}$:** Once an appropriate $Q_{\max}$ is identified, it is fine-tuned to a point where the signal in $F(Q)$ intersects or closely approaches the baseline (the $F = 0$ line). This final adjustment ensures the analysis captures the structural details while maintaining clarity in the PDF data.

It is also worth mentioning that even before refining the data through a structural model, we can extract information from the peak positions (bond distances of atom pairs in the sample), peak intensities, peak width and shape in the $G(r)$ data. Ideally, these would appear as delta functions. Still, in an actual material, there will be a broadening of the peaks due to strain or atomic displacements, defined by a Gaussian broadening term ij given by:

$$\sigma_{ij} = \sigma'_{ij} \sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} - Q_{\text{broad}}^2 r_{ij}^2}. \quad (2.8)$$

The first term in the expression, σ'_{ij} , is the peak width given by the atomic displacement parameter tensors for the atoms [53]. In contrast, the delta functions (δ_1 and δ_2), a refinable parameter in PDF, are the correction parameters that describe the correlated atomic motion, which contains detailed information about the bonding and the atomic potential in the materials [58]. Another important term is the Q_{broad} , a broadening factor resulting from the finite limit of the experimental Q resolution that also leads to a decreasing peak amplitude for larger r values. This effect also follows a Gaussian shape, modelled by multiplying the calculated profile by:

$$B(r) = e^{\left(\frac{r^2 Q_{\text{damp}}^2}{2}\right)}. \quad (2.9)$$

Thus, before applying and refining the structural model, we need to obtain these two terms, Q_{damp} , an instrumental resolution parameter [59], and Q_{broad} . To do so, we perform a calibration step of an assumed perfectly crystalline material, typically Ni, and fix these obtained values to the PDF data model of the sample we wish to refine. After doing this, we can refine the PDF data by creating a crystallographic model containing information about the atoms, their positions, and dynamics (atomic displacements and site occupancies). Then, following the refinement order of first the scale factor and the lattice parameters, the atomic displacements (isotropic or anisotropic) and δ_1 or δ_2 , never both at the same time and finally the atomic positions, we obtain a G_{calc} , which is then compared with the data $G_{\text{obs}}(r)$, building an R_w , expressed as:

$$R_w = \sqrt{\frac{\sum_{i=1}^n w(r_i) [G_{\text{obs}}(r_i) - G_{\text{calc}}(r_i)]^2}{\sum_{i=1}^n w(r_i) G_{\text{obs}}(r_i)}}, \quad (2.10)$$

where (w_{r_i}) is the inverse of the estimated standard deviation of each data point [53]. This figure of merit is minimized by varying the chosen parameters by a least squares refinement, just like in the whole profile Rietveld refinement.

2.2.3 Scanning Electron Microscopy

SEM is a highly versatile advanced instrument used to examine and characterize materials on the nanometer (nm) to micrometer (μm) length scale. This characterization technique can produce three-dimensional high-resolution images with a spatial resolution of approximately 1 nm [60].

SEM works by focusing a high-energy electron beam, typically in the range of 1 keV to 30 keV [61], produced in the electron gun at the top of the instrument. Then, a condenser lens reduces the beam diameter until the final lens, the objective lens, focuses the beam on the sample surface, which is mounted on a stage in an adequate chamber area (under vacuum). Furthermore, the electron beam position on the sample is controlled by the scan coils that are situated above the objective lens, allowing it to scan over the X-Y plane. A visual illustration of this typical SEM setup is depicted in Fig. 2.3 a).

Moreover, as the beam interacts with the sample, it generates various signals, including secondary electrons, backscattered electrons, and characteristic X-Rays, as seen in Fig. 2.3 b), which are then collected by the detectors and analyzed on an external computer with proper software.

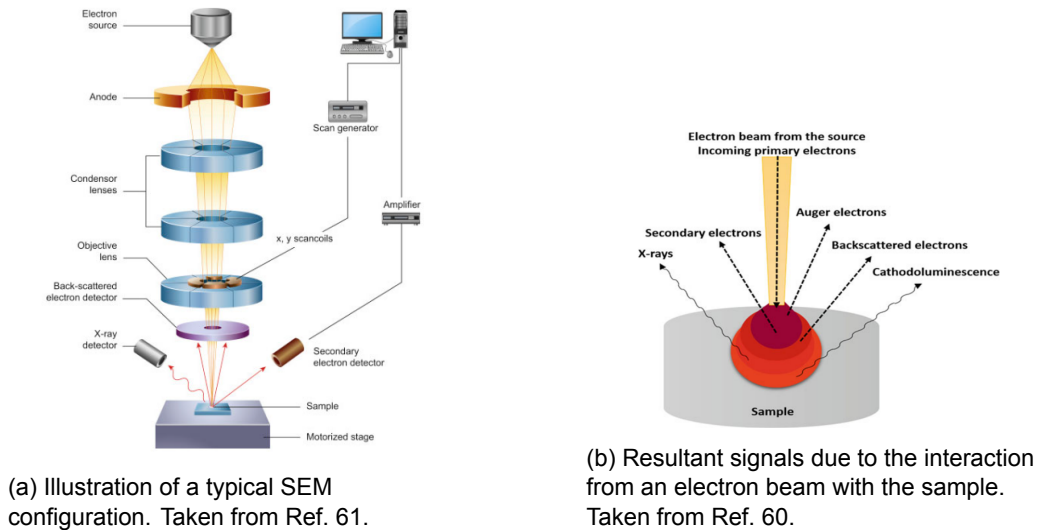


Figure 2.3: Working principle of a Scanning Electron Microscopy.

From the produced signals in SEM, the most commonly used are the secondary and backscattered electrons. The first is produced by inelastic scattering interactions between the electron beam and the sample's valence electrons, making them responsible for generating high-resolution images of the sample's surface topography. On the other hand, the backscattered electrons are elastically scattered from the sample's surface and used for distinguishing different elements based on their atomic number, with heavier elements producing stronger signals, appearing brighter in the contrasting images. It is worth mentioning that when performing an SEM analysis, we can also perform an elemental analysis, thanks to EDS.

2.2.4 Energy Dispersive X-Ray Spectroscopy

As shown in Fig. 2.3 b), characteristic X-Rays are emitted as the atoms return to their ground state, with each element having its unique energy value, allowing the identification of the sample's elemental composition. As previously mentioned, Energy Dispersive X-Ray spectroscopy (EDS or EDX) utilizes the characteristic X-Rays emitted from the interaction of the electron beam with the sample during SEM imaging. This technique is a fast and non-destructive method of elemental detection on the micron scale, used in the materials science field, geology, and life science (biological cellular samples) [62].

This characterization method takes advantage of the fundamental principle that each element has a unique electronic structure, producing X-Rays unique to the element and allowing for posterior identification. A visual representation of this process is shown in Fig. 2.4, which summarizes the key steps: a) Depicts the interaction between the electron beam and the atom, which is ionized, ejecting valence electrons. If this occurs in the inner electron shell, an electron from a higher energy shell fills the created hole. Thus, electromagnetic radiation is created, equal to the surplus difference between the two energy shells, classified as X-Rays. b) shows a schematic view of the EDS detector paired with SEM imaging. c) demonstrates that the created X-Ray spectrum is a semi-quantitative elemental "fingerprint". d) displays a spatially mapped count, revealing the relative elemental composition.

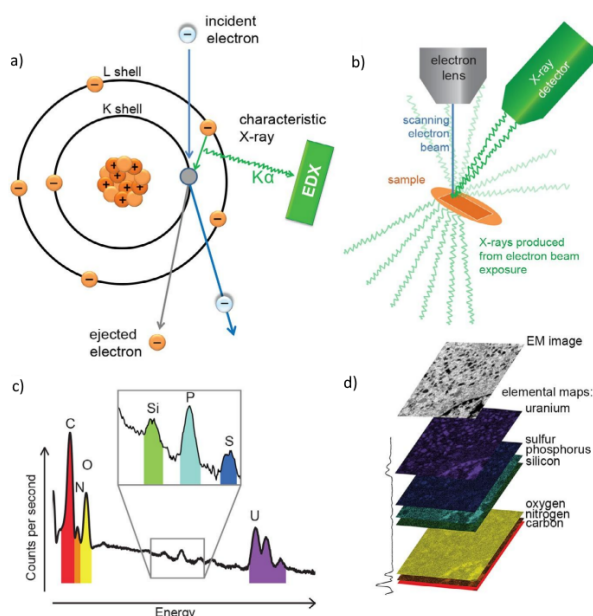


Figure 2.4: a) Interaction between the electron beam and the atom, which is ionized, ejecting valence electrons. If this occurs in the inner electron shell, an electron from a higher energy shell fills the created hole. Thus, electromagnetic radiation is created, equal to the surplus difference between the two energy shells, classified as X-Rays. b) Schematic of the EDS detector paired with SEM imaging. c) The created X-Ray spectrum is a semi-quantitative elemental "fingerprint". d) The spatially mapped count reveals the relative elemental composition. Adapted from Ref. 63.

In detail, as the incident electron beam hits an atom within the sample, it may excite an electron in an inner shell, ejecting it and creating an electron hole, which is then filled with another electron from an outer shell since this configuration is not stable. As this occurs, X-Ray radiation, resulting from the difference in energy between the higher and lower energy shells, is emitted and captured by a detector. This detector measures the relative abundance of X-Rays to their energy, thus obtaining an EDS spectrum, which provides a

semi-quantitative elemental fingerprint. The counts for each element are spatially mapped to reveal their relative elemental composition. It is worth mentioning that for samples containing oxygen, the results do not accurately identify this specific element's relative abundance in the sample.

2.2.5 Magnetic Properties Measurements

In the ultrasensitive electric and magnetic measurement systems industry, SQUIDs have played a key role in their development, offering the ability to make measurements that no other methodology can. SQUIDs can be described in four quantum effects: superconductivity, Meissner effect, Flux quantization, and Josephson effect [64]. Their differential high sensitivity arises from their ability to convert minor magnetic flux variations into measurable voltage changes. Hence, they can measure any physical quantity that can be transformed into magnetic flux, for example, magnetic fields and susceptibilities, currents, or voltages.

SQUIDs can be divided into two main categories, Radio Frequency (RF) SQUID and DC SQUID. On the one hand, the first consists of a single Josephson junction mounted on the superconducting ring. When we apply an oscillating current, there is a voltage fluctuation due to the interaction of the junction and the ring, allowing for the measurement of the magnetic flux. On the other hand, the second uses two Josephson junctions in parallel, as seen in Fig. 2.5 a) and its equivalent electric circuit in Fig. 2.5 b), thus, depending on the strength of the magnetic field on the loop, shows quantum interference due to the electrons tunnelling through the junctions. Furthermore, the voltage across is a periodic function of the external magnetic flux that flows through the ring with a period equal to the flux quantum Φ_0 [65], making it more sensitive.

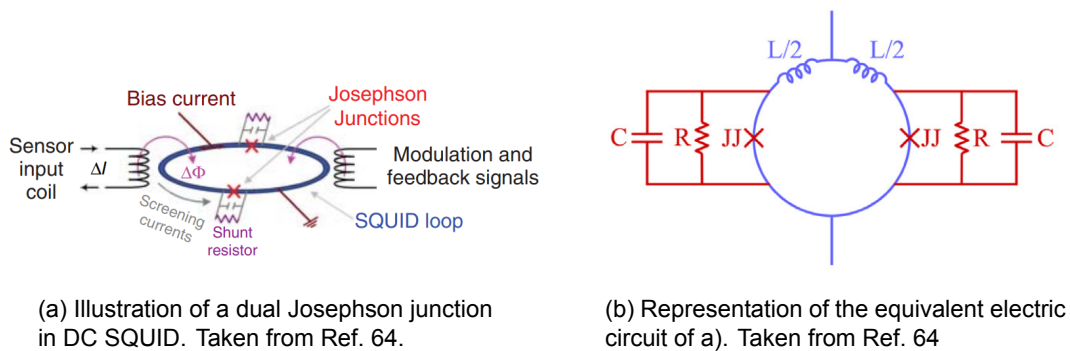


Figure 2.5: Working principle of a DC SQUID.

In this thesis, the magnetic measurements were performed using a SQUID magnetometer (MPMS from Quantum design). Here, we will discuss their definitions, following the reference [66], that will be later used in the study of the magnetic properties of Y_2NiMnO_6 . Firstly, a magnetic material is described as having many atoms with magnetic moments, where M is the magnetization, defined as the magnetic moment per unit volume. If this vector field is linearly related to the magnetic field H , we can write the following expression:

$$M = \chi H, \quad (2.11)$$

where χ is the magnetic susceptibility. Furthermore, this dimensionless property can also be tabulated in terms of the molar magnetic susceptibility, as $\chi_m = \chi V_m$, or as mass susceptibility, $\chi_g = \frac{\chi}{\rho}$. By studying the behaviour of magnetic susceptibility, we can infer how atomic magnetic moments are ordered. For example, if the susceptibility is negative, the material is dominated by diamagnetism, and if it is positive, it is dominated by paramagnetism. In the latter one, the temperature dependence of the susceptibility, at low field regime, is given by the Curie law, defined as:

$$\chi = \frac{C}{T} = \frac{n\mu_0\mu_{eff}^2}{3k_B T}, \quad (2.12)$$

where C is the Curie constant and μ_{eff} is the effective paramagnetic moment, which can be expressed as:

$$\mu_{eff} = g_J\mu_B\sqrt{J(J+1)}, \text{ where } g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}. \quad (2.13)$$

Here, J is the angular momentum quantum number ($J = L + S$), μ_B is the Bohr magneton, and g_J is the Landé g-factor. Low-field magnetization measurements can be performed to obtain the material's Curie temperature or the Néel temperature, which is similar to the previous one (ferromagnetism) but used as an order parameter for antiferromagnets. To do so, the thermal dependence of low-field magnetization $M(T)$ is acquired after the sample has been cooled with a magnetic field and/or without an applied magnetic field.

In Field Cooling (FC), we cool the sample to the desired temperature under an applied magnetic field. Then, under a constant applied magnetic field, we take measurements

while heating the sample (FCH) or cooling (FCC) in the same temperature range. Meanwhile, in Zero Field Cooling (ZFC), the sample is cooled without a magnetic field to the lowest temperature. We apply the constant magnetic field and take the magnetization measurements while sweeping the temperature to the desired range.

Another important magnetic measurement is the isothermal curves, $M(H)$, which can be used to evaluate, *e.g.*, the saturation magnetization. In addition, these curves can also be helpful, *e.g.*, for calculating the magnetic entropy variation (ΔS_m) of a magnetic sample. The Magnetocaloric Effect (MCE) is a thermodynamic property that changes the temperature in a magnetic sample through magnetic field variation, which can be estimated from the Maxwell thermodynamic relation [67]:

$$\Delta S_M(T, \Delta H) = \int_0^H \left(\frac{\partial M(H, T)}{\partial T} \right)_H dH, \quad (2.14)$$

in addition, to determine the potential of the sample as a magnetic refrigerator, we can also calculate the Relative Cooling Power (RCP), described in equation 2.15, where $\Delta S_m^{\max}$ is the peak value on the $\Delta S_m(T)$ curve plotted for a specific field change and ΔT_{FWHM} is the full width at half maxima of the same curve [67].

$$RCP = \Delta S_m^{\max} \times \Delta T_{FWHM}. \quad (2.15)$$

To calculate the MCE, first, we cool the sample to the lowest temperature, and then after stabilizing at this temperature, we begin measuring by varying the field from zero up to a certain maximum, typically around 50 kOe. It is worth mentioning that in each step, the magnetization is measured at a fixed temperature but in a sweeping field mode. Once the maximum chosen field is reached, we perform the measurements on a decreasing field until 0 Oe is reached again. At this point, we heat the sample until it reaches its paramagnetic region (typically 20 K above); only then is the sample cooled again to perform the same measuring cycle, but at a higher temperature than the previous one set. This resets the sample magnetic state (see Ref. 68 for loop method details).

2.2.6 Heat Capacity and Resistivity Measurements

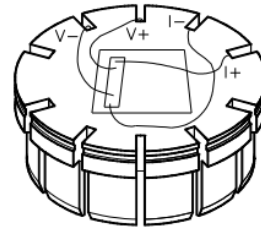
Other sample characterization technique used were, Heat Capacity and Resistivity Measurements using a PPMS, designed by Quantum Design, the same producer as the

MPMS previously mentioned. This device is a versatile and advanced automated low-temperature and magnet system. Some of its available measurement options are electrical transport, Ferromagnetic Resonance (FMR) spectroscopy, magnetometry, thermal measurements, multi-function probes, and optics [69], where sample environment controls include fields up to 9 T and a temperature range of 1.9 - 400 K. In this thesis, we used the DC Resistance option in the electrical transport to calculate a sample's Resistivity and Heat Capacity option in the thermal measurements.

In the DC resistance option, we add to the PPMS controller a configurable resistance bridge board, a device mounted on Fig. 2.6 a), where, since none of the four channels on the user bridge board is fixed to a specific system operation [70], we can perform a four-wire resistance measurement. This is of special interest because this configuration greatly reduces the contribution of the leads and joints to the resistance measurement [70]. Here, current is passed through a sample via two current leads, while two separate voltage leads that draw very little current measure across the sample the potential difference, as seen in Fig. 2.6 b). This way, using Ohm's law, we can accurately determine the material's resistance since we know the current and the voltage drop across the sample to a high degree of certainty. PPMS supports resistance from $10 \mu\Omega$ to $5 \text{ M}\Omega$, in addition to a current range of 2 nA to 8 mA. It can also limit the voltage, current, or power applied to the sample so that more delicate devices are not damaged.



(a) Example of a test station, from Quantum Design, with a puck mounted. Taken from Ref. 69.



(b) Schematic of a four-wire resistance measurement on the sample. Taken from Ref. 70.

Figure 2.6: Electrical Transport - DC Resistance measurement details.

As mentioned before, another physical property that will be studied, and also PPMS excels in, is the Heat capacity (C_p), an important thermodynamic property of a material. This system can perform high-precision microcalorimetry experiments, allowing the observation of the Heat Capacity as a function of temperature, an essential property in identifying possible electronic or magnetic phase transitions in materials. To do this measurement on

the PPMS, we begin by loading the sample, which should not be bigger than a 3x3 mm size, onto a Heat Capacity puck. Fig. 2.7 illustrates the sample mounting station for a Heat Capacity measurement on the PPMS system. Furthermore, the samples must be attached to the platform with a thermal grease to provide a thermal link between them. In doing so, we need to account for the Heat Capacity of the puck and grease. Thus, we make an addenda measurement with just these two components first, and only then can we make the actual sample measurement [71]. With these two data sets, PPMS automatically makes the necessary corrections, ensuring that only the sample's Heat Capacity is recorded.



Figure 2.7: Heat Capacity sample mounting station. Taken from Ref. [72].

In this way, we can measure the Heat Capacity as a function of temperature over a broad range, which was performed in this thesis, more specifically, from 10 K to 300 K, for the sample Y_2NiMnO_6 . The Heat Capacity, C_p , is measured by monitoring the amount of heat required to raise the sample's temperature by a small increment and is typically expressed in terms of Joules per Kelvin (J/K) [69]. This measurement is essential for understanding phase transitions in materials, as changes in C_p are often associated with transitions between different electronic, magnetic, or structural states [71]. These transitions can reveal valuable information about the material's behaviour, such as the presence of magnetic ordering (like ferromagnetic or antiferromagnetic transitions) or electronic phase transitions (ferroelectricity), shown as an anomaly in the data, contributing to the understanding of its multiferroic properties [71].

The precision of the Heat Capacity measurement is crucial as it allows for detecting subtle changes in the material's thermodynamic response. The PPMS system provides highly accurate data, typically down to 10^{-8} J/K at 2 K (for Zero Field) [69], enabling the observation of phase transitions that might otherwise be difficult to detect. The temperature-controlled environment, combined with the precise calorimetric capabilities, make the PPMS an ideal tool for studying materials that undergo complex phase transitions, especially those with competing ferroic orders like the multiferroic Y_2NiMnO_6 [9].

3. Double Perovskite Study - Y_2NiMnO_6

Double perovskites, such as the one studied in this thesis Y_2NiMnO_6 , have brought a lot of attention to the scientific community due to their multifunctional properties arising from the strong interplay between spin, orbital and charge degrees of freedom [73]. These properties allow the integration of a variety of cation species due to the flexible crystal structure of perovskites, which provides unique magnetic, electronic, and thermal properties, positioning them as promising candidates for a wide range of applications, including optics, photonics, electronics, and catalysis [74].

In the preceding chapters, we introduced the fundamental concepts of this double perovskite and outlined the experimental techniques used in this study, including the synthesis methods and characterization tools. In this following chapter, we provide a comprehensive analysis of the structural, morphological, chemical, and magnetic characterization of bulk Y_2NiMnO_6 , as well as Heat Capacity and Resistivity measurements of the sample, which has been synthesized by two different methods, sol-gel and solid-state reaction. Thus, we aim to elucidate the relationships between synthesis routes, macroscopic characteristics, and functional properties of Y_2NiMnO_6 , providing valuable insight into the optimization of double perovskite materials for future technological advancements.

3.1. Experimental details

For the synthesis of Y_2NiMnO_6 we employed two distinct methods: the solid-state and the sol-gel process. In addition, in the solid-state reaction, while following the same synthesis steps, we used two different Mn-based reagents, as described in Fig. 3.1. The synthesis process for the solid-state reactions followed the ones described in the articles [75, 76] and for the sol-gel process in the paper [77].

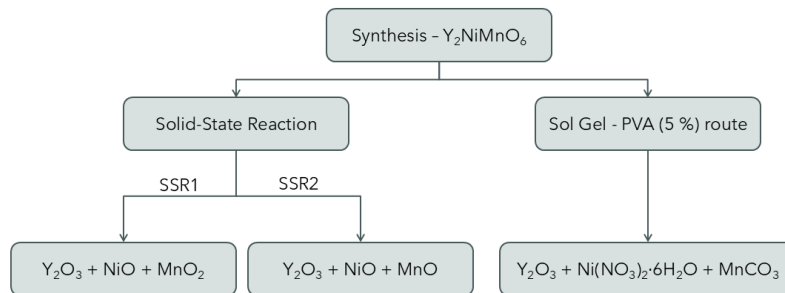


Figure 3.1: Y_2NiMnO_6 sample synthesis path.

3.1.1 Solid-State Reaction

Starting with the solid-state reaction method, polycrystalline samples of Y_2NiMnO_6 were synthesized with high purity reagents: Y_2O_3 (99.99 %), NiO (99.998 %), and either MnO_2 (99.996 %) or MnO (99.99%) for the SSR1 and SSR2 methods, respectively. All reagents were purchased from Alfa Aesar.

First we determined the stoichiometric proportions of each reagents for the SSR1 and SSR2 methods, in order to obtain a final sample of Y_2NiMnO_6 weighing 2 grams, which were then mixed and grounded in an Agatha mortar, pressed into pellets, and then calcined at 800 °C for 12 hours. Subsequently, several intermediate grinding, pressing and sintering cycles were carried out to achieve a homogeneous sample. After each cycle, X-Ray powder diffraction measurements were performed in continuous scanning mode using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with the Rigaku SmartLab high-resolution X-Ray diffractometer [78] to analyse the crystalline structure of the sample. Finally, the sample was sintered at 1250 °C for 24 hours. A summary of this process is described in Fig. 3.2, and Fig. 3.3 shows the X-Ray evolution of the sample with each completed cycle.

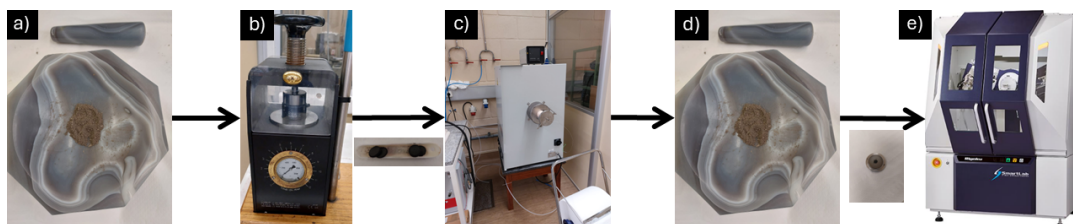


Figure 3.2: Synthesis process cycle of the Y_2NiMnO_6 sample. a) and d) illustrates the grinding of the powder in a Agatha mortar, b) shows the pressing process of the grounded powder into a pellet, c) shows the Termolab furnace used for the synthesis, and e) the Rigaku SmartLab [78] high-resolution X-Ray diffractometer used.

Its also worth noting that the synthesis steps for both the SSR1 and SSR2 methods were identical, including the duration of the grinding process, an important parameter to achieve a homogeneous powder. Fig. 3.3 illustrates the X-Ray diffraction pattern evolution of both SSR1 and SSR2 samples, taken after each grinding, pelleting and sintering cycle. The symbols shown represent the phase each peak is indexed to, where initially we identify the peaks that do not correspond to the pure phase Y_2NiMnO_6 , in order to track their disappearance throughout the synthesis process. Nevertheless, after the final treatment, a residual NiO secondary phase remains in both synthesis routes.

Moreover, as seen in Fig. 3.3, there are no significant differences in the XRD results between SSR1 and SSR2. Due to the higher volatility of the Mn-based reagents, an extra

5% of these reagents was added twice during the synthesis to compensate for material loss. This adjustment helped to reduce the residual Y_2O_3 and NiO peaks observed in the intermediate X-Ray diffraction patterns. However, despite these efforts, the final samples for both SSR1 and SSR2 exhibited a minor secondary phase of NiO , indicating incomplete reaction or phase separation during the synthesis. Thus, only the SSR1 sample will be used in the following sections for comparison with the SG sample.

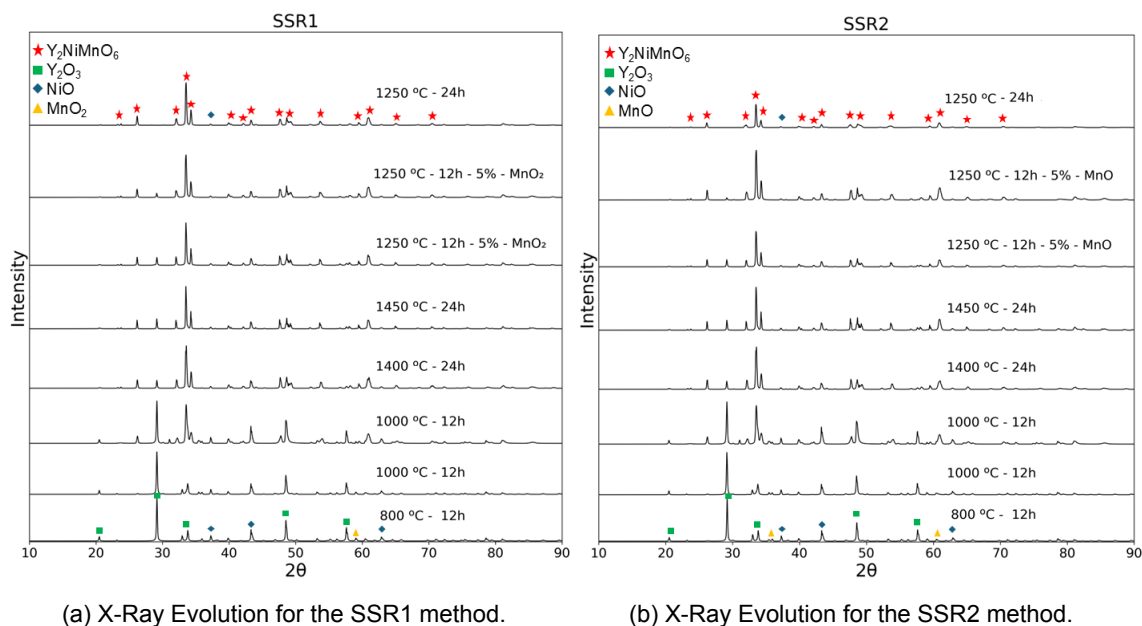


Figure 3.3: X-Ray patterns as a function of the sintering temperature and time of the Y_2NiMnO_6 samples produced by the solid-state reaction.

3.1.2 Sol-Gel Process

As for the sol-gel process, to obtain as well 2 grams of Y_2NiMnO_6 , we used stoichiometric proportions of high purity Y_2O_3 (99.99 %), MnCO_3 (99.9+ %) and $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (99 %). We started by preparing a 5 % Polyvinyl Alcohol (PVA) solution, made by dissolving PVA powder (98-99 %) in deionized water at 80 °C. Then we added 5 ml of nitric acid (HNO_3) to the beakers containing the reagents Y_2O_3 and MnCO_3 . The resulting mixtures were then transferred into a flask containing 50 ml of the PVA solution. Separately, $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was dissolved in 5 ml of HNO_3 , and added to the flask. Furthermore, the beakers were rinsed with approximately 10 ml of deionized water to recover any residual material, and the combined mixture was stirred overnight at 360 rpm.

In the following day, the mixture was heated on a hot plate at 130 °C for 4 hours while maintaining the same stirring speed. This step allowed most of the water to evaporate and increased the solution's viscosity, and again, with no heat, left stirring overnight at

the same speed. Subsequently, the temperature was raised to 140 °C, and the mixture was stirred for 3 hours until it formed a colloid. To initiate the expansion and combustion process, the temperature was rapidly increased to 550 °C. During this step, the material darkened, generated bubbles and emitted smoke until the combustion was complete, leaving a dry residue. A visual representation of the sol-gel process of different stages of the mixture evolution is shown in Fig. 3.4.

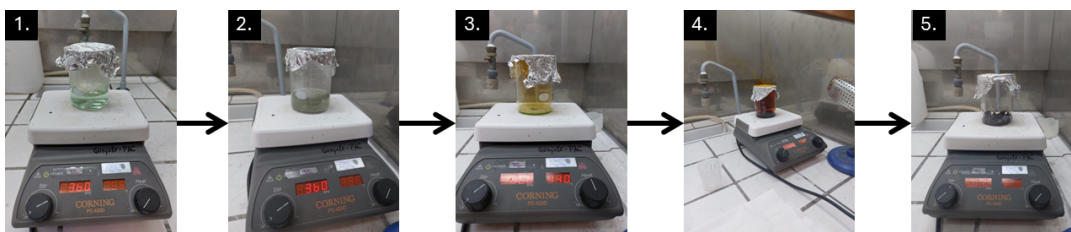


Figure 3.4: Sol-gel evolution of the mixture.

The resulting material was scraped, ground into a fine powder, and calcinated at 650 °C for 12 hours. This was followed by two additional thermal treatments at 1200 °C and 1300 °C, each lasting 12 hours. Finally, the material was sintered at 1250 °C for 24 hours. The evolution of the material's crystal structure was monitored using XRD after each synthesis step. The results, along with a comparison to the theoretical XRD pattern of Y_2NiMnO_6 , calculated using VESTA, are presented in Fig. 3.5.

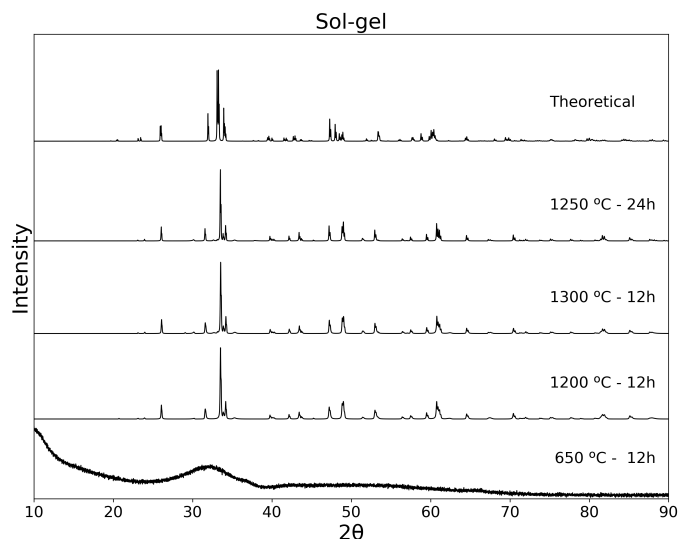


Figure 3.5: X-Ray patterns as a function of the sintering temperature and time for the sol-gel method and comparison with the theoretical XRD calculated using VESTA.

Given these results, the sol-gel and solid-state reaction methods could benefit from further improvements to reduce secondary phases and increase crystallization. In particular,

for the SSR method, additional grinding cycles could enhance the homogeneity of the mixture, leading to a better diffusion during the sintering and possibly a further addition of a small amount of the Mn-based reagent could also minimize the residual NiO phase. As for the SG process, ensuring a more thorough mixing of the precursors during the gel formation stage could improve uniformity at a lower scale, reducing unwanted phase formation and leading to more well-defined diffraction peaks.

From the XRD analysis, no significant differences were observed between the SSR1 and SSR2 samples, confirming that the choice of manganese precursor (MnO_2 or MnO) did not substantially affect the final phase composition. However, a slight difference was noted for the SG sample, particularly around $\theta = 48^\circ$, where the diffraction pattern deviates from the theoretical one. In other words, a simple observation of the pattern suggests a scenario where a triplet of peaks should be observed but instead we observe only two peaks, indicating that the middle peak has merged with the one on the right. This phenomenon could be attributed to several factors: (i) the presence of larger quantities of secondary phases; (ii) cation disorder and atomic deficiencies within the lattice; or (iii) instrumental effects, such as errors in calibration or diffraction geometry, which might distort the peak position [79].

3.2. Macroscopic Characterization

In ordered double perovskites ($\text{A}_2\text{BB}'\text{O}_6$), such as the one studied, the material is composed of a layered type superstructure with alternate stacking of $\text{BO}_6/\text{B}'\text{O}_6$ octahedra to minimize the electrostatic energy due to the different charges of the two cations, and/or reduce the elastic energy arising from their distinct ionic sizes [73]. Here, if the radius or the charge of the B and B' cations are similar, the probability of partial occupation of B cations in B' sites (and vice versa) increases up to a fully disordered state, allowing for tuning of the macroscopic properties of the material. Additionally, these can be influenced by the synthetic conditions or post-synthesis treatments [80].

Furthermore, understanding the macroscopic properties of Y_2NiMnO_6 is essential to define potential future scientific and industrial applications. Thus in this section, we analyse the structural, morphological, chemical, and magnetic characteristics of bulk Y_2NiMnO_6 . Moreover, we perform and study the Heat Capacity and Resistivity measurements, giving insight into the electronic and thermodynamic properties of the material. These analyses were carried out on samples synthesized using both sol-gel and solid-state reaction

methods, enabling a comparison of how different synthesis routes influence the material's macroscopic behaviour.

3.2.1 Structural characterization

In terms of the structural characterization of the synthesized samples, Fig. 3.6 a) and b) present the latest XRD of the Y_2NiMnO_6 samples produced via the SG and SSR method, respectively. These measurements were performed in continuous scanning mode using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) with the Rigaku SmartLab high-resolution X-Ray diffractometer. Meanwhile, Fig. 3.6 c) illustrates the graphical output of the Le Bail refinement performed, at room temperature, to the XRD pattern of the Y_2NiMnO_6 sample SSR. In particular, the black dots represent the experimental pattern (Yobs), the fit curve is shown as a red line (Ycalc), the residual difference (Yobs - Ycalc) is the blue line, and the Bragg reflections are the green vertical lines (|).

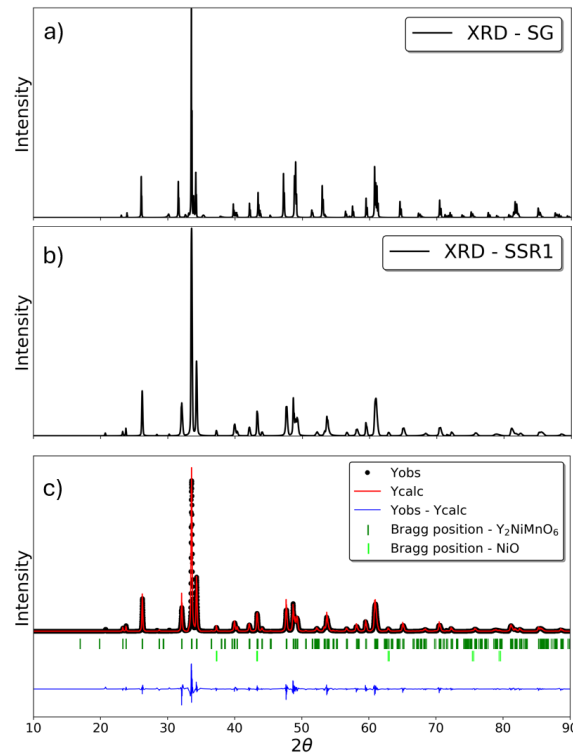


Figure 3.6: a) XRD of the sample Y_2NiMnO_6 produced by sol-gel method. b) XRD of the sample Y_2NiMnO_6 produced by solid-state reaction method. c) Le Bail refinement at room temperature of the XRD powder sample Y_2NiMnO_6 synthesized by the solid-state reaction method.

The double perovskite Y_2NiMnO_6 was indexed to the monoclinic space group $P2_1/n$ (No. 14), with lattice parameters $a = 5.23 \text{ (\AA)}$, $b = 5.57 \text{ (\AA)}$, $c = 7.47 \text{ (\AA)}$, and $\beta = 89.92^\circ$, as expected, accounting for most of the diffraction peaks. However, as previously mentioned,

a minor secondary phase of NiO , indexed to the cubic space group $Fm\bar{3}m$ (No. 225), is also present, corresponding to a small fraction of the sample (less than 5 %). The refinement results are summarized in Table 3.1 and show good agreement with the values reported in the literature [9, 10, 81, 82]. In addition, the statistical analysis presented in Table 3.1, in particular the high values of R_{wp} and R_{exp} , suggests that our model could be further improved, indicating that our sample is not only described by the space group $P2_1/n$. In other words, this discrepancy highlights the presence of additional complexities in the material structure that were not fully captured by the current model. These findings suggest that additional synthesis treatments, such as prolonged annealing or adjustments to the precursor ratios, may be necessary to reduce secondary phases and improve phase purity.

Table 3.1: Structural parameters of Y_2NiMnO_6 at room temperature.

Space Group: $P2_1/n$			
a (Å) = 5.23	b (Å) = 5.57	c (Å) = 7.47	β (°) = 89.92
R_{wp} = 31.5 %	R_{exp} = 29.04 %	χ^2 = 1.18	

Lattice parameter error of 0.01 (Å).

3.2.2 Morphological and chemical characterization

The surface morphology and chemical composition of the Y_2NiMnO_6 samples, prepared by the SG and SSR method, were analysed using SEM and EDS. These were conducted at the Materials Centre from the University of Porto (CEMUP) using an FEI Quanta 400FEG ESEM equipped with an EDAX Genesis X4M. Fig. 3.7 and Fig. 3.8 show SEM images with different magnifications (from a) to c)). In both cases, the elemental compositions were estimated using EDS analysis of X-Rays in zone Z1, as shown in d). While ideally, multiple zones should have been analysed, the atomic elemental percentages obtained for the SG and SSR methods are detailed in e) of Fig. 3.7 and Fig. 3.8, respectively.

In particular, for the SG sample, we obtain an approximate elemental composition of Y/Ni/Mn/O (2.2:0.5:2.3:4.1), while for the SSR sample, the composition is (2.2:1:1.5:4.2), roughly. Both these results deviate from the theoretical stoichiometric composition of Y/Ni/Mn/O (2:1:1:6), with the solid-state reaction (SSR method) exhibiting a much closer match to the theoretical composition than the sol-gel method, which shows, approximately, a (5:1) ratio of Mn to Ni. It is also worth mentioning that the oxygen measurements

in EDS analysis are less reliable due to challenges in detecting lighter elements with high precision and accuracy. Such inaccuracies arise from limitations in the energy resolution of EDS detectors and the likelihood of surface oxidation or contamination skewing the results.

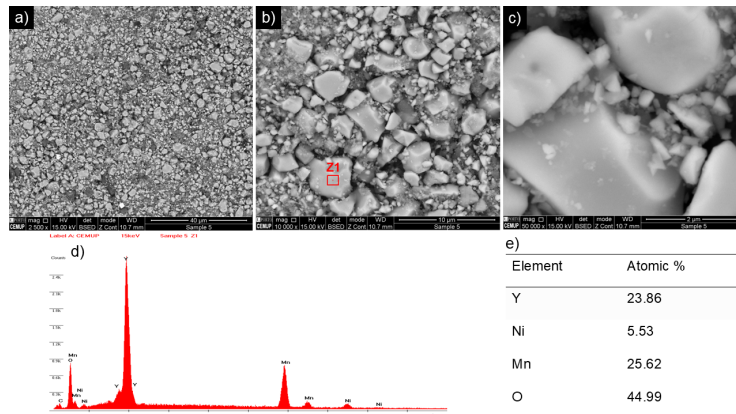


Figure 3.7: SEM images of the sample Y_2NiMnO_6 synthesized by the method SG with a magnification: a) 2500x, b) 10000x and c) 50000x. d) shows the EDS results of zone Z1 indexed in b). Finally, table e) shows the determined elemental composition of the sample.

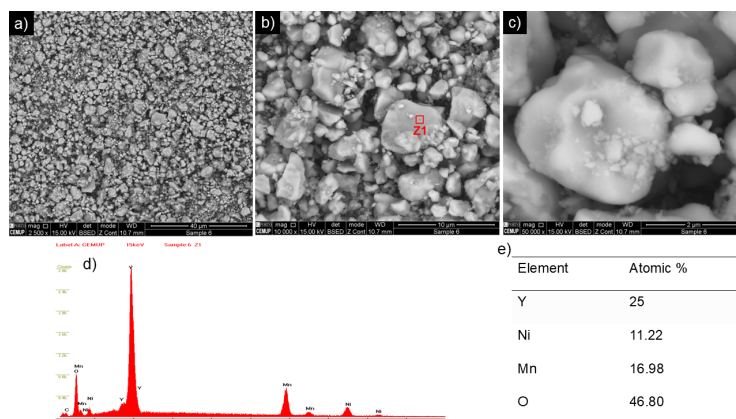


Figure 3.8: SEM images of the sample Y_2NiMnO_6 synthesized by the method SSR1 with a magnification: a) 2500x, b) 10000x and c) 50000x. d) shows the EDS results of zone Z1 indexed in b). Finally, table e) shows the determined elemental composition of the sample.

Furthermore, by analysing the SEM images, we can estimate the grain size of the samples synthesized by the different methods. As shown in Fig. 3.7 and Fig. 3.8, particularly in panel (b), the images seem to hint that the grain sizes associated with the SG method are smaller than those produced by the SSR method, which is expected, since the SG process is typically used for nanoparticles, yielding smaller particle sizes [83]. Nevertheless, a more in-depth analysis is required to confirm this observation.

Pairing these results with the XRD findings, it is evident that both synthesis methods need further improvement, although to different extents. In particular, the sol-gel method shows significant deviations from the theoretical elemental composition, suggesting incomplete incorporation of key elements and the presence of secondary phases. These discrepancies suggest that some synthesis conditions, for example precursor ratios, processing time, or sintering temperatures, should be revisited and adjusted to achieve a more homogeneous and phase-pure material. In contrast, the solid-state reaction method exhibits a much closer match to the theoretical elemental composition, requiring only some minor refinements to further reduce secondary phases and enhance phase purity, supported as well by the XRD data.

3.2.3 DC magnetization

The temperature-dependent magnetization curves under both zero field cooled (ZFC) and field cooled (FC) conditions are shown in Fig. 3.9 and Fig. 3.10, for the samples synthesis by the SG and SSR methods, respectively. The magnetization was taken in a temperature range between 5 K and 250 K under two different applied magnetic fields: 100 Oe (for both ZFC and FC conditions) and 1 kOe (only FC measurement). Both graphs show a clear bifurcation between the FC and ZFC curves at an applied magnetic field of 100 Oe. This bifurcation occurs below 100 K for the SG sample and below 80 K for the SSR sample, indicating the presence of magnetic frustrations or randomness [9, 40].

Moreover, as an inset in Fig. 3.9 and Fig. 3.10, to investigate the magnetic phase transitions, the first order derivate of the FC curve concerning temperature is shown for different external magnetic fields. In the SG sample, two minima are shown, one at 28 K and the other at 44 K, indicating more than one phase transition, where an increase in the applied magnetic field increases the contribution of the lower temperature minima. As for the SSR sample, it has again two minima. Still, the second occurs at a higher temperature (64 K), and an increase in the external magnetic field has less impact on the lower-temperature minima (28 K). These results show clear competing magnetic interactions in the samples, where in this system the expected oxidation states of Mn and Ni are 4+ and 2+, respectively. Thus, the main super-exchanges are $\text{Mn}^{4+}-\text{O}^{2-}-\text{Ni}^{2+}$ (FM), $\text{Ni}^{2+}-\text{O}-\text{Ni}^{2+}$ (AFM) and $\text{Mn}^{4+}-\text{O}-\text{Mn}^{4+}$ (AFM). The first is the dominant interaction responsible for the ferromagnetic behaviour, and the latter are the antiphase boundaries' consequences [40]. Nevertheless, in addition to these interactions, the elements may have different oxidation

states, resulting in different magnetic interactions, described as follows: $\text{Mn}^{3+}-\text{O}^{2-}-\text{Ni}^{3+}$ (FM), $\text{Ni}^{3+}-\text{O}-\text{Ni}^{3+}$ (AFM) and $\text{Mn}^{3+}-\text{O}-\text{Mn}^{3+}$ (AFM) [40].

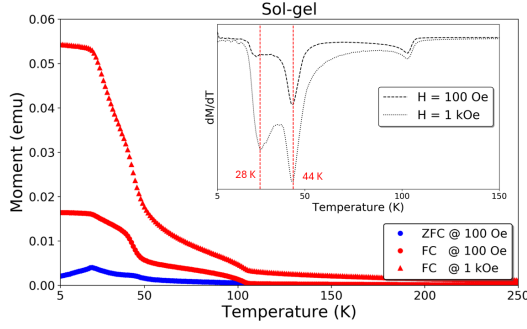


Figure 3.9: DC magnetization SG with an applied magnetic field of 100 Oe and 1 kOe. Inset figure shows the first order derivative of the FC data.

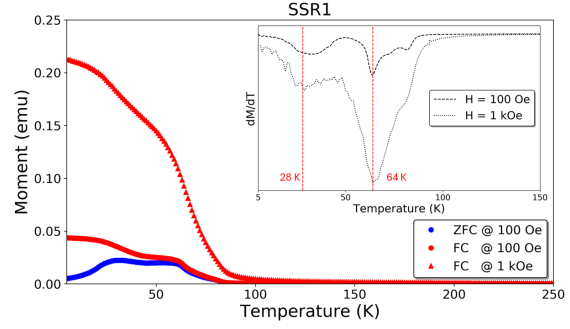


Figure 3.10: DC magnetization SSR with an applied magnetic field of 100 Oe and 1 kOe. Inset figure shows the first order derivative of the FC data.

Therefore, to explain the dual magnetic phase transitions and the lower Curie Temperature (T_C) observed in both samples (see Table 3.3), Table 3.2 presents the Néel temperatures of the Mn-based reagents used in the synthesis of bulk Y_2NiMnO_6 via both the SG and SSR methods. In particular, the lower T_C value (around 28 K) can be attributed to the presence of unreacted Mn-based precursors, which exhibit a similar Néel Temperature (T_N). Moreover, recalling the EDS results in the previous section, SG sample contained 2.5 times more Mn than expected, further supporting its role in the formation of the minimum at 28 K and its increasing influence under a higher applied magnetic field. As for the SSR sample, although there is still a Mn influence (second magnetic phase transition), the T_C is closer to the reported value, which is around 88 K [9], but still with other competing magnetic interactions lowering this value (second phase of NiO).

Table 3.2: Summary of the Néel temperature of Mn-based reagents used in the SG and SSR.

Competing magnetic interactions		
Reagent	T_N (K)	Reference
$\delta\text{-MnO}_2$ (SSR1)	20	[84]
MnCO_3 (SG)	32	[85]

To further understand the magnetic behaviour of the SG sample, we studied the relationship between the magnetization (M) and the magnetic field (H), as illustrated in Fig. 3.11.

The measurement was done in two different temperatures, one at 10 K, in the ferromagnetic zone (lower than T_C), and the other at 300 K, in the paramagnetic state. As expected, the sample shows a linear behaviour in the paramagnetic state. In contrast, at 10 K, a clear magnetic hysteresis is observed, confirming the presence of ferromagnetic ordering. Notably, even at an external magnetic field of 70 kOe, the magnetization has not yet saturated, a result consistent with the findings reported in the work [40], where for an applied magnetic field of 7 T (70 kOe), a unsaturated magnetization slightly above 40 emu/g was obtained.

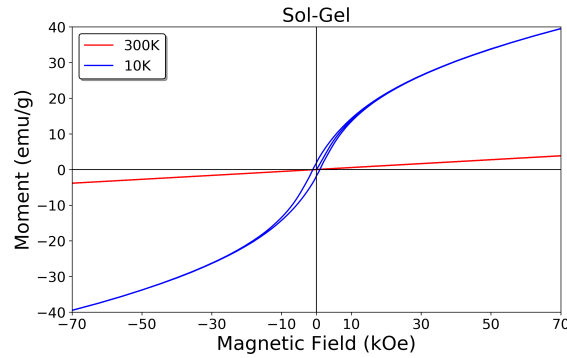


Figure 3.11: $M(H)$ in the ferromagnetic (10 K) and paramagnetic zone (300 K) for the SG sample.

From the FC data, we can also represent the inverse susceptibility as a function of temperature and determine key magnetic parameters (see Equation 2.12). Fig. 3.12 and Fig. 3.13 show the inverse susceptibility as a function of temperature for an applied magnetic field of 1 kOe for the SG and SSR samples, respectively.

Additionally, we fitted the Curie-Weiss law (black line) to the data in the paramagnetic region, and the obtained parameters are summarized in Table 3.3, as well as a comparison to values reported in the literature for this material. In particular, when analysing the SG sample, Fig. 3.12, in the paramagnetic state, we observe two step-like fall anomalies below 200 K. Therefore, we fitted the Curie-Weiss law in three different temperature ranges: 250-200 K, 195-115 K, and 95-50 K, which correspond to Regions 1, 2, and 3, respectively. Such deviations have also been seen in other materials. For example N. Marcano et al. [86] studied the static magnetization and dynamic susceptibility responses of the compound $\text{Tb}_{5-x}\text{La}_x\text{Si}_2\text{Ge}_2$ and attributed similar step-like anomalies to the emergence of short-range magnetic clusters in the paramagnetic state, representing the "fingerprint" of a Griffiths phase, where the different slopes observed indicate different sizes of the ferromagnetic clusters within those temperature ranges.

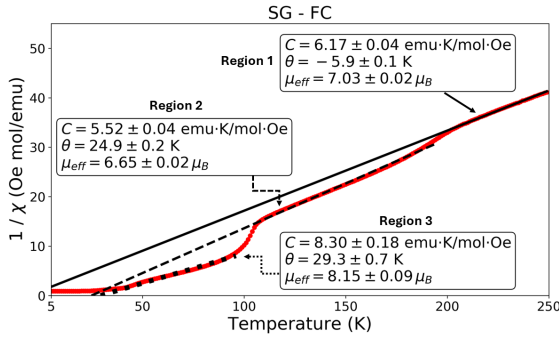


Figure 3.12: Inverse susceptibility as a function of temperature of the SG sample for an applied magnetic field of 1 kOe.

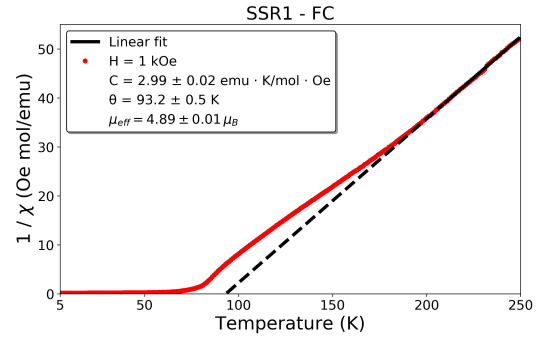


Figure 3.13: Inverse susceptibility as a function of temperature of the SSR sample for an applied magnetic field of 1 kOe.

Moreover, Table 3.3 shows that, although the T_C value for the SSR sample is still lower than other reported values, it has a Curie constant and Weiss temperature similar to those expected. In contrast, the SG sample deviates significantly from the expected values, further emphasizing the need for improvements in the synthesis process. Interestingly, in Region 1, we obtain a negative value for the Weiss temperature, which suggests the presence of antiferromagnetic interactions in this temperature range.

Table 3.3: Summary of the Curie-Weiss parameters of the SG and SSR samples with other already reported on Y_2NiMnO_6 .

Curie-Weiss linear fit parameters				
Sample Synthesis	T_C (K)	$\Theta_{CW}(K)$	C (emu · mol ⁻¹ K ⁻¹)	μ_{eff} (μ_B)
SG - Region 1	44	-5.9	6.17	7.03
SG - Region 2	44	24.9	5.52	6.65
SG - Region 3	44	29.3	8.30	8.15
SSR1	64	93.2	2.99	4.89
SG - [10]	67	57.6	-	-
CG - [9]	88	96.630	2.605	4.56
SG - [40]	84	88.19	2.94	4.87

CG - Citrate-gel.

In addition, the effective paramagnetic moment was calculated using the following equation 2.12 [9], and as for the theoretical value of the effective paramagnetic moment for Y_2NiMnO_6 , it can be determined using the following equation 2.13 and the spin only version ($J = S$) [66]:

$$\mu_{\text{eff}} = \sqrt{\mu_B^2 g^2 [S(S+1)_{\text{Ni}} + S(S+1)_{\text{Mn}}]}, \quad (3.1)$$

where g is the Landé g-factor, which is equal to 2 in the case of spin-orbit interaction, and S , the total spin quantum number, is equal to 1 for Ni^{2+} , 1.5 for Ni^{3+} , 2 for Mn^{3+} , and 1.5 for Mn^{4+} . Therefore, the theoretical magnetic moment value (oxidation states 2+ and 4+, for Ni and Mn, respectively) is $\mu_{\text{eff}} = 4.8 \mu_B$, meanwhile, for example, with the oxidation states 3+ for Mn and Ni, we obtain a $\mu_{\text{eff}} = 6.3 \mu_B$.

It is worth mentioning that this calculation is based on the assumption that both B cations, Ni and Mn, are in a 1:1 ratio. Deviations from this ratio would lead to different results, even if the oxidation states remained the same. Thus, comparing these theoretical values with the experimental μ_{eff} of each sample, the higher value observed for the SG sample (in particular, Region 2) suggests that Ni and Mn are predominantly in the 3+ oxidation state rather than the expected 2+/4+ combination. This deviation leads to a dominant ferromagnetic interaction via the $\text{Mn}^{3+}-\text{O}^{2-}-\text{Ni}^{3+}$ superexchange pathway. To confirm this, X-Ray Photoelectron Spectroscopy (XPS) should be employed to determine the exact oxidation states of Ni and Mn, to provide more insight into the material's electronic structure and validate the presence of the $\text{Mn}^{3+}-\text{O}^{2-}-\text{Ni}^{3+}$ interaction.

3.2.4 Heat capacity

To gain further insight into the magnetic ordering in Y_2NiMnO_6 , we measured the specific heat at ambient constant pressure (Heat Capacity (C_p)) as a function of temperature for the sample synthesized by the SG method in the range of 10 K to 300 K in zero fields, using the heat capacity option of the Quantum Design (PPMS). It is worth mentioning that the measurements were performed from the lowest temperature to the highest (Heating) and from the highest to the lowest temperature (Cooling). This analysis helps validate the findings from DC magnetization, as anomalies in C_p often correlate with critical temperatures observed in magnetic and structural transitions.

In order to better locate possible anomalies in the Heat capacity data, we divide C_p by the temperature and plotted the resulting C_p/T as a function of temperature. Fig. 3.14 illustrates C_p/T as a function of temperature in zero applied magnetic field, for both the heating and cooling measurements, where no visible difference is seen between the two. In other words, our measurements show no hysteresis, suggesting that we are likely dealing with weak first or second order thermodynamic transitions [87].

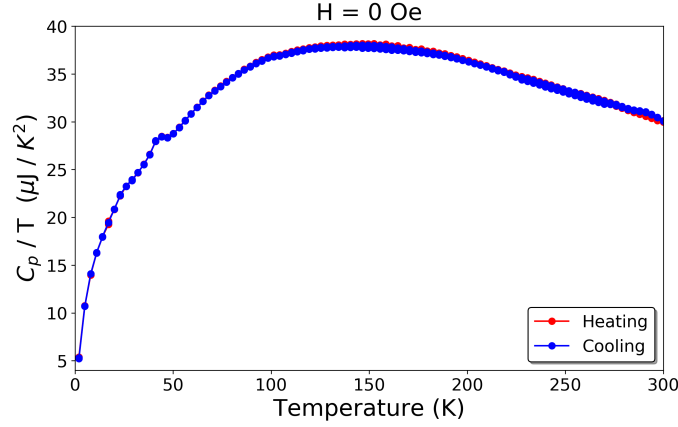


Figure 3.14: C_p/T as a function of temperature in a zero applied magnetic field for the sample synthesized by SG method.

As previously mentioned, this representation is particularly useful near phase transitions, as it often reveals sharper anomalies, making it easier to pinpoint possible transition temperatures. In fact, a distinct anomaly appears around 44 K, coinciding with the T_C value (second magnetic phase transition) observed in the first-order derivative of the FC data for the SG sample (see Fig. 3.9). A similar result was reported in the work Ref. [10], where a sharp anomaly was observed in C_p as a function of temperature around T_C of 67 K.

3.2.5 Magnetocaloric Effect

Another important magnetic measurement that we can take from the isothermal curves ($M(H)$) is the magnetic entropy variation (ΔS_m). Summarized, when a magnetic material is exposed to an external magnetic field (H), the magnetic atomic moments try to align along the direction of H . Since it is an adiabatic process, the total entropy of the system remains constant. When the magnetic moments align in response to the applied magnetic field, the system loses magnetic disorder, resulting in a decrease in magnetic entropy. To compensate for this and maintain constant total entropy, the lattice entropy must increase. This manifests as an increase in the material's temperature [75]. Reciprocally, the temperature decreases when the external magnetic field is removed adiabatically.

This effect is called the Magnetocaloric Effect (MCE), being related to the magnetic entropy variation (ΔS_m), see section 2.2.5. In recent years, magnetic refrigeration, which relies on the MCE, has made significant advancements and is emerging as a promising cooling technology for both RT and cryogenic applications, where conventional cooling systems are helium-based [88]. Therefore, in the following section, we measured the ($M(H)$) isotherms at different temperatures ($\Delta T = 3$ K), covering the range from 5 K to

185 K, which is particularly relevant for cryogenic applications. The results for the two distinct synthesis methods are illustrated in Appendix A, Fig. A1 and Fig. A2.

In addition, the $M(H)$ curves can be used to calculate the variation in magnetic entropy (ΔS_m) of a magnetic material under the influence of an applied magnetic field, both during an increase and a decrease in the field. This is important for understanding the material's magnetocaloric effect and potential applications in refrigeration technologies. To better visualize this, Fig. 3.15 presents the temperature dependence of the magnetic entropy change ($-\Delta S_m$) with respect to increasing and decreasing applied magnetic field for both the sol-gel and solid-state reaction samples. The values of ΔS_m were calculated using equation 2.14. The applied magnetic field was varied between 1 T and 7 T for both samples, and the maximum value of the magnetic entropy change is provided in Table 3.4. The graphs show that both the sol-gel and solid-state reaction samples exhibit a broad peak around their corresponding T_C value, at 44 K and 64 K, respectively. However, for the solid-state reaction sample, the peak is notably broader for both increasing and decreasing applied magnetic fields. This broadening suggests that the solid-state sample has better potential for application in magnetic refrigeration, as the wider magnetic entropy peak offers advantages for use in the Ericsson cycle [89], which relies on such broad peaks for efficient heat transfer and energy conversion.

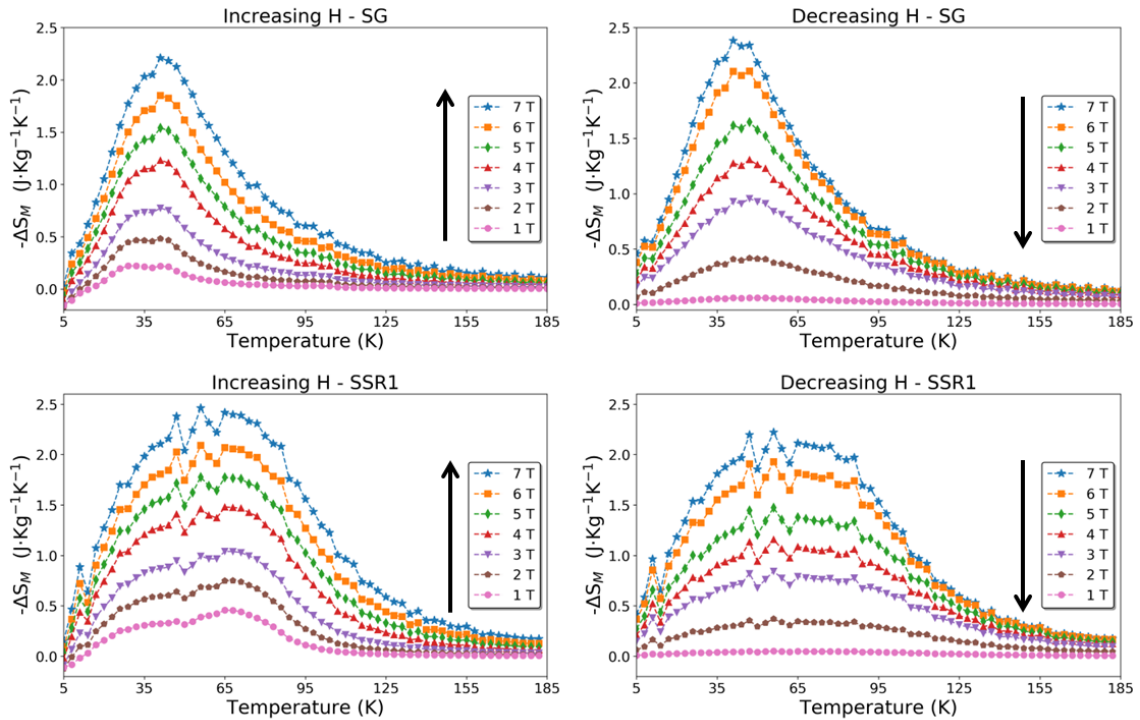


Figure 3.15: ΔS_m as a function of temperature of the two samples. Left image is with increasing applied magnetic field and the right image is with decreasing applied magnetic field.

Furthermore, another crucial parameter for evaluating the material's performance in magnetic refrigeration is the cooling efficiency, often quantified as the relative cooling power (RCP), which can be calculated using equation 2.15. It is worth noting that there is on-going debate regarding the most appropriate figure of merit for magnetocaloric materials. While RCP is widely used, there are several other alternatives that could have also been considered [90].

To obtain the RCP, we first calculate the (FWHM) of the magnetic entropy change curve. This parameter provides insight into the breadth of the entropy change, which is directly related to the material's efficiency in transferring thermal energy during the refrigeration cycle. A visual representation of the FWHM calculation is shown in Appendix A, Fig. A3. Once the FWHM is determined, we multiply it by the maximum value of the magnetic entropy change ($\Delta S_m^{\max}$) observed at the highest applied magnetic field of 7 T. The resulting product provides the RCP, which serves as a key indicator of the material's performance in magnetic refrigeration applications. In our analysis, we consider both the increasing and decreasing magnetic field scenarios once again.

Table 3.4: Summary of the magnetocaloric performance of the SG and SSR samples with other already reported on Y_2NiMnO_6 .

Magnetocaloric Properties			
Sample	T (K) of $ \Delta S_m ^{\max}$	$ \Delta S_m^{\max} $ ($\text{J} \cdot \text{Kg}^{-1} \text{K}^{-1}$) / ΔH	RCP ($\text{J} \cdot \text{Kg}^{-1}$) / ΔH
SG - Up	41	2.21 / 70 kOe	110.98 / 70 kOe
SG - Down	41	2.38 / 70 kOe	125.40 / 70 kOe
SSR - Up	56	2.46 / 70 kOe	207.85 / 70 kOe
SSR - Down	56	2.22 / 70 kOe	193.09 / 70 kOe
[75]	83	2.9 / 20 kOe	74.88 / 20 kOe
[82]	85	6.57 / 80 kOe	134 / 80 kOe
[67]	85	4.95 / 50kOe	191.3 / 50kOe

The relevant values are summarized in Table 3.4 and also compared with other reported values on this material. From this, we see that the SSR sample, in comparison with the sample synthesized by the SG method, gives a higher RCP value, specifically, in an increasing applied magnetic field scenario. In addition, it is also worth mentioning that the MCE is usually higher around the temperature where $\sum \frac{\partial M}{\partial T}$ is maximum, which in the case of ferromagnetic materials happens near T_C [75].

3.2.6 DC transport properties

For the DC transport properties, as previously mentioned in the section 2.2.6, we used the DC Resistance option in the PPMS, designed by Quantum Design, and performed a four-wire resistance measurement in order to obtain the resistance, and also the resistivity, described in equation 3.2, of the Y_2NiMnO_6 sample produced by the sol-gel method.

$$\rho = R \cdot \frac{A}{L} \quad (3.2)$$

The temperature dependence of the DC Resistance was measured between a temperature of 212 K to 300 K under various applied magnetic fields (ranging from $H = 0$ Oe to $H = 250$ Oe), as seen in Fig. 3.16. We applied different magnetic fields in order to explore potential magnetoresistance effects (change in electrical resistance when a magnetic field is applied), which have been observed in related compounds. For instance, Yuqiao Guo et al. [91] studied the temperature-dependent resistivity of the double perovskite $\text{La}_2\text{NiMnO}_6$ in the temperature range 200 K to 400 K under zero applied magnetic field and under an applied field of 200 Oe. They observed not only a semiconducting-like behavior throughout the entire temperature range, but also a decrease in resistivity when a magnetic field was applied, indicating the presence of a negative magnetoresistance effect in the material.

Additionally, the inset in Fig. 3.16, shows the I - V curve taken at 300 K, exhibiting a smooth increase in current with the applied voltage (-2 to 2 V), following Ohms law (linear behaviour). The choice of these voltage limits, as well as the restricted temperature range (212 K as the lowest temperature), is due to the limitations of the PPMS and need to protect the sample. At lower temperatures, due to the semiconducting behavior of Y_2NiMnO_6 , the resistance levels were excessively high, falling out of the allowed PPMS range.

Figure 3.16 illustrates the increase in resistance with decrease in temperature, a typical behavior of semiconducting materials [9, 92], where, at RT, the resistance value is 2435Ω . Naphat Albutt et al. [93] studied the electrical impedance of Y_2NiMnO_6 samples at room temperature, reporting resistance values (real part) ranging from 1080Ω to 6150Ω . In addition, no significant difference was observed between the resistance measurements taken under zero field and under the maximum applied magnetic field of 250 Oe. This seems to suggest that the magnetoresistance effect in this compound is either very weak or negligible within the studied temperature range and field strength.

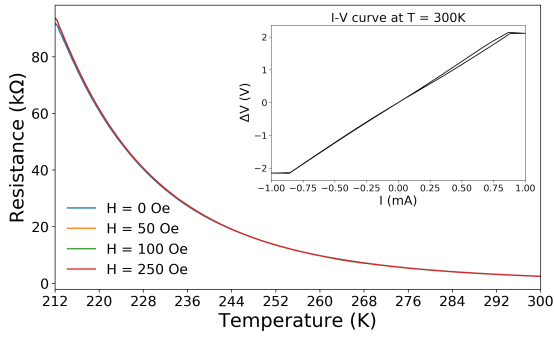


Figure 3.16: Temperature dependence of resistance from 212 K to 300 K. Inset figure I - V curve at a temperature of 300 K.

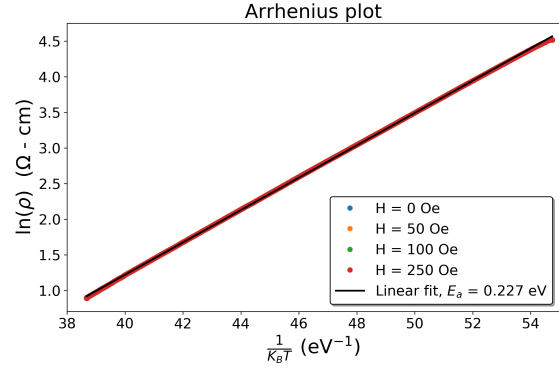


Figure 3.17: Arrhenius plot of the sol-gel sample.

Furthermore, we can also obtain the activation energy, which is a measure of the energy required to surpass the barrier (not just electronic or even thermal) [94], from the Arrhenius equation, described as follow:

$$\ln(\rho) = \ln(\rho_0) + \frac{E_a}{k_B T} . \quad (3.3)$$

Where, E_a is the activation energy, obtained from the slope of the linear fit from the Arrhenius plot. Fig. 3.17 shows the Arrhenius plot, which is the variation of the logarithm of the resistivity of the sample as a function of the inverse temperature, showing, as expected, a linear trend [95] and an activation energy of 0.227 eV, a value close to that obtained in a similar double perovskite structure ($\text{La}_2\text{NiMnO}_6$) [96, 97].

4. Macroscopic and local study on ErCrO_3

In the previous chapter, we focused on the double perovskite oxide Y_2NiMnO_6 , identifying its crystal structure and investigating its magnetic, thermal, and electrical properties due to the interplay of the two distinct transition metals occupying the B -sites. While double perovskites offer a unique platform to explore complex phenomena arising from such cation ordering, it is essential to first understand the basic properties and behaviour of simpler perovskite oxide structures before delving further into these even more complex systems. Therefore, the following section will focus on studying single perovskite oxides. In particular, we aim to address uncertainties related to the crystal structure of ErCrO_3 , more specifically, the existence of possible local distortions that could explain the appearance of ferroelectricity (or even potential new physical properties), which is still shrouded in some debate to these types of materials.

4.1. Overview

As a recap of section 1.2.1, ErCrO_3 belongs to the family rare-earth orthochromite perovskite oxides (ABO_3), where in this case the A -site is occupied by a rare-earth ion, Er^{3+} , and the B -site by a transition metal ion, Cr^{3+} . Unlike the ideal cubic perovskite structure, ErCrO_3 has an orthorhombic structure, indexed to the $Pbnm$ space group, due to the tilting of the CrO_6 octahedra. This structural distortion is critical in determining the material's physical properties, particularly its magnetic and electrical behaviour.

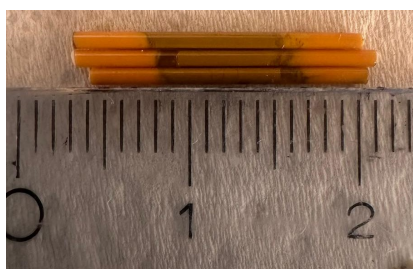
Rare-earth orthochromites (RCrO_3) are known for exhibiting rich and varying physical properties, such as magnetic, ferroelectric and multiferroic properties. Therefore, they are of valuable interest to theoretical and applied research scientists, with the development of suitable applications dependent on a better understanding of their fundamental properties. Regarding ErCrO_3 , in terms of its magnetic properties, the Cr^{3+} spins (Cr^{3+} - Cr^{3+}) order antiferromagnetically below the $T_N = 133$ K, then at 22 K a spin reorientation ($\Gamma_4 \rightarrow \Gamma_1$) occurs (the interplay between Cr^{3+} - Er^{3+} becomes more significant), and at [6-13] K (T_N^{Er}) the second magnetic sub-lattice ordering occurs (Er^{3+} - Er^{3+} interactions). In terms of its electrical properties, it is described in the literature as a ferroelectric material [25]. However, there is still a debate about its actual existence and origin [1, 25, 31, 98, 99] as a ferroelectric material with a claimed ferroelectric transition temperature (T^*) arising around 460 K.

In fact, these types of materials (rare-earth orthochromites) are at the centre of considerable debate regarding the actual existence of ferroelectricity and its possible origin. For example, ferroelectricity is revealed in the perovskites SmCrO_3 [100] and HoCrO_3 [101], where polar order with a structural origin is observed at temperatures of 220 K and 240 K, respectively, both higher than their T_N . It is also worth noting that, in the work reported in Ref. 25, the ferroelectric transition temperature for HoCrO_3 is reported to occur at an even higher temperature, near 445 K. In addition, since the crystalline structure of RCrO_3 perovskites are indexed to a well-understood orthorhombic structure, which does not allow for ferroelectricity to appear, this property might arise from local structural features that long-range average models cannot describe. Thus, a need for local studies emerges as a clear necessity.

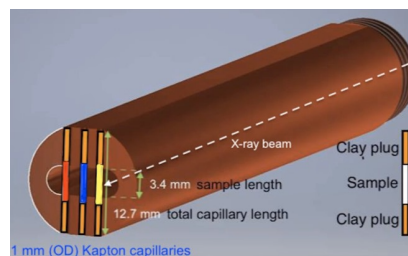
In this context, the Pair Distribution Function (PDF) surged as a method that had the potential to provide meaningful additional knowledge about these materials. In this thesis, ErCrO_3 will be examined as a prototype of a single perovskite oxide that could, in the future, be used to elucidate the underlying mechanisms that govern the structural properties of similar types of materials. By connecting the macroscopic behaviour (XRD) to local structural distortions (PDF), the present study aims to provide a clearer picture of how single perovskite oxides function at both the atomic and macro scale, setting the stage for a future deeper understanding of more complex materials like the case of the double perovskite oxides.

4.2. Experimental Details

The samples of ErCrO_3 , see Fig. 4.1 a), used here are the same as in Ref. 1, which were prepared by SSR of mixed stoichiometric quantities of Er_2O_3 and Cr_2O_3 . Then, were pressed into pellet form and followed by a 15-hour heat treatment at 1073 K. Finally, two more grinding and consecutive heating steps were performed at 1573 K for 48 hours. The measurements of the XRD and PDF of the sample ErCrO_3 were performed at the Brookhaven National Laboratory (National Synchrotron Light Source II), with the PDF setup shown in Fig. 4.2, where the sample was mounted as demonstrated in Fig. 4.1 b). Furthermore, the data was collected in two different sets. First, starting from the lowest temperature (5 K) to the highest (500 K), which will denote as Up, then going back from the highest to the lowest temperature, Down.



(a) Sample ErCrO_3 prepared from a solid-state reaction.



(b) Sample ErCrO_3 in the capillary tube for the PDF. Taken from Ref. 102.

Figure 4.1: Sample preparation of ErCrO_3 .

Room temperature XRD measurements of the sample were performed both before and after the sequential measurements, which can be seen in Appendix B, Fig. B1. Additionally, the area under the XRD diffraction pattern, calculated using the trapezoidal rule, was 1313 and 1307, for the before and after RT measurement, respectively. Given the alignment of both XRD patterns and the minimal difference in the areas under the diffraction patterns, the sample did not suffer any changes during the measurements, reinforcing the reliability of the data. It is also worth mentioning that, in the same temperature, the XRD was measured first, and then the PDF, before heating/cooling the sample for a new temperature measurement dataset.

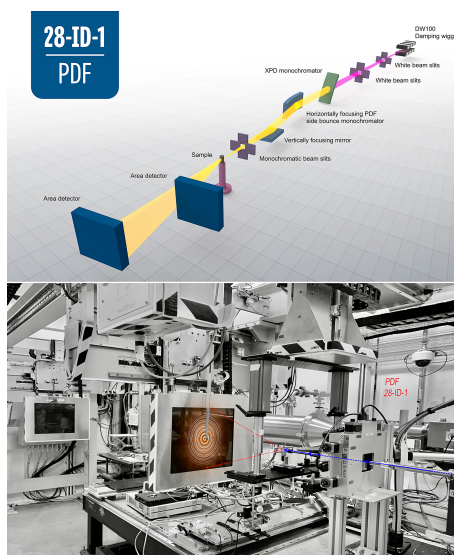


Figure 4.2: Experimental setup of PDF at the Brookhaven National Laboratory (National Synchrotron Light Source II). Taken from Ref. 103.

4.3. Macroscopic Study - XRD

This section will focus on the macroscopic study of the sample ErCrO_3 by doing a sequential Rietveld refinement, using the FullProf software, in the 5 – 500 K temperature

range in 5 K intervals. As previously mentioned, the data was acquired in two different settings, going from the lowest temperature to the highest (Up) and from the highest to the lowest temperature (Down). In the upcoming analysis, the Up dataset was chosen for presentation purposes, however the same analysis was also performed for the Down dataset, which can be seen in Appendix B, Fig. B2, but since both datasets yield similar results, we will primarily discuss the Up dataset.

Nevertheless, before examining the refinement results, it was important to first perform a preliminary analysis of the raw data, as valuable information can already be obtained from this, such as possible phase transitions or defects, seen as changes in the position, shape, or appearance of new peaks. Additionally, it is also crucial to exclude external effects, in particular signal variations caused by changes in the sample's density, such as the movement of powder within the capillary, which could result in a reduced volume analysis. It is also important to verify that the beam intensity remained constant throughout the measurements to ensure data reliability. Two methods that help see this are the 2D contour plot and the study of the area under the entire diffraction pattern or of a specific peak. A complete discussion and the corresponding figures can be found in Appendix C.

Furthermore, we also investigated the validity and consistency of the XRD Rietveld refinement results applied to the Up sequence dataset by analyzing the goodness of fit (χ^2) and Bragg R factor obtained through three different refinement models. Additionally, a comparison with the integrated area under the diffraction patterns, derived from a preliminary analysis of the raw data, supports the conclusion that the observed temperature-dependent variations are intrinsic to the sample. Further insights and a detailed examination of these results are also presented in Appendix C, section C3.

4.3.1 Strain and Crystalline size

Calculating strain and crystalline size is essential for understanding the properties and performance of materials, especially at the nanoscale. Together, strain and crystalline size analyses allow us to tailor materials for various applications by understanding and controlling their structural properties [104, 105]. The strain in materials, deformation that occurs when a material is subjected to stress, either from external forces or internal factors, and the crystalline size, the average size of crystallites within a material, have a significant effect on its properties: mechanical strength, electronic or optical properties,

chemical reactivity, or even thermal stability. Appendix D presents a comprehensive analysis of strain and crystalline size, carried out using the Williamson-Hall method.

4.3.2 Lattice Parameter

One of the most important physical characteristics of a material is its thermal expansion, which is described as a response to anharmonic terms in the expansion of the ionic interaction energy about its equilibrium value [106]. In order to properly describe the lattice parameters' temperature dependency, we must select an adequate model. For this thesis, we used a relatively simple model that is based on an Einstein approximation, which assumes that all atoms vibrate with the same angular frequency [107–109], expressed as:

$$d(T) = d_0 + \frac{E}{\exp\left(\frac{\Theta_E}{T}\right) - 1}, \quad (4.1)$$

where d_0 is the zero-temperature lattice, Θ_E is the effective Einstein temperature that characterizes the typical vibrational energy of atoms in the lattice, and E is the Einstein constant, related to the average energy of the oscillators in the lattice [110].

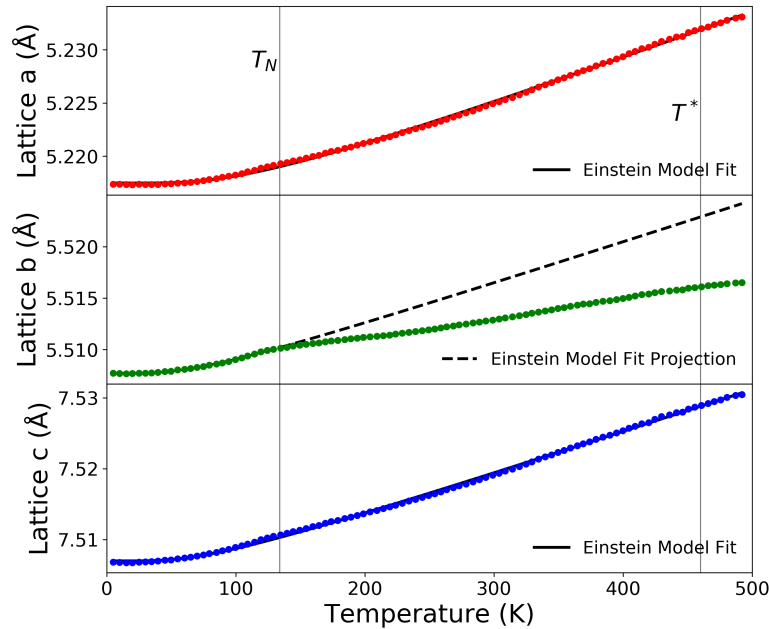


Figure 4.3: XRD: lattice parameters fitted using the Einstein model (black line) as a function of temperature.

Figure 4.3 shows the evolution of the lattice parameters a , b and c with rising temperature, where for each lattice parameter, the previously discussed model was fitted (full black

line). It is worth mentioning that near the magnetic phase transition, T_N , all the three lattice parameters show a deviation from the Einstein model, and in particular, in the lattice b , at higher temperatures than T_N , the model deviates and can not describe its thermal expansion. So, for this lattice, only the temperatures smaller than T_N were considered for the fitting, and extrapolation is shown as a dashed black line for higher temperatures.

Figure 4.4 illustrates the temperature dependence of the unit cell volume, along with the corresponding fit using the previously described Einstein model. Notably, two deviations from the model are observed: one occurring near T_N (134 K) and another within the temperature range of approximately 200-300 K. Similar anomalies near T_N have been reported in other antiferromagnetic perovskites, for example in $\text{Ba}_4\text{NaRu}_3\text{O}_{12}$ [111] and BiFeO_3 [112], suggesting a possible correlation between magnetic ordering and lattice behavior. In addition, an inset is included to compare the relative change in each lattice parameter, defined by the following expression:

$$\Delta d = \frac{d(T) - d_0}{d_0} . \quad (4.2)$$

From this comparison, it is evident that above T_N , the lattice parameter b exhibits a smaller thermal expansion than the other two. In other words, the material presents an anisotropic thermal expansion.

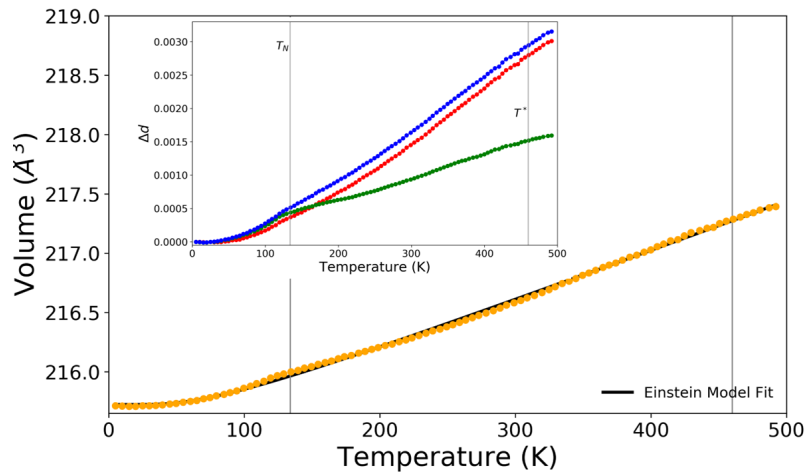


Figure 4.4: XRD: unit cell volume fitted using the Einstein model (black line) as a function of temperature. The inset shows the relative change (Δd) of each lattice parameter, highlighting anisotropic thermal expansion.

In Table 4.1, the parameters extracted from the model are shown, as well as its correspondence for the calculated volume. Additionally, first-principle calculations based on

Density Functional Theory (DFT) have been performed for rare-earth chromites (RCrO_3) by Jianhang Shi et al. [113]. The lattice parameter values obtained using the Hubbard U correction (SCAN+U) for the ErCrO_3 sample are also included in Table 4.1. Notably, our experimentally determined zero-temperature lattice parameters, derived using the Einstein model, are smaller than those predicted by the DFT calculations.

Lattice parameter	Space Group $Pbnm$			
	a	b	c	V
d_0 ($\text{\AA}, \text{\AA}, \text{\AA}, \text{\AA}^3$)	5.21749	5.50772	7.50697	215.71549
d_0 - DFT (SCAN+U) [113]	5.241	5.535	7.548	218.939
Θ_E (K)	307.6	189.2	212.0	204.49
E	0.0137	0.0077	0.0128	0.86683
R^2	0.9993	0.9975	0.9993	0.9989

Table 4.1: Summary of the Einstein model fitting of the lattice parameters from the XRD refinement.

4.3.3 Atomic Displacement Parameter

The atomic displacement parameter, often an isotropic value referred to as B or Debye-Waller factors (B_{iso}), is a measurement of the root-mean-square displacement amplitude of an atom from its average position in a crystal, which can be due to the vibration of the atoms and/or due to static disorder [109].

In Fig. 4.5, we present the temperature dependence of the isotropic atomic displacement parameter of Er, Cr, O1 and O2, which are the crystallographic sites defined by the $Pbnm$ space group. It is important to note that, due to the symmetry constraints of this space group, the oxygen atoms are divided into two distinct sites: O1, which corresponds to the apical oxygen atoms, and O2, which represents the equatorial oxygen atoms within the octahedral structure. As expected, the B factor for the lighter element (O) has a higher error associated with it since the X-Ray scattering factor depends on the atomic number (Z), making it challenging to locate these lighter atoms in the presence of heavy atoms [48]. The B factors for Er and Cr follow the same trend, with an overall increasing value with rising temperature (see Fig. 4.5). In addition, we see that only at $T > T_N$ does B_{iso} start to increase, unless in the temperature range 280-400 K, where an abnormal decreasing behaviour is shown.

These results are similar (inverse trend) to those observed in the raw data analysis of the area under the diffraction pattern (see section C2), which is expected since this parameter describes the effect on the XRD diffracted intensities due to the lattice vibrations [114].

In other words, a decrease in the area under the diffraction pattern suggests a reduction in overall scattering intensity, indicating variations in the atomic displacement parameter. Thus, this consistency further supports the validity of the fitting process, indicating that the results reflect real physical phenomena rather than artefacts.

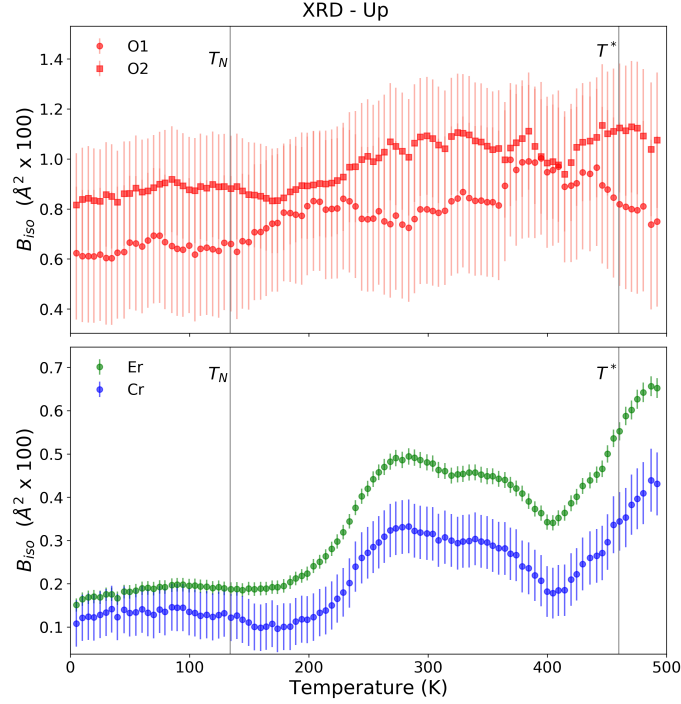


Figure 4.5: XRD: Isotropic ADPs of the Er, Cr, O1 and O2 atoms.

4.3.4 Atomic Position Evolution

Table 4.2 shows the symmetry constraints for the space group $Pbnm$ and the atomic positions for each atom, taken from the sequential refinement (Up dataset) at RT. The atomic positions of Cr, as well as the z -coordinates of Er and O1, are fixed due to these constraints. It should be noted that, in this space group, all three angles are 90° . Therefore, each lattice vector corresponds directly to a Cartesian direction, with a , b , and c aligning with x , y , and z , respectively. Furthermore, to study the relative change (Δd) of these refinable atomic positions, we used the previously mentioned expression 4.2.

Figure 4.6 a) illustrates the variation in Δd for the atomic positions of Er as a function of temperature. For $T < T_N$, in both the x and y direction, the atomic position stays roughly constant, only moving for higher temperatures. For temperatures higher than T_N , in the x -direction, the atomic position stays constant, except in the temperature ranges (180-250) K and (400-500) K, where it increases. In contrast, in the y -direction, for $T > T_N$, the atomic position of Er decreases with increasing temperature. Moreover, the trend

observed in the x -direction of the atomic position of Er closely resembles that of the B_{iso} parameter (see Fig. 4.5). It is also worth noting that the unusual behaviour shown in the y -direction (decreasing value with increasing temperature), aligns with the smaller anisotropic thermal expansion of the lattice parameter b (y -direction) at temperatures above the magnetic phase transition temperature, T_N .

<i>Pbnm</i> - Atomic Positions ErCrO_3 - RT		
Sites	Symmetry (atomic coordinates)	Atomic position (refinement)
Er^{3+} (4c)	$x, y, \frac{1}{4}; \bar{x}, \bar{y}, \frac{3}{4}$	$x = -0.0172$ $y = 0.0672$
Cr^{3+} (4b)	$\frac{1}{2}, 0, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; 0, \frac{1}{2}, 0$	
O_1^{2-} (4c)	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{4}; \frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{4}$	$x = 0.1077$ $y = 0.4568$
O_2^{2-} (8d)	$\pm(x, y, z); \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z;$ $\bar{x}, \bar{y}, \frac{1}{2} + \bar{z}; \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$	$x = -0.3082$ $y = 0.3019$ $z = 0.0580$

Table 4.2: XRD: Atomic positions of ErCrO_3 at RT. Adapted from Ref. 115.

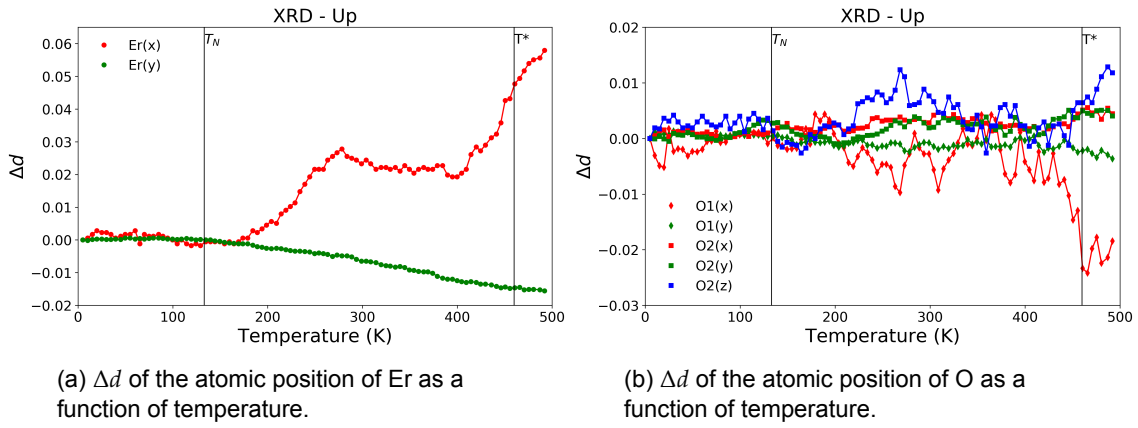


Figure 4.6: XRD: Δd of the atomic positions as a function of temperature.

Figure 4.6 b) illustrates the temperature dependence of the atomic positions of O within the space group $Pbnm$, as previously discussed. Throughout the entire temperature range, these atomic positions remain roughly constant with increasing temperature, except for noticeable variations in the x -direction for O1 and the z -direction for O2. In addition, these anomalies in $\text{O1}(x)$ and $\text{O2}(z)$, which occur only at temperatures above T_N , seem to compensate for one another, with the most significant variation observed around T^* .

Furthermore, these observed atomic position variations are within the allowed limits imposed by the space group $Pbnm$, which, according to symmetry constraints, should respect the irreducible representations (IRREPs) of the space group [116, 117]. In other words, there is no indication that a symmetry lowering is required to explain the observed data. It should be noted, however, that the Fullprof software does not allow the refinement of atomic positions that do not conform to the symmetry of the chosen space group. For example, positions such as 0, 0.25, 0.5, 0.75 are fixed, as previously mentioned. To refine these fixed atomic positions (and subsequently check if is required to lower the symmetry), we need the PDF method, which will be used and discussed later (see section 4.4).

Nevertheless, we performed a Rietveld refinement of the XRD data at RT using space groups with lower symmetry ($P2_1/m$ and $P2_1$). However, these refinements did not significantly improve the χ^2 value, and thus our fitted model (using space group $Pbnm$) remains sufficient to explain the observed experimental data.

4.3.5 Octahedral Environment Study

In perovskites, there are three main sources of structural distortions: rotation (tilting) of the BO_6 octahedra (B-O-B bond angle), Jahn-Teller distortions (B-O bond length changes) [118], and polar cation displacements [33], which are associated with ferroelectricity [119]. Therefore, studying the interactions between the B-site and oxygen anions is important since it provides valuable information about the basic properties of the material. For example, the degree of tilt of the octahedron gives rise to various crystal fields, leading to different electronic and optical properties [119]. It is worth mentioning that, in our case of ErCrO_3 , the Cr^{3+} (the atom sitting at B-site) does not exhibit Jahn-Teller distortion since its t_{2g}^3 configuration is not degenerate.

To facilitate the visual interpretation of this analysis, we used in parallel the software VESTA to examine the exported crystallographic information file (CIF) from the Rietveld refinement of the XRD data previously obtained. Notably, according to the constraints of the space group $Pbnm$, and confirming using VESTA, we can distinguish between two types of Cr-O bonds: Cr-O1 and Cr-O2. The Cr-O1 bonds consist of two equivalent bond lengths, while the Cr-O2 bonds are divided into four possible bond lengths, grouped into two equal sets, as depicted in the inset of Fig. 4.7.

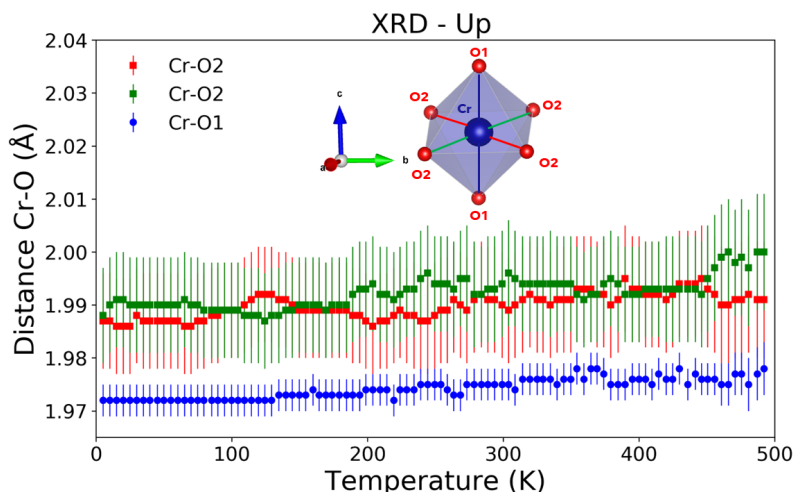


Figure 4.7: XRD: Analysis of the Cr-O distances in the octahedron with rising temperature.

Notably, although the Cr-O2 bonds are split, their values are constant and equal within the associated error margins. Interestingly, possible anomalies appear in the temperature range of 180-250 K and around 460 K (T^*), with the latter being more evident. Fig. 4.7 demonstrates the distance evolution with rising temperature for each of the bond lengths: Cr-O1 corresponds to the blue points (apical), while the Cr-O2 bond (equatorial) is split into two different lengths, shown as red and green points. Additionally, we see that no significant changes occur throughout the entire temperature range, staying roughly constant. This suggests that there is no evidence of structural distortions in the octahedron with respect to the bond lengths.

As for the angle dependence study, Fig. 4.8 illustrates the temperature dependence of the bond angles between Cr-O1-Cr (along the vertical axis, corresponding to the c -direction), represented by the blue points, and Cr-O2-Cr (within the horizontal plane, corresponding to the a - and b -directions), depicted by the red points, as the temperature increases. It should be noted that while there are other bond angles between Cr-O1-Cr and Cr-O2-Cr, they exhibit similar trends; therefore, only these two are presented for clarity. Additionally, the inset provides a visual representation of these angles formed between the octahedra. For this analysis, the bond angles at RT are taken as reference values, and once again, the results indicate that these angles remain relatively constant across the entire temperature range. However, the data seem to hint at subtle deviations near the 200 K and 460 K regions (more pronounced here). Nevertheless, we cannot confidently assert that these variations represent a genuine change in the bond angles due to the current data statistics and the associated error margins.

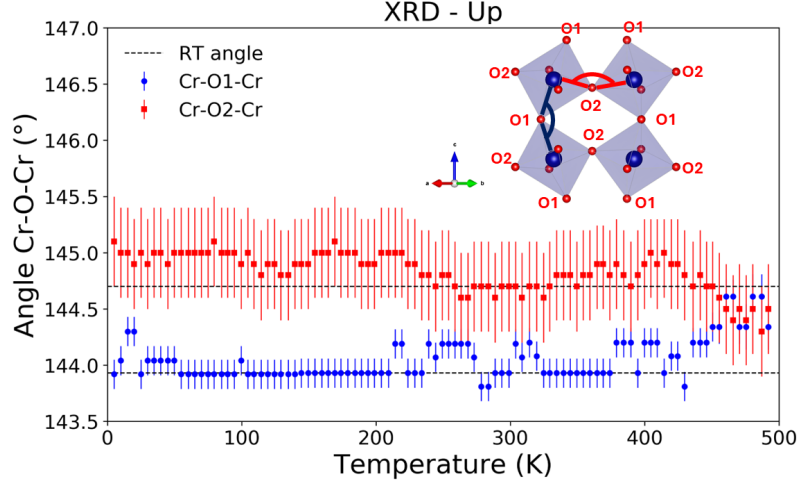


Figure 4.8: Analysis of the Cr-O angles inside the octahedron. The reference angle chosen was the one at RT.

4.4. Local Study - PDF

Until now, the analyses focused on the average structure of the material's crystalline structure, and from the results presented, there is no clear evidence to indicate a need to lower the symmetry in order to characterize the data. In other words, throughout the entire temperature range, the perovskite ErCrO_3 is described by the space group $Pbnm$. Nevertheless, some abnormal behaviours appear in the study of some of the properties of this material in other works Ref. [25]. For example, the dielectric constant, at different frequencies, was examined as a function of temperature. Near T^* , a large dispersion of the dielectric constant is seen for ErCrO_3 , having a broad peak and a frequency dependence, a commonly observed behaviour in relaxor ferroelectrics [25].

In addition, in the work of G. Oliveira et al [1], using the PAC technique, which is a local probe study, measurements on a polycrystalline ErCrO_3 sample, which is the same sample used in this thesis, revealed two clear signs of local environment changes, one also near the supposed ferroelectric phase transition temperature, T^* , and the other below 250 K. It is also worth mentioning that in another work Ref. [98], the electric polarization in this material was investigated in the temperature range 5-370 K, and no uniform ferroelectric ordering was found in any direction, but an electrical polarization induced by restricted polar domains of structural origin was observed.

Thus, in the following section, we will analyse the PDF data of this sample in hopes of giving a better understanding of these physical phenomena documented, as they are believed to have a local origin, which could not be studied through the Rietveld refinement of the long-range XRD data previously shown. Nevertheless, before examining the

sequential refinement results of the PDF data, a pre-data treatment process was performed in order to determine the key parameters required for the accurate generation of the $G(r)$ function. This includes defining instrumental and analysis-related quantities such as $Q_{\text{max-inst}}$, Q_{max} , and Q_{min} , as well as the calibration-specific parameters Q_{damp} and Q_{broad} . A detailed explanation of this procedure and the corresponding evaluation can be found in Appendix E.

In addition, similar to the the analysis of the XRD data, a preliminary study of the raw X-Ray data used to obtain the PDF data, $G(r)$, was performed, both as a 2D contour plot and of the area under the diffraction pattern. Once again, the same study was conducted on the highest intensity peak (112). A complete discussion and the corresponding figures can also be found in Appendix E.

4.4.1 Fit Ranges

As a reminder, the PDF method provides the probability of locating an atom at a given distance r from another atom. Thus, it can be thought of as a weighted distribution of bond lengths [120]. Additionally, since it allows the user to fit different structural models over various distance ranges, we can study how the local structure transitions into the average structure of the material, in other words, revealing characteristic length scales associated with local correlations [121]. In this work, we have chosen the r range from a $r_{\text{min}} = 1.8 \text{ \AA}$ to $r_{\text{max}} = 30 \text{ \AA}$, which will be defined as the "All Range". When refining the data, we separate them into three ranges: the already mentioned one, the "Low range", which is from r_{min} to $r = 7.8 \text{ \AA}$, and finally, the "High range", which is from $r = 15 \text{ \AA}$ to r_{max} .

This segmentation allows us to analyse different structural regimes. In the Low range (shorter distances), fewer atom pairs contribute to the statistical analysis, making it more sensitive to local variations and short-range correlations. Conversely, in the High range (larger distances), which is dominated by the periodicity of the crystal lattice, there are more atom pairs that contribute to the statistical analysis, diluting any captured distortions in the Low range. As a result, these distortions become less apparent in the PDF analysis. An intuitive way to picture this is by imagining a shell of thickness dr at different distances r . As r increases, the number of atom pairs within this shell grows. Therefore, we are effectively probing different layers, each influenced by a different number of contributing atoms.

A visual representation of this is shown in Fig. 4.9. Here, we present not only the theoretical $G(r)$ for this data—depicted as the blue “all-all” plot—considering the space group $Pbnm$ at 5 K (the lowest temperature, where the peaks are most well-defined), but also the contributions from every possible atomic pair in the studied perovskite ErCrO_3 under the same conditions. Additionally, as seen in Fig. 4.9, at higher r values, our theoretical $G(r)$ function “all-all” becomes dominated by the pairs containing Er, more precisely the pair Er-Er.

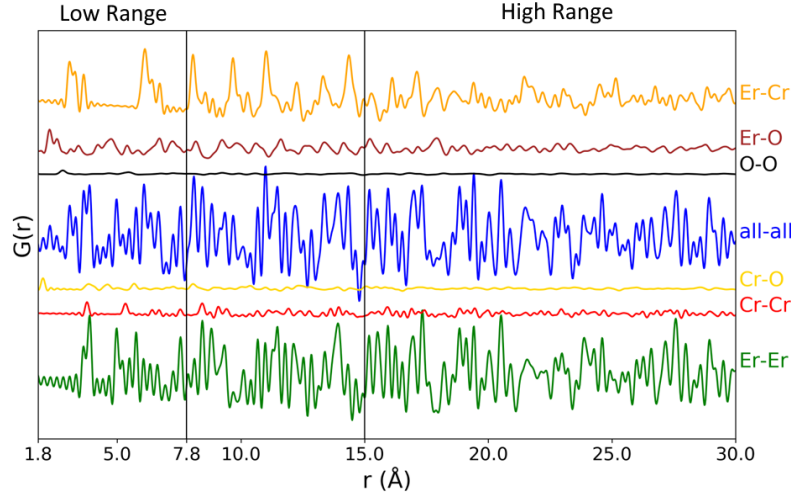


Figure 4.9: PDF: Theoretical $G(r)$ of ErCrO_3 using a space group $Pbnm$ at a temperature of 5 K.

4.4.2 R-value Analysis

As mentioned earlier, one method to evaluate the fit quality in describing the PDF data is an analysis of the equation 2.10, the R_w . Therefore, using the three previously defined r ranges, we refined our PDF data (using the space group $Pbnm$) and collected the corresponding R_w parameter for each temperature.

Fig. 4.10 illustrates the evolution of R_w , using the space group $Pbnm$ that was indexed through the XRD analysis, as a function of temperature for the three defined r ranges. Throughout the entire temperature range, the R -value stayed roughly constant (within the baseline shown in red), except in the Low range, where a clear distortion is seen in two distinct temperature regions: one between 180-250 K (highlighted in purple shaded area in Fig. 4.10) and the other near the claimed ferroelectric phase transition, T^* . To further confirm the local origin of the distortion, we see that in the High range, there is no dispersion of the R_w value, since, as previously mentioned, the local variations are diluted.

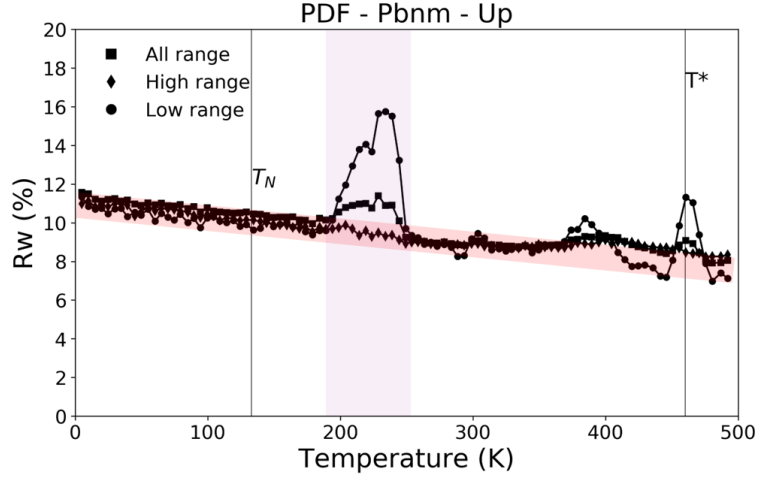


Figure 4.10: R_w of the three r ranges, as a function of temperature, used for refining the data with a space group $Pbnm$.

The purple-shaded region highlights the temperature range (180-250 K) of the first and most prominent anomaly. By contrast, the red shaded area represents a baseline for the R_w , serving as a visual indicator of the expected fit quality (for the $Pbnm$ space group) when no structural distortions are present. Therefore, outside of the temperature ranges mentioned, the space group $Pbnm$ can well describe the PDF data in the three r ranges; therefore, there is no sign of a phase transition for a corresponding unique temperature. It is also worth mentioning that the results shown here all agree with those presented in previous works found in literature [1, 25, 98].

4.4.3 Lattice parameter

In this subsection, the thermal behaviour of the lattice parameter a , b , and c , derived from the PDF analysis, will be examined. The same Einstein model, equation 4.1 and previously employed in the XRD study, has been used here. The extracted parameters from the fitting are summarized in Table 4.3, and are similar to those obtained in XRD, see Table 4.1.

Lattice parameter	Space Group $Pbnm$			
	a	b	c	V
d_0 (Å, Å, Å, Å ³)	5.21642	5.50756	7.50744	215.69005
Θ_E (K)	303.1	223.1	209.7	221.8
E	0.0168	0.0124	0.0148	1.1914
R^2	0.9970	0.9861	0.9961	0.9957

Table 4.3: Summary of the Einstein model fitting of the lattice parameters from the PDF refinement.

Figure 4.11 illustrates the evolution of the lattice parameters a , b and c with rising temperature, where for each lattice parameter, we fitted the Einstein model (full black line). Similar to the results seen in section 4.3.2, at T_N , lattice b deviates from the model and exhibits a smaller thermal expansion than the other two lattices, indicative once again of its anisotropic thermal expansion. The dashed black line represents an extrapolation based solely on the data collected up to T_N for the lattice parameter b . In comparison with the lattices obtained from the XRD data, the linear region (higher temperatures) shows more variation, which follows the observations from the raw data analysis of the Gaussian centre, as shown in Fig. E2 b).

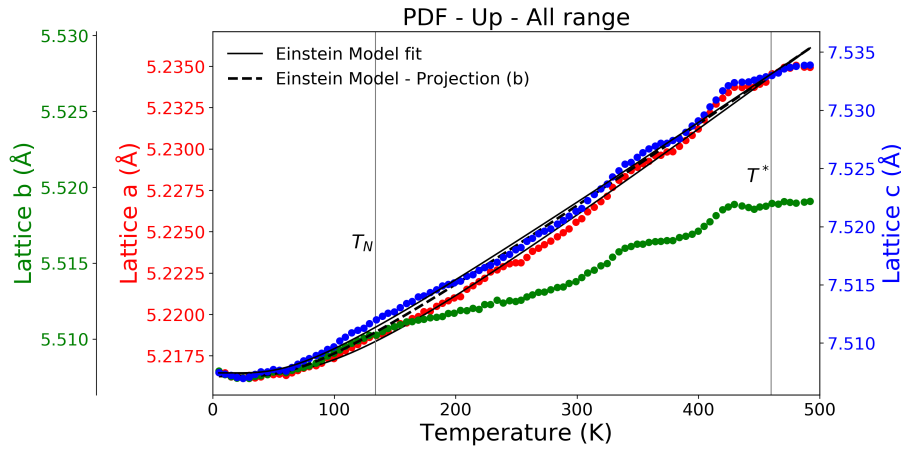


Figure 4.11: Lattice parameters as a function of temperature, extracted from the PDF method using the space group $Pbnm$ and the r all range. The solid black line represents the fitting of the Einstein model and the dashed black line the extrapolation of the same model for b using only temperatures smaller than T_N .

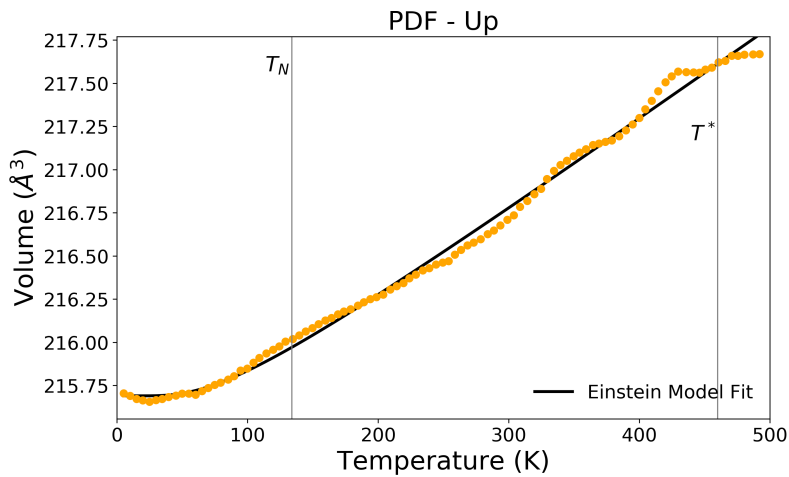


Figure 4.12: PDF: Unit cell volume as a function of temperature.

Figure 4.12 illustrates the temperature dependence of the unit cell volume, along with the corresponding fit using the Einstein model. Compared to the unit cell volume derived

from the XRD data (see Fig. 4.4), the volume derived from the PDF data exhibits more deviations from the model, particularly in the higher temperature range. In addition to the two anomalies already observed in the XRD data (one occurring near T_N (134 K) and another within the temperature range of approximately 200-300 K), a third deviation is clearly visible just below T^* . This discrepancy also explains the small differences in the parameters extracted from the Einstein model between the two methods, where in both cases, they are smaller than the first-principle calculations based on DFT [113], see Table 4.1.

4.4.4 Atomic Displacement Parameter

Understanding the evolution of the ADPs with rising temperature can provide valuable insights into the local dynamics of ErCrO_3 , since this parameter is modelled from the PDF peak width, containing information on both the static disorder and thermal diffuse scattering [122].

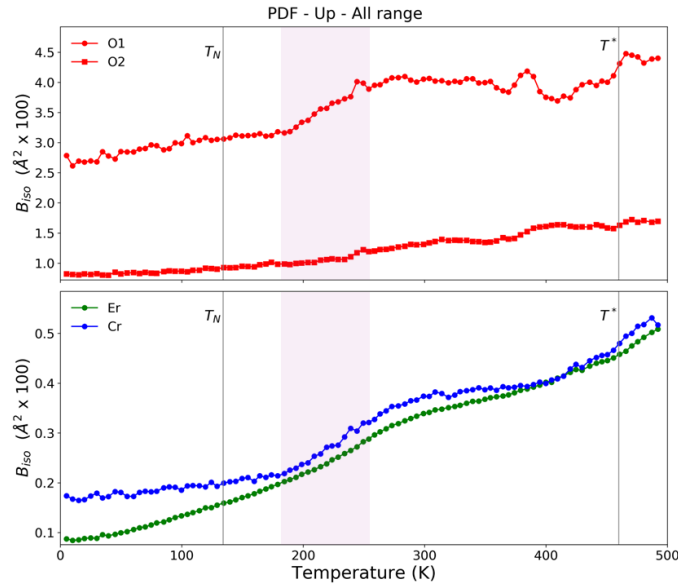


Figure 4.13: PDF: Atomic displacement parameter as a function of temperature.

Figure 4.13 illustrates the temperature evolution of the isotropic atomic displacement parameter (B_{iso}) for each refinable atom, constrained by the space group $Pbnm$. For the heavier atoms (Er and Cr), they follow roughly the same trend and have identical values. As the temperature increases, their B_{iso} values remain roughly constant, until a temperature of 180 K, which is the beginning temperature for the local distortion seen in the subsection 4.4.2 (purple shaded area), where it starts to rapidly increase until a temperature of 250 K (end of purple shaded area). Then they remain approximately stable until

460 K (T^*), where a sharp increase is observed, indicating another structural change at this temperature. Additionally, a similar trend is observed for both O1 and O2, although in the latter it is much more evident.

These findings suggest that Cr and O play a dominant role in the structural distortions observed within the temperature regions identified in the R -value analysis for different r ranges. In particular, the B_{iso} values for these atoms remain constant at lower temperatures, below the Néel temperature (T_N), indicating that the magnetic ordering of the material may suppress these distortions as the temperature decreases from higher values. Similarly, Yuling Su et al. [31] observed a decrease in polarization (possible local distortion origin) near T_N with increasing temperature, suggesting a coupling between magnetic and ferroelectric order parameters, where the magnetic field suppresses the polarization.

4.4.5 Atomic Position Evolution

The following subsection demonstrates the atomic position evolution with rising temperature, given by the space group $Pbnm$, which was already discussed in Table 4.2. All the results are presented in the Δd form, expressed by equation 4.2. Figure 4.14 a) demonstrates the variation in the x - and y - direction of the atomic positions of Er as temperature rises. In addition, Fig. 4.14 b) shows the evolution on rising the temperature of the atomic positions generated using the mentioned space group for the element O.

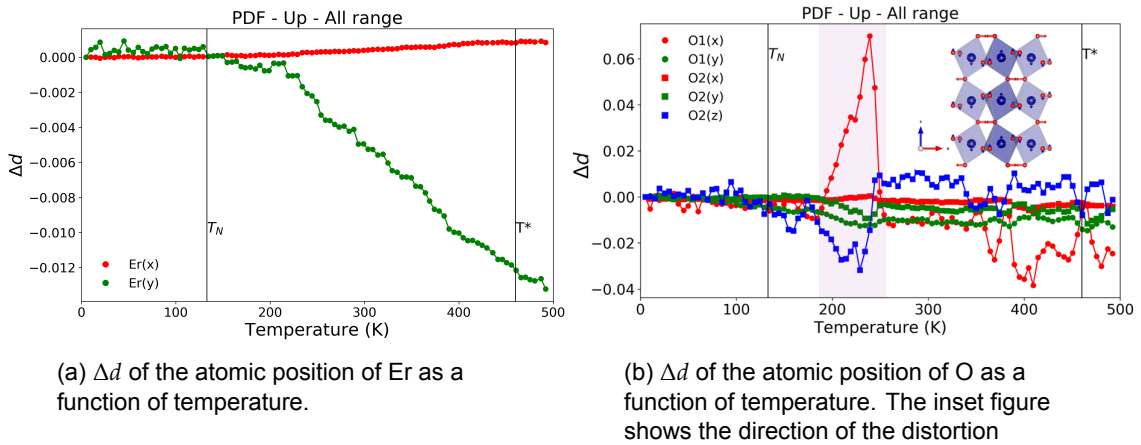


Figure 4.14: PDF: Δd of the atomic positions as a function of temperature.

In comparison with the XRD Δd of Er, see Fig. 4.6 a), an atypical behaviour of this parameter is still observed along the y -direction (for temperatures higher than T_N , the atomic position decreases), which coincides with the smaller thermal expansion identified in the lattice b in both sample characterization methods. Moreover, in the x -direction, unlike in the XRD analysis, where a significant shift in the atomic position of Er is seen,

here it remains roughly constant across the entire temperature range, as demonstrated in Fig. 4.14 a).

As for the Δd O, shown in Fig. 4.14 b), they all remain constant with rising temperature, except O1, in the x -direction, and O2, in the z -direction, which appear to compensate for each other. It should be noted that in Fig. 4.6 b), these are also the only two atomic positions that vary with rising temperature, although, for the PDF case, the fluctuations are more pronounced. In particular, the most notable variation is observed in $\text{O1}(x)$, which is consistent with the temperature range (180-250 K) of the local distortion seen in Fig. 4.10.

These results suggest that the local distortions seen in the temperature region of 180-250 K are associated with variations in the x - and z -directions of the O1 and O2 atomic positions, respectively. Additionally, as demonstrated in the inset of Fig. 4.14 b), the direction of these anomalies in the O1 and O2 atomic positions points to a possible tilting of the CrO_6 octahedra.

4.4.6 Study of local distortions

Investigating local distortions is crucial for understanding the functional properties of complex perovskite-like oxides, as even slight deviations from the average crystal structure can significantly impact electronic, magnetic, and thermal behaviour, which are often missed by traditional techniques like the Rietveld refinement performed in section 4.3. Other rare-earth orthochromites, such as YCrO_3 [33], SmCrO_3 [123], and GdCrO_3 [110] have been under strong debate with respect to their ferroelectric properties, whose local study have been conducted to clarify its origin. As shown in the PDF analysis until now performed, local distortions were detected in specific temperature ranges, suggesting short-range structural complexities not captured by the XRD analysis. In the following subsections, we will delve deeper into the origin of these temperature-dependent local distortions, utilizing the advantages of PDF for short-range structural analysis.

4.4.6.1 Symmetry lowering study

The study of Irreducible representation (IRREP) (symmetry lowering) can be a powerful tool in understanding structural phase transitions due to symmetry changes in materials. For complex perovskite-like oxides, analysing these symmetry changes helps identify possible distortions that can contribute to unique physical properties, like ferroelectricity. Some examples of other studies on similar rare-earth orthochromites, such as YCrO_3 [33]

and SmCrO_3 [123], which both exhibit an average crystal structure characterized by the $Pnma$ space group, have demonstrated that the local structural distortions can be indexed to the non-centrosymmetric space group $P2_1$ that allows for ferroelectricity (spontaneous polarization) due to a cation B -site displacement.

For ErCrO_3 , we propose a similar scenario with the same symmetry reduction from the centrosymmetric space group $Pbnm$ (No. 62) to the non-centrosymmetric $P2_1$ (No. 4). To achieve this, we followed and studied the sequence that involves a stepwise reduction described in Fig. 4.15, following the IRREP associated with lowering symmetry ionic displacements (Γ -point). The first reduction leads to the non-centrosymmetric $Pna2_1$ (No. 33), associated with the irreducible representation $\Gamma 4^-$. This transition breaks inversion symmetry and allows for the possibility of ferroelectricity. The second reduction pathway ($Pbnm$ to $P2_12_12_1$ (No. 19)) is driven by the $\Gamma 1^-$ IRREP, which, although lacks inversion symmetry, it does not have a polar axis, meaning it is not ferroelectric. The third pathway from $Pbnm$ leads to $P2_1/m$ (No. 14), driven by the $\Gamma 4^+$ mode, which, since it preserves inversion symmetry, does not allow for the existence of ferroelectricity. Finally, we can lower the symmetry from the space group $P2_1/m$ to $P2_1$ by removing the centre of symmetry located at the B -site [33]. This is achieved by slightly displacing the B atom, which, in this case, is Cr, the element situated within the octahedron.

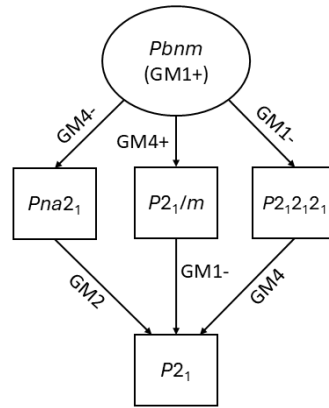


Figure 4.15: Possible structural phase transitions sequence from $Pbnm$ (62) to $P2_1$ (4). Adapted from ref. 124.

It is worth mentioning that the decision to investigate such a significant symmetry reduction is motivated by the PDF analysis previously shown. As highlighted earlier, in the "Low range" (short-range), the experimental $G(r)$ function reveals local distortions that cannot be described by higher symmetry space groups, like the $Pbnm$ that can, over all the temperature range, describe the average structure of the material. Therefore, for a

temperature that previously showed a distortion, in this case 234 K, we fitted the experimental data with the possible different space groups that followed a stepwise symmetry reduction for different r ranges, where the obtained R_w parameter is shown in Table 4.4.

Table 4.4: Summary of the R_w values for different r -ranges at 234 K.

Refinement at T = 234 K - R_w (%)					
Space group	$Pbnm$	$Pna2_1$	$P2_12_12_1$	$P2_1/m$	$P2_1$
All Range	11	11	11	10	10
High Range	10	12	10	11	10
Low Range	16	16	15	14	12

All value errors are less than 1%.

From the analysis, it is evident that for the "All Range" and "High Range" fits, the R -value remained approximately constant, indicating that the higher symmetry space group, $Pbnm$, is sufficiently accurate to describe the experimental data in these ranges. However, in the "Low Range", where local distortions are more prominent, reducing the symmetry leads to a noticeable improvement in the agreement between the model and the experimental data, with the lowest symmetry space group $P2_1$, having the best agreement. It is important to emphasize that this space group is non-centrosymmetric and allows for a Cr displacement.

Following this, we further analyzed the $G(r)$ graphs at this temperature for the space groups $Pbnm$ and $P2_1$ to identify the specific peaks where the higher symmetry space group can not describe the experimental data. In the $G(r)$ function, peaks can be attributed to specific atom pairs or multiple atom pairs' contributions if they share the same bond length. Additionally, in many cases, the first 2-3 peaks occur in the region where the baseline can be clearly seen, and there are no overlapping peaks [125]. This is where the PDF method stands out by allowing us to identify and extract this information. In this thesis, these calculations were performed using the designated option (Calculations) in the PDFgui software [56], which can be seen in Fig. 4.9.

Figure 4.16 illustrates the refined $G(r)$ function using two different space groups, $Pbnm$ and $P2_1$, at a temperature of 234 K. Refinement was performed using the Low range, as local distortions were observed at this temperature (indicated by the disparity in the R_w

parameter). Additionally, we identify the atom pairs associated with some of the peaks that are of particular interest to this study.

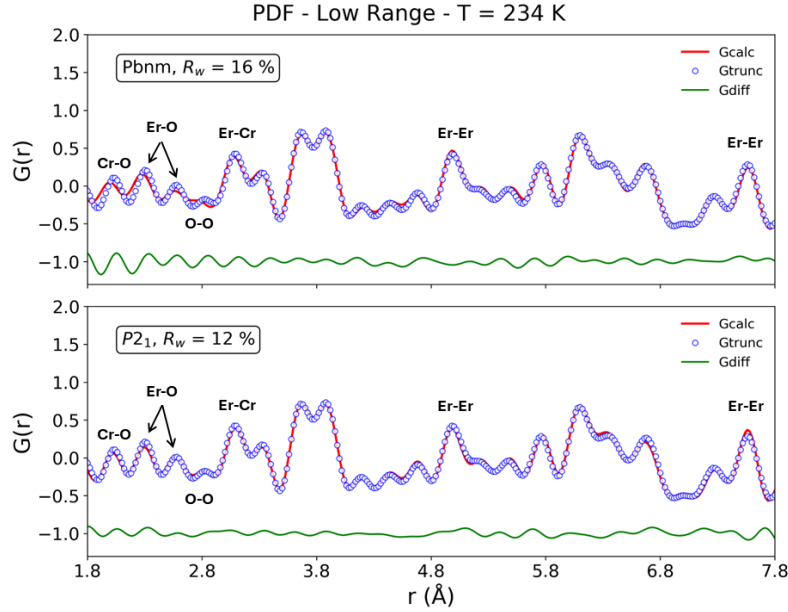


Figure 4.16: PDF: $G(r)$ at a temperature of 234 K, fitted using a space group $Pbnm$ and $P2_1$.

In particular, Figure 4.16 shows PDF experimental data (G_{trunc}) represented by blue points, the model fits (G_{calc}) shown as red lines and the residuals (G_{diff}) (green line) for each space group model fit. Moreover, we see that the anomalies are mainly due to atom pairs with oxygen, where the two most significant distortions are the peak at approximately $r = 2 \text{ \AA}$, which corresponds to the Cr-O bond, indicating a possible displacement of the Cr, and the O-O bond length, at approximately $r = 2.8 \text{ \AA}$. In particular, the Cr-O and O-O bonds suggest that the $P2_1$ space group provides the best fit for the local environment (both are corrected by the space group $P2_1$), similar to the findings in [33, 123], indicating that comparable distortions may be at play in ErCrO_3 . In addition, peaks involving Er-Er pairs, on the other hand, remain consistent across both models, indicating no significant distortions in the rare-earth sublattice. However, for higher values of r , in the space group $P2_1$, they start to deviate from the experimental data.

4.4.6.2 Cr displacement

Now, we will examine the displacement of the Cr within the crystal structure of ErCrO_3 , as suggested by the previous analysis. As mentioned, the potential off-centring of this atom is essential to the appearance of ferroelectricity since a non-centrosymmetric phase emerges. Our analysis is also motivated by the findings of K. Ramesha et al. [33] on

YCrO_3 , where a PDF study revealed local distortions not captured by the higher-symmetry space group $Pbnm$, especially seen in the Cr-O bond length at $r = 2 \text{ \AA}$.

To perform this, we selected three temperatures: 234 K and 460 K (T^*), both of which exhibited local distortions, and 492 K, which did not. Using the space group $Pbnm$, we refined our PDF data in the Low range, following the same procedure as before but first modifying the atomic position of the Cr atom. In other words, we conducted systematic refinements to investigate the influence of the Cr displacement along specific crystallographic directions, and the model that provided the best fit was the Cr off-centring along the c -axis (lattice with the highest value), specifically in the z direction. Fig. 4.17 illustrates the resultant R_w values for the different displacement values along the c -axis at the selected temperatures. Moreover, Fig. 4.17 shows that for temperatures with local distortions, a clear minimum in the parameter R_w is observed for a Cr displacement of approximately $0.008 \text{ \AA}$ in the first local distortion range (234 K) and $0.01 \text{ \AA}$ in the second, near T^* . Additionally, in a temperature that showed no local distortion (492 K), a Cr off-centring only gave a worst fit to the experimental data. These results presented are similar to those reported by K. Ramesha et al. [33] for the rare-earth orthochromite YCrO_3 .

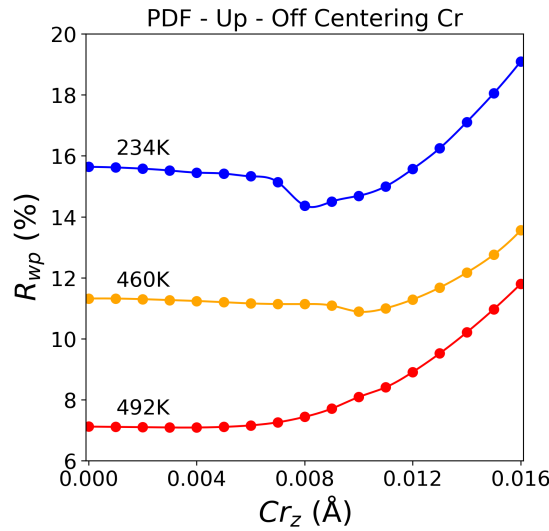


Figure 4.17: PDF: Off centring of the Cr atom in the z direction.

It is worth mentioning that if such a displacement were coherent throughout the entire crystal structure, it would be expected that in the Rietveld refinement (XRD), the non-centrosymmetric model $P2_1$ would give better results upon fitting the experimental data. This was not observed in section 4.3, which indicates that this displacement is not uniform

throughout the material but rather in a disordered manner [33]; in other words, the off-centring is local, leading to regions with lower symmetry while maintaining an overall high symmetry average structure.

4.4.6.3 Octahedral Environment Study

We further investigate the impact of distortions in the CrO_6 octahedra by examining various angles and distances both within and between the octahedra. This analysis uses VESTA, with the Crystallographic Information File (CIF) from the refinement and the space group $P2_1$ for the temperature at which the distortion is most pronounced (234 K). An illustration of these angles and distances can be seen in Fig. 4.18, and they are summarized in Table 4.5 and Table 4.6, respectively. Additionally, a comparison of the results is made with the XRD values and for the PDF, but using the space group $Pbnm$, for the "All range" and "Low range", in the same temperature. It is worth mentioning the distinction between solid and dashed lines used to represent the various angles and distances, illustrated in Fig. 4.18 and summarized in Table 4.5 and Table 4.6 (first column). This visual convention becomes particularly useful in the analysis of the Low range PDF data refined using the space group $P2_1$, as will be discussed later.

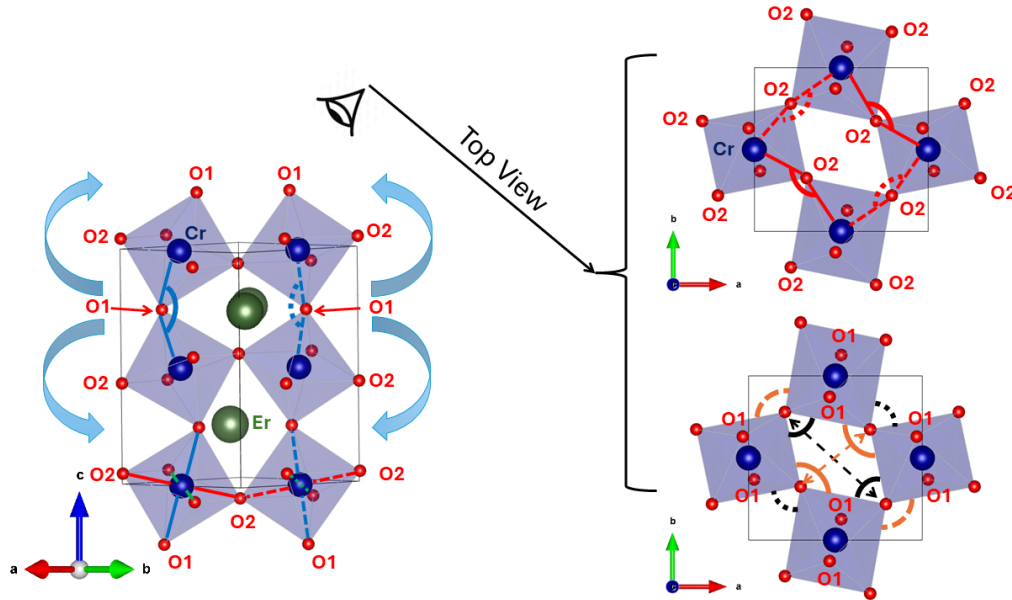


Figure 4.18: Schematic view of the octahedra distortion in ErCrO_3 . The left image shows the tilting of the octahedrons, and the right image shows the top view, where in the space group $P2_1$, the values are divided into two sets.

In particular, Table 4.5 shows that when using the space group $Pbnm$, the angles measured from the CIF in Vesta, obtained through both XRD and PDF characterization techniques, are identical when taking into account the r -range All range, except for the angle

depicted in red (see right of Fig. 4.18). These results are expected, as this r -range reproduces the long-range average atomic structure. Additionally, still considering the space group $Pbnm$, the angular values in the Low range differ from the XRD results only for the blue and red angles, which correspond to the octahedral bond angles Cr-O₁-Cr and Cr-O₂-Cr, respectively. Furthermore, when we reduce the symmetry to the space group $P2_1$ and analyse the Low range r -region (short-range), we observe that the data splits into two different sets (which, within the unit cell, correspond to adjacent columns), one that yields similar results to those obtained from XRD using the space group $Pbnm$ (angles shown as solid lines), while the other exhibits noticeable distortions (angles shown as dashed lines).

Table 4.5: Angles: Refinement at a temperature of 234 K.

Angle ($\angle$)	XRD - $Pbnm$	PDF - $Pbnm$		PDF - $P2_1$ - Low Range (12%)	
	R_{wp} (6.3 %)	All Range (11%)	Low Range (16%)	—	---
— / ---	113.4(6)	113.0	112.4	112.8	109.7
— / ---	66.6(6)	67.0	67.6	67.3	70.3
— / ---	143.9(6)	142.8	140.9	139.0	139.8
— / ---	144.8(5)	146.7	147.0	144.5	148.3

The PDF angle errors are 0.1%.

As for the bond length analysis, Table 4.6 once again highlights the similarity between the values obtained from XRD and PDF when considering the All range dataset for the space group $Pbnm$. Meanwhile, when analysing the Low range values, a greater discrepancy is observed, which is expected since local distortions are more pronounced in this r -range. Moreover, upon lowering the symmetry to the space group $P2_1$ (which provides the best fit to the experimental data when considering the Low range, see Table. 4.4), the values are again divided into two distinct sets (except for the bond lengths shown in orange and black, which are O₂-O₂, and in blue, which is the Cr-O₁). In this case, all the values from the different sets exhibit distortions, and their average approximates the bond lengths obtained from the XRD analysis using the space group $Pbnm$.

Table 4.6: Bond Lengths: Refinement at a temperature of 234 K.

Distance ($\leftrightarrow$)	XRD - $Pbnm$	PDF - $Pbnm$		PDF - $P2_1$ - Low Range (12%)	
	R_{wp} (6.3 %)	All Range (11%)	Low Range (16%)	—	---
— / ---	4.706(19)	4.67	4.65	4.44	4.44
— / ---	3.094(19)	3.09	3.11	2.96	2.96
— / ---	1.976(4)	1.98	2.00	2.01	2.00
— / ---	1.989(10)	1.97	1.95	1.93	2.06
— / ---	1.993(10)	1.99	2.01	1.92	2.03

The PDF bond length errors are 0.01%.

To further confirm the local origin and amplitude of these distortions, we conducted a study on the variation of the bond lengths Cr-O, which, based on previous analysis, appears to be one of the primary sites of distortion, across different r -ranges. In particular, we fixed the $r_{\min}$ at 1.8 Å and varied $r_{\max}$, refining the model (using the space group $Pbnm$) to fit the experimental data, and using Vesta extracted the value of the bond lengths. This was performed for two different temperatures: 134 K, where no distortion was observed, and 234 K, where the distortion was most pronounced.

The results of this analysis are illustrated in Fig. 4.19, where we observe that at 134 K, the Cr-O bond lengths are independent of the r -range chosen for the refinement, remaining roughly constant. In contrast, at 234 K, the bond lengths depend on the chosen $r_{\max}$, where for smaller $r_{\max}$ (Low range), local distortions are still present and have not been averaged out by statistical sampling over a larger structural region. These values tend to stabilize and remain constant when the refinement is carried out for an $r_{\max}$ value of roughly 16 Å or beyond.

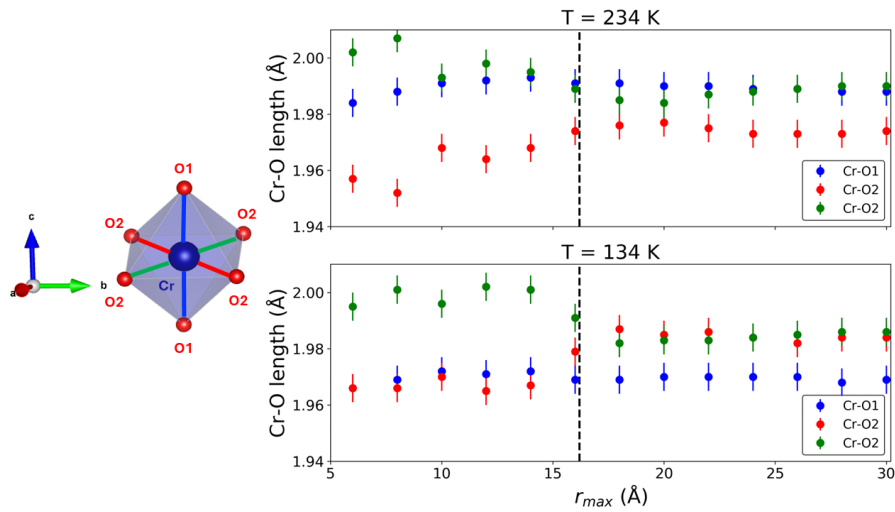


Figure 4.19: Cr-O bond lengths extracted from the PDF refinement using $Pbnm$ at different temperatures.

Therefore, this study allows us to extract the size of the cluster of the distortion region, which is around this length scale, before the values approximate the XRD average [120]. Moreover, the data suggest that for both temperatures, when $r_{\max} < 16$ Å, we can distinguish between two Cr-O2 bond lengths (depicted as red and green lines). However, for higher $r_{\max}$ values this separation no longer exists and there is only one bond length associated with Cr-O2, although for the temperature where local distortions are seen (234 K), there remains a slight difference between the two bond lengths.

4.4.7 Correlation Length Study

To determine the correlation length, we examine the evolution of the parameter R_w as a function of the fit range (r) for two different temperatures: one with local distortions (234 K) and the other without them (492 K). In other words, using the space group $Pbnm$, we refine the experimental data at both temperatures over the full r -range (from $r_{\min}$ of 1.8 Å to $r_{\max}$ of 30 Å), fix the refined parameters, and systematically vary $r_{\max}$. It is worth noting that, since the PDFgui software does not allow obtaining the R_w with zero parameters refined, we allowed the scale factor parameter to refine. However, it could have been, for example, one of the lattice parameters, as it is a value that is not expected to change with the decreasing r -range.

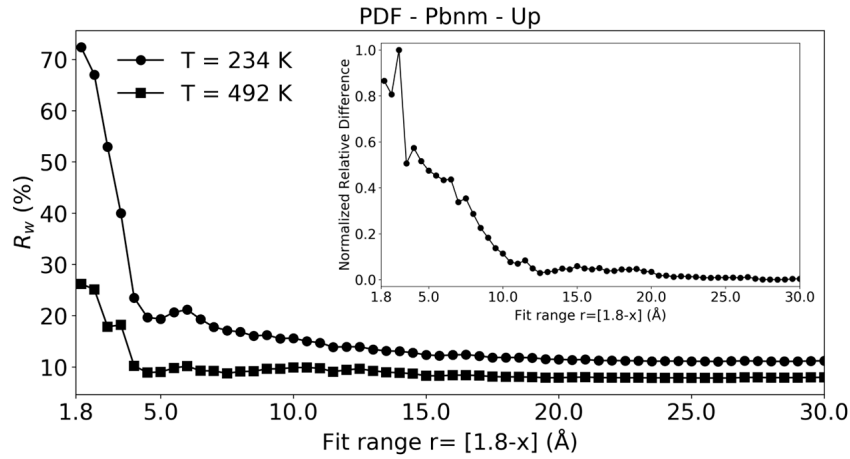


Figure 4.20: Correlation length: R_w as a function of the r -range. Inset figure shows the relative difference between the two datasets.

Figure 4.20 illustrates the variation of the R_w value at two different temperatures, one where local distortions are observed (234 K) and one where they are not (492 K), as a function of the fit range (where $r_{\min}$ is fixed). As the $r_{\max}$ decreases, particularly near 10–15 Å, disparities in the R_w values become evident, especially at the temperature which exhibits local distortions. These disparities are of similar value to those observed in the Cr-O bond lengths ($r = 16$ Å), and they highlight how the local structural features, which are averaged out at larger $r_{\max}$ -ranges (long-range), start to influence the refinement results. In addition, the inset figure shows the relative difference between the two datasets, using the temperature without local distortions as the baseline. This further emphasizes the disparities in the R_w parameter, particularly around 10–15 Å. Furthermore, we can also determine from Fig. 4.20 that the correlation length is on the order of 5 Å, which corresponds approximately to the size of the unit cell.

5. Conclusions and future work

In this chapter, we summarize the main conclusions and key findings of this thesis, based on the study of the two perovskite oxide materials, Y_2NiMnO_6 and ErCrO_3 . Additionally, we will give an outlook on possible directions for future work.

5.1. Conclusions

Perovskite materials have been well known for their diverse and tunable properties, making them highly attractive for a wide range of technological applications. Therefore, a comprehensive understanding of their crystal structure is crucial, as it directly influences their physical and chemical properties. In this thesis, we investigated two distinct perovskite oxides: the single perovskite ErCrO_3 and the double perovskite Y_2NiMnO_6 , representing different classes of perovskites exhibiting promising characteristics for multifunctional device applications.

We have synthesized Y_2NiMnO_6 using two different methods: the solid-state reaction and the sol-gel process techniques. The X-Ray diffraction analysis of both samples confirmed the space group $P2_1/n$ (No.14), with the solid-state route producing a sample of better quality, although it contained a second phase of NiO , which slightly impacts its properties, mainly the magnetic. In addition, the elemental composition analysis using the technique Energy Dispersive X-Ray Spectroscopy further confirmed the superior quality of the solid-state sample, as its chemical composition closely matched the theoretical values, whereas the sol-gel sample had a significant deviation. Despite these challenges, we performed a comprehensive analysis of the magnetic properties of both samples, along with electrical and thermal measurements for the sol-gel sample.

As for the magnetic properties, our investigation showed the existence of competing magnetic interactions within the material, as evidenced by the dual-phase magnetic transitions observed in both samples. The solid-state sample exhibited the highest transition temperature (T_C) at 64 K, along with an effective magnetic moment of $4.89 \mu_B$, which is in close agreement with the theoretical value. Additionally, this dual transition temperature and lower (T_C) can be attributed to the presence of unreacted Mn-based reagent and the minor second phase of NiO , respectively, both of which were more pronounced in the sol-gel sample. This was further supported by the higher effective magnetic moment observed in the sol-gel sample, which is likely due to variations in the oxidation states of Ni

and Mn compared to the expected values. We have also calculated the magnetocaloric effect and found that the solid-state sample has better potential for application in magnetic refrigeration, which exhibited a maximum entropy change of $2.46 \text{ J}\cdot\text{Kg}^{-1} \text{ K}^{-1}$ and a RCP of $207 \text{ J}\cdot\text{Kg}^{-1}$ at an applied external magnetic field of 70 kOe. Finally, the Heat Capacity measurement in the sol-gel sample confirmed the presence of the magnetic phase transition, and the DC resistance measurement indicated that the sample has a room temperature resistance of 2435Ω , as well as a semiconductor behavior, which was then further confirmed by obtaining a activation energy, calculated from the Arrhenius plot, of 0.227 eV.

In the current literature regarding rare-earth orthochromites, some doubts still persist about the potential existence of a ferroelectric phase transition, and what could be its origin, as understanding this is crucial for developing potential applications in multifunctional devices that rely on both magnetic and electric properties. Therefore, the primary goal of our work on ErCrO_3 was to compare the macroscopic and local structural characteristics, which could potentially explain the actual existence and origin of any ferroelectric (transition) behavior.

In terms of the macroscopic analysis, the XRD confirmed that the space group $Pbnm$ accurately described the crystal structure across the entire temperature range studied. Although some anomalies were observed, they were within the acceptable limits imposed by the space group and always occurred above the Néel temperature (T_N). Regarding the local study, the PDF analysis demonstrated that local structural distortions appeared in the low r range (short-range), specifically between 180-250 K and around 460 K. In these same temperature ranges, no such anomalies were observed in the high r range (long-range).

Moreover, these distortions, which have been previously reported in similar orthochromites, were primarily due to the displacement of Cr ions along the c -axis (z -direction), with a displacement of around $0.08 \text{ \AA}$. Additionally, a tilting of the octahedra, attributed to a displacement of oxygen atoms $\text{O1}(x)$ and $\text{O2}(z)$, was observed. Consequently, reducing the symmetry to the $P2_1$ space group yielded the best fit to the PDF data, although this was only evident when analyzing the low r range and within the previously mentioned temperature ranges, which supports the presence of local distortions. Furthermore, when we reduce the symmetry to the space group $P2_1$ and analyse the low range r -region, we observe that the data splits into two different sets (which, within the unit cell, correspond

to adjacent columns), one that yields similar results to those obtained from XRD using the space group $Pbnm$, while the other exhibits noticeable distortions. The correlation length study revealed a correlation length of approximately 5 Å, close to the size of the unit cell, and the distortions can be indexed to a cluster size of roughly 16 Å.

Given these findings, our analysis not only confirms previous reports of local distortions in ErCrO_3 , but also suggests that these distortions arise from the displacement of Cr ions and the tilting of the octahedral units. However, despite these local structural changes, we were unable to assign a temperature to a potential ferroelectric phase transition. Furthermore, these local distortions are effectively suppressed by the magnetic phase transition at T_N , suggesting that any possible ferroelectric behavior in this material is suppressed by the strong magnetic interactions.

5.2. Future work

For future investigations on Y_2NiMnO_6 , further refinement of the synthesis methods, particularly in the sol-gel process, could improve the purity of the samples. This would involve more extensive grinding and possibly alternative synthesis routes to minimize secondary phases or incomplete reactions. In addition, although the SEM images seem to hint that the grain sizes associated with the SG method are smaller than those produced by the SSR method, a more in-depth analysis is required to confirm this observation, for example a common approach is to use the software ImageJ to determine the mean particle size from the fitting of their particle size distribution [126]. Additional analyses, such as Williamson-Hall and Scherrer methods, should also be performed to obtain the crystallite size and microstrain of both samples.

Additionally, one could pair with the sample characterization technique X-Ray photoelectron spectroscopy (XPS) in order to confirm the valence states of the different magnetic ions involved and compare them with their expected value. Once improved samples are obtained, their potential for thin-film applications should be explored, particularly for usage in devices such as solar cells. The study could also extend to determining the stability and efficiency of these thin films under various conditions to understand their applicability in energy-related technologies.

In the case of ErCrO_3 , further analysis of the down dataset, which is currently ongoing, could provide additional insights into the material's behavior, particularly its thermal expansion upon cooling. Furthermore, Raman spectroscopy could offer complementary

information about the vibrational modes and structural distortions in the material, helping to establish a clearer connection between its local and macroscopic structural features. In addition, measuring polarization versus electric field loops at different temperatures could help identify possible ferroelectric behavior associated with the structural distortions observed at certain temperature ranges, further supporting our findings and providing a comparison with other rare-earth orthochromites, where ferroelectricity has been linked to local structural distortions. Finally, additional symmetry analysis through IRREP studies could provide valuable insights into the evolution of distortions with temperature, helping to clarify the pathways taken during the material's structural transitions.

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Appendix A - Magnetocaloric Effect

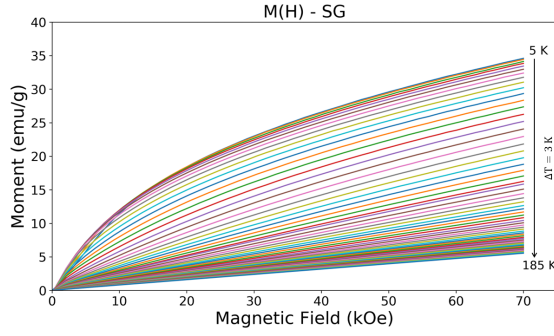


Figure A1: Isothermal M - H curves for SG.

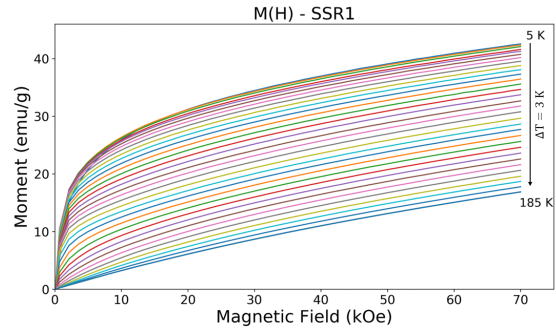


Figure A2: Isothermal M - H curves for SSR.

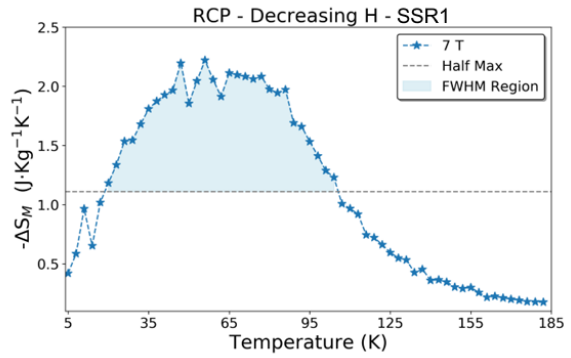
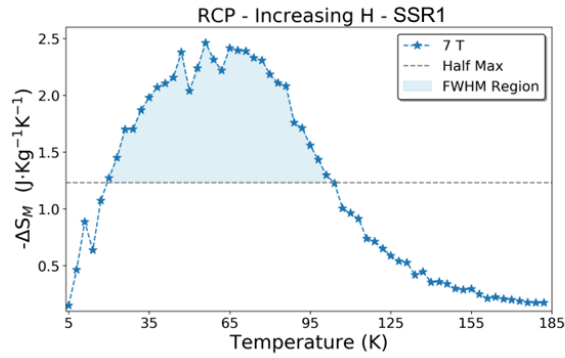
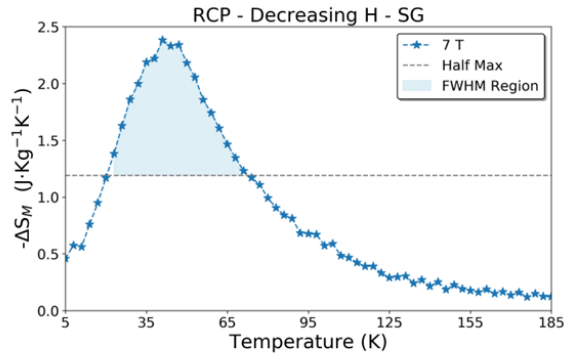
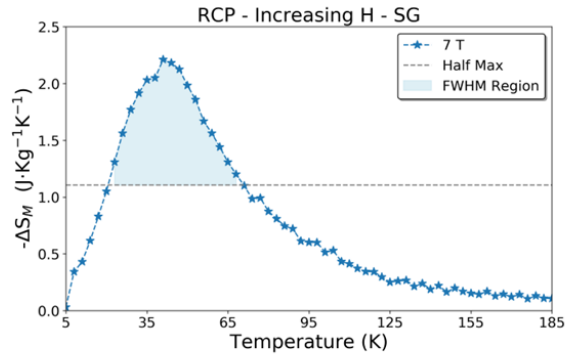


Figure A3: Determination of the FWHM for the RCP of the SG and SSR samples.

Appendix B - Raw Data

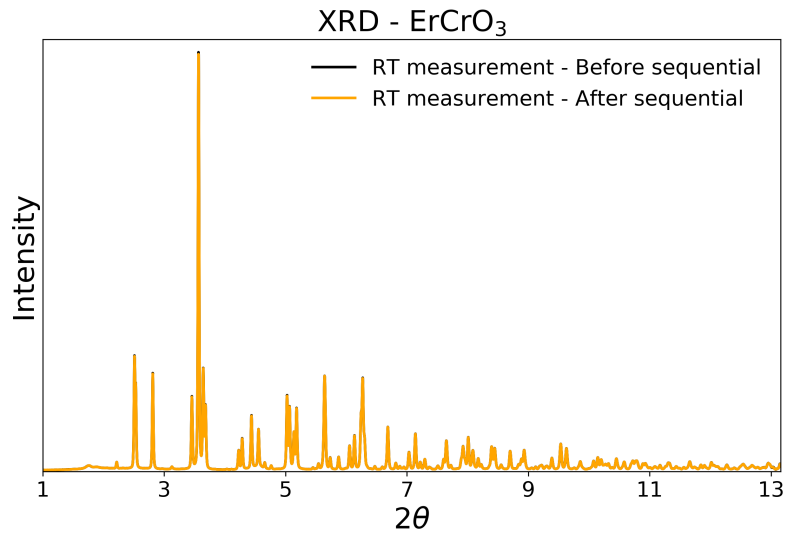


Figure B1: XRD: Room temperature measurement before and after the sequential measurements. The area under the diffraction pattern (calculated using the trapezoidal rule) was 1313 and 1307, for the before and after RT measurement, respectively.

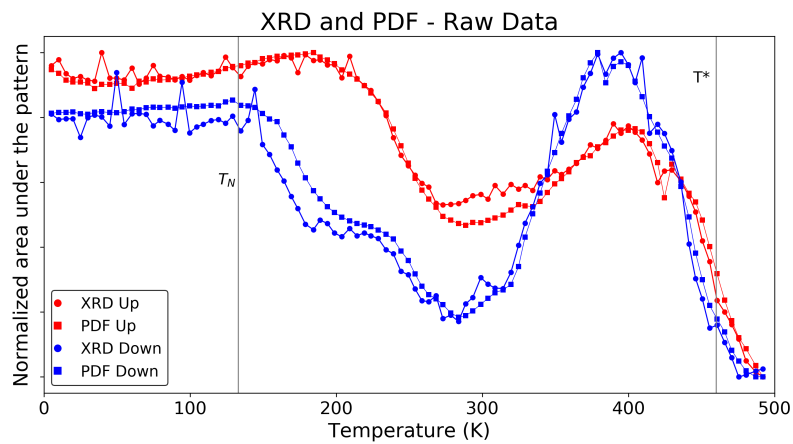
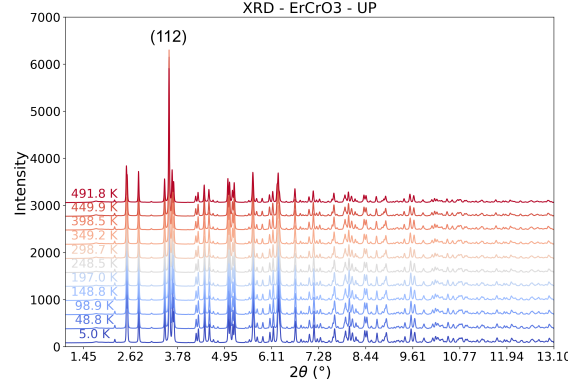


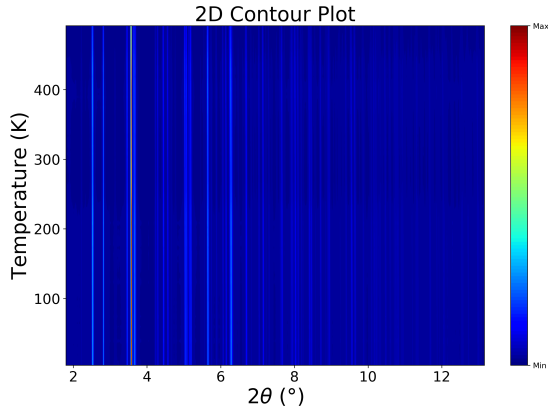
Figure B2: XRD and PDF analysis of the area under the diffraction pattern in the Up and Down dataset.

Appendix C - XRD Data

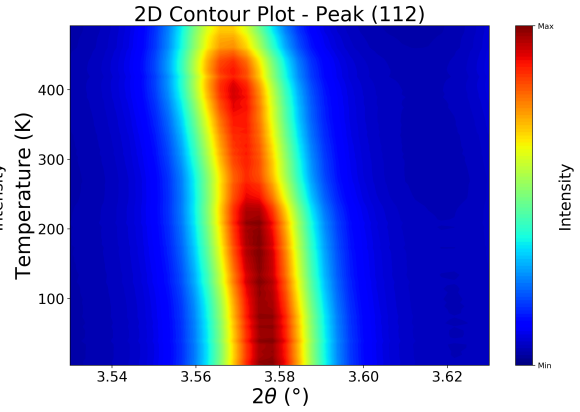
C1 2D Contour plot



(a) Temperature-dependent synchrotron X-Ray Diffraction, where the peak with the highest intensity has the (112) Miller index.



(b) Overall 2D Contour plot of the Synchrotron X-Ray diffracted spectra.



(c) Zoom of the 2D Contour plot of the highest intensity peak.

Figure C1: X-Ray Diffraction Contour plot of ErCrO_3 sample with rising temperature.

Figure C1 a) presents the temperature-dependent synchrotron X-Ray diffraction, where the peak with the highest intensity was identified with the (112) Miller index (see Fig. C1 a)). Additionally, on Fig. C1 b) an overall 2D Contour plot of the synchrotron X-Ray diffraction spectra is shown and on Fig. C1 c) a zoom on the highest intensity peak is shown. From the analysis of Fig. C1 a) and Fig. C1 b), with rising temperatures, we find neither the appearance nor splitting of any Bragg peaks overall 2θ range. In addition, as we zoom in on the highest intensity peak (112), we observe not only a shift of the peak towards lower 2θ , indicative

of thermal expansion, but also a change in the peak's intensity. This latter phenomenon becomes more apparent through analysis of the peak area, which we will examine in detail later.

C2 Area under the peak

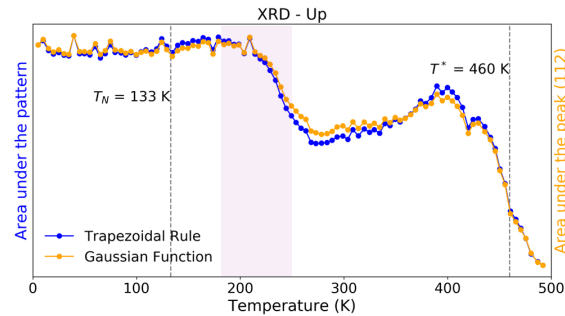
As previously mentioned, to ensure that the sample did not shift, lose density, or undergo other changes that could affect the measurements [127], an analysis of the area under the peak was performed. For that, two methods were employed to examine the broadening of the peaks: the trapezoidal rule [128], which was used to analyse the area under the entire diffraction pattern, and the Gaussian function [129], described in equation C1, used for a particular peak (in this case, the (112)), as a function of the temperature.

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}. \quad (\text{C1})$$

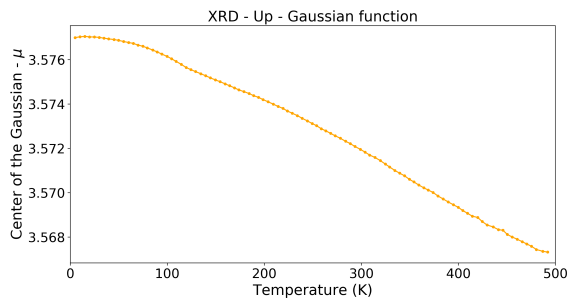
The results from these analyses are plotted in Fig. C2 a). Starting from the lowest temperature, both methods follow the same trend, with significant variations in the area under the (112) peak or the diffraction pattern only appearing at temperatures above 180 K, marking the beginning of the purple-shaded region (180-250) K. Additionally, a significant deviation is observed at another critical temperature, T^* , suggesting a potential change in the material's system. Furthermore, the Gaussian function reveals the temperature dependence of the (112) peak center as the temperature increases (Fig. C2 b)). Here, all three lattice axes come into play, allowing us to correlate it to the cell volume variation, where no anomalies are observed that would suggest abrupt structural distortions within the studied temperature range. Additionally, Fig. C2 c) illustrates the temperature evolution of the Gaussian variance parameter, which remains relatively unchanged.

In addition, we observe that the variation of the area under the diffraction pattern, as well as under the highest intensity peak (112), is reversible for both the XRD and PDF measurements during the Up and Down sequences, in other words, follows the same trend, as shown in Appendix A, Fig. B2. These results indicate that the sample did not undergo significant density changes due to displacement

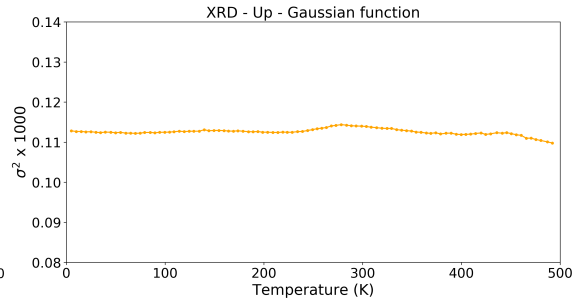
within the capillary. Therefore, we can conclude that no external effects influenced the measurements, ensuring the reliability of the XRD data for the subsequent analysis.



(a) Area under the diffraction pattern, calculated using the trapezoidal rule, and the area under the peak (112), fitted using the Gaussian function.



(b) Center of the Gaussian function of the peak (112) as a function of temperature.



(c) Gaussian function parameter variance of the peak (112) as a function of temperature.

Figure C2: Analysis of the area under the diffraction pattern and under the highest peak (112) as a function of temperature.

C3 Goodness of fit - Analysis

The Rietveld refinement was done considering the space group $Pbnm$ for the Up sequence dataset. In addition, to ensure the validity of the results and minimize systematic errors arising from the inherent systematic nature of the fitting procedure, we have divided the sequential refinement into three models: the first (Model 1) starting the refinement from the lowest to the highest temperature, the second model (Model 2) starting from the highest to the lowest temperature, and finally, in the third model (Model 3), the data was divided into two sets, starting from RT, one going to the lowest temperature and the other going to the highest temperature.

It is worth mentioning that we allowed the refinement of the same parameters in the three different models (models 1 to 3), as described in Fig. C3.

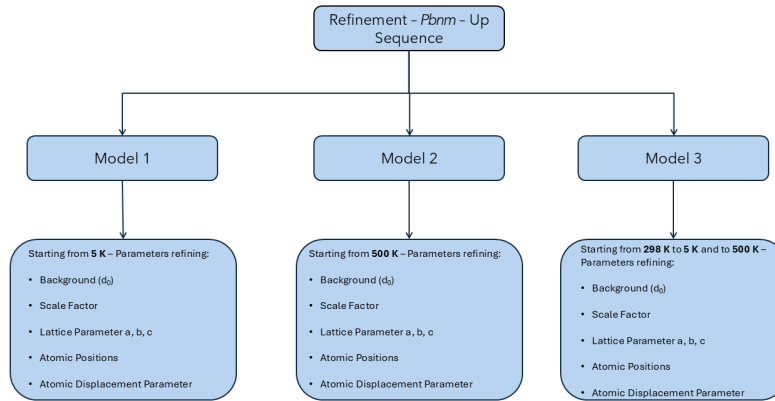


Figure C3: Three different ways the Up data was refined considering the space group *Pbnm*.

As discussed before (see section 2.2.1.2), to find the best fit, we use numerical figures of merit * to quantify the quality of the fit. In Fig. C4, we analyse not only the goodness of fit, described in equation 2.4, for the three presented models, but also the evolution of the Bragg *R* factor (Model 1) as a function of temperature, which is particularly useful to analyse since it shows the agreement between the reflection intensities calculated from the crystallographic model and those measured experimentally, in other words, depends on the fit of the structural parameters and not the profile parameters [51].

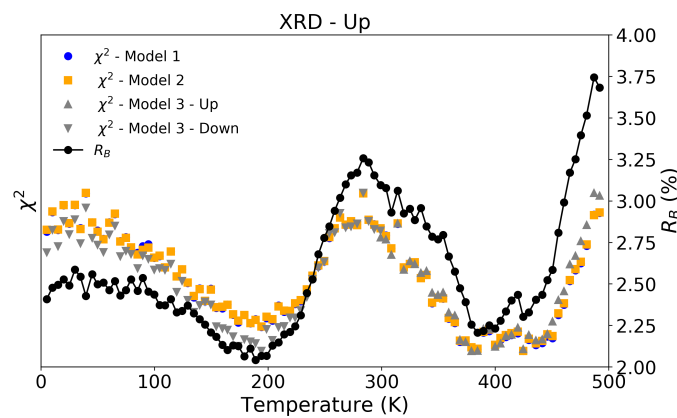


Figure C4: Figure of merit Bragg *R* factor and the goodness of fit (χ^2) of the three different ways the Up data was refined as a function of temperature.

*Here, we define "figures of merit" based on our analysis criteria, though this is not a standard classification universally adopted by the scientific community.

In the goodness of fit analysis, all three models follow the same trend, so for the rest of the refinement analysis, Model 1 was the one adopted. Furthermore, we see that the variation of the area under the diffraction pattern (Fig. C2 a)), which is a preliminary study of the raw data done before the Rietveld refinement, has a similar trend (inverse) to that observed in the goodness of fit and Bragg R factor analysis, showing that these temperature-dependent variations observed are of intrinsic (sample) origin and not fitting artefacts.

Appendix D - Strain and Crystalline size

The Williamson-Hall plot [104] is an important analysis method since size-induced and strain-induced broadening can be determined by examining the peak width as a function of 2θ , which is described in equation 2.3. In this study of the sample ErCrO_3 , the λ is 0.1665 Å, and K , which is the Debye-Scherrer constant, was considered to be 0.94 (approximation for spherical crystallites) [130]. Fig. D1 a) shows the Williamson-Hall plot for a temperature of 5 K, where the slope represents the mean strain and the line interception with the YY axis, gives the inverse particle size, from which we were able to obtain a $\epsilon = 0.0016(3)$ and $D = 72(22)$ nm, with a $R^2 = 0.7749$.

In addition, Fig. D1 b) illustrates the evolution of ϵ , D , and R^2 as the temperature increases, revealing an almost constant trend across the entire temperature range, suggesting that no significant structural distortions occur as the material is heated.

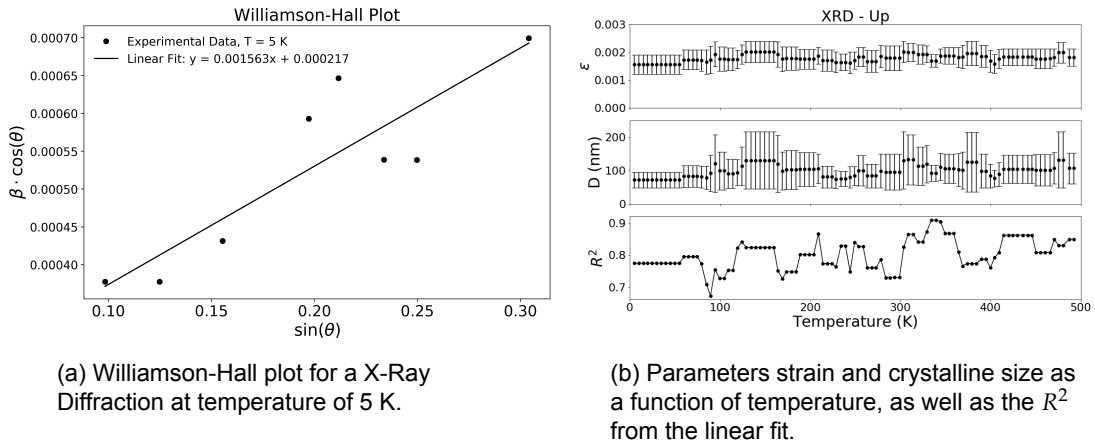


Figure D1: Williamson-Hall plot for a temperature of 5 K (a) and strain and crystalline size as a function of temperature (b).

Appendix E - PDF Data

E1 Pre-Data Treatment

To determine crucial parameters to create the right $G(r)$ function for the PDF analysis, such as the $Q_{\text{max-inst}}$, which gives the highest Q -value that defines the range of $I(Q)$ that the polynomial function is fitted over, and the Q_{max} which alongside Q_{min} gives the range of the diffraction data that is Fourier transformed to obtain the PDF, a pre-data treatment was performed. In addition, two other important parameters that have been mentioned in subsection 2.2.2 are the Q_{broad} and the Q_{damp} , which are determined using a standard or calibration data set, in this case, it was Ni.

PDF Parameters	
Parameter	Value
$Q_{\text{max-inst}} (\text{\AA}^{-1})$	26.0
$Q_{\text{min}} (\text{\AA}^{-1})$	0.1
$Q_{\text{max}} (\text{\AA}^{-1})$	24.1
$r_{\text{max}} (\text{\AA})$	30.0
$r_{\text{min}} (\text{\AA})$	1.8
$r_{\text{step}} (\text{\AA})$	0.02
r_{poly}	0.9

Table E1: Summary of the parameters used for generating the $G(r)$ function in the ErCrO_3 PDF analysis.

For the data reduction process and Ni calibration, we followed the already mentioned procedure in section 2.2.2, to obtain the optimal parameters for a high-quality $G(r)$ function. In addition, we followed this outlined data reduction procedure for the lowest temperature data, using the xPDFsuite software, with the determined terms summarized in Table E1 below, which were then applied to the rest of the datasets.

Moreover, as previously mentioned, the two instrumental terms Q_{damp} and Q_{broad} are obtained using a highly crystalline material, such as Ni, and refining the data, typically taken at RT [131]. The results of this calibration are presented in the following Table E2, where they show good agreement with the expected values for a well-calibrated Ni standard.

Ni Calibration	
Parameter	Value
R_w (%)	4.989
Scale Factor	0.3233
δ_2 Factor	2.4422
$a = b = c$ (Å)	3.5233
B_{iso} (Å ²)	0.00443
Q_{broad}	0.0171
Q_{damp} (Å ⁻¹)	0.0368

Table E2: Summary of refinement parameters from the Ni calibration.

E2 2D Contour plot

Figure E1 a) illustrates the overall 2D contour plot of the synchrotron X-Ray diffraction spectra used for the PDF analysis and on Figure E1 b) a zoom on the highest intensity peak (112) is shown as a function of temperature. Additionally, these results are similar to those of the XRD analysis, see section C1, where no signs of splitting or appearance of new peaks in the 2D contour plot are presented. Moreover, in the peak (112) analysis, although less evident, we still see a deviation of the peak toward lower 2θ , and here for the PDF data, a much broader peak is also shown, but with a similar change in intensity to that of the XRD, which will be discussed in the following section.

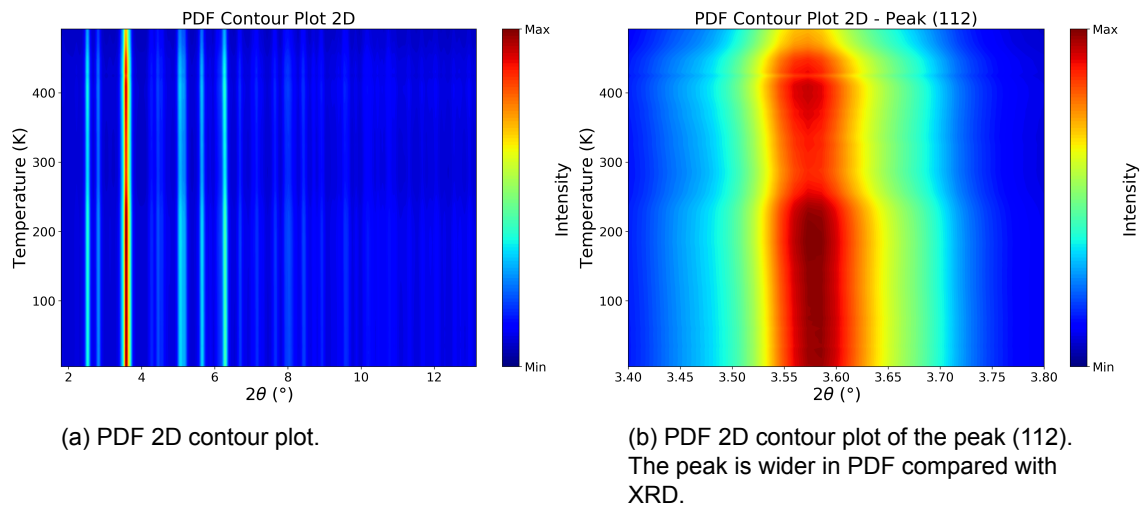
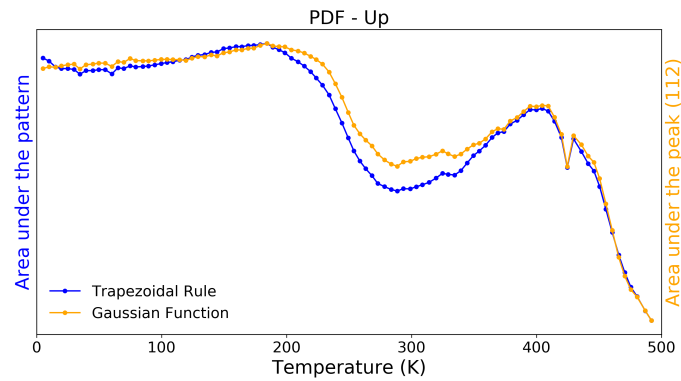


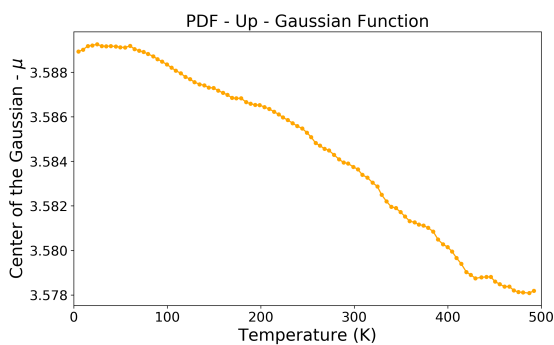
Figure E1: PDF: 2D contour plot of all the diffraction patterns and of the highest peak (112).

E3 Area under the diffraction pattern

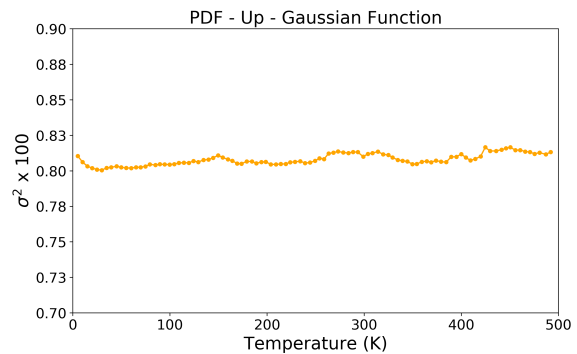
As previously discussed, two methods were employed to study the area under the diffraction pattern and the peak (112): the trapezoidal rule and the Gaussian function for the latter. Fig. E2 a) shows that not only do both methods follow a similar trend but also that the change in the area (peak broadening) is identical in the raw data used for the analysis in the two different characterization techniques, as seen in Fig. C2 a). Furthermore, since the data acquisition of the X-Rays for the XRD and PDF analysis were executed at different times, a non-identical number of photons was used for both measurements. In other words, since the results obtained are similar in these two techniques, the outcome is independent of this parameter.



(a) Area under the diffraction pattern, calculated using the trapezoidal rule, and the area under the peak (112), fitted using the Gaussian function.



(b) Center of the Gaussian function of the peak (112), as a function of temperature.



(c) Gaussian function parameter variance of the peak (112), as a function of temperature.

Figure E2: PDF: Analysis of the area under the diffraction pattern and the peak (112).

Figure E2 b) illustrates the evolution of the highest peak center as a function of temperature, where the results shown are similar to those found in Fig. C2 b), although there is more variance in the data, there is no evidence of an abrupt

structural distortion within the studied temperature range. Additionally, Fig. E2 c) presents the temperature evolution of the Gaussian variance parameter, which remains relatively constant. These findings indicate that, once again, the sample did not experience significant density changes due to displacement within the capillary, thus ensuring the reliability of the XRD data (used to obtain the PDF) for the subsequent analysis.