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Master Thesis in
Chemical and Process Engineering

*Development, investigation and characterization of
Perovskites-type Polycationic Oxides*

Relatore: CANU PAOLO, Università degli Studi di Padova

Correlatori: GLISENTI ANTONELLA, Università degli Studi di Padova

BERRIER ELISE, Unité de Catalyse et de Chimie du Solide du Lille

Laureanda: ELENA CIFANI

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Supervisor: Dr. Berrier Elise

Co-Supervisor: Dr. Richard Melissandre



*A mio fratello Edoardo,
sarò per sempre il tuo porto sicuro,
la tua casa e la tua spalla quando ne avrai bisogno.
Spero di averti reso orgoglioso di me,
così come io lo sono di te.
Ti dedico tutto.*

*A chi sta ancora
cercando la storia che ha dentro.*

Abstract

In the realm of catalysis, perovskite-based oxides have emerged as intriguing candidates owing to their unique structural properties and versatile functionalities.

This thesis presents a systematic study on the synthesis, structural characterization, and redox behavior of lanthanum-based perovskite-type polycationic oxides, with the aim of elucidating structure–function relationships. Different compositions were synthesized via auto-combustion, including La_xFeO_3 , La_xMnO_3 , and multicationic variants doped at both A and B sites such as $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The materials were characterized using Raman spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), BET surface area measurements, and temperature-programmed reduction/oxidation (TPR/TPO). XRD confirmed phase purity and crystallinity, while BET and TGA provided insights into porosity and thermal stability. TPR/TPO analyses revealed distinct redox profiles, highlighting the role of dopants in oxygen mobility and reducibility.

A-site substitution with Sr promoted oxygen vacancy formation and enhanced reducibility, whereas Ca improved thermal robustness. B-site doping with Mn and Ni modified the electronic environment, enabling multivalent redox cycling. Mixed A/B-site compositions exhibited synergistic effects, broadening redox profiles and increasing surface reactivity.

The findings demonstrate that compositional tuning can influence the physicochemical and redox properties of perovskite oxides.

Riassunto

Nel campo della catalisi, gli ossidi a base di perovskite si sono rivelati candidati interessanti grazie alle loro proprietà strutturali uniche e alle loro versatili funzionalità.

Questa tesi presenta uno studio sistematico sulla sintesi, la caratterizzazione strutturale e il comportamento redox degli ossidi policationici di tipo perovskite a base di lantanio, con l'obiettivo di chiarire le relazioni struttura-funzione. Sono state sintetizzate diverse composizioni tramite autocombustione, tra cui La_xFeO_3 , La_xMnO_3 , e varianti multicationiche dopate sia nel sito A che nel sito B, includendo $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

I materiali sono stati caratterizzati utilizzando la spettroscopia Raman, la diffrazione dei raggi X (XRD), l'analisi termogravimetrica (TGA), le misurazioni dell'area superficiale BET e la riduzione/ossidazione programmata in temperatura (TPR/TPO). La XRD ha confermato la purezza di fase e la cristallinità, mentre la BET e la TGA hanno fornito informazioni sulla porosità e sulla stabilità termica. Le analisi TPR/TPO hanno rivelato profili redox distinti, evidenziando il ruolo dei droganti nella mobilità dell'ossigeno e nella riducibilità.

La sostituzione del sito A con Sr ha favorito la formazione di vuoti di ossigeno e migliorato la riducibilità, mentre il Ca ha migliorato la robustezza termica. Il drogaggio del sito B con Mn e Ni ha modificato l'ambiente elettronico, consentendo un ciclo redox multivalente. Le composizioni miste dei siti A/B hanno mostrato effetti sinergici, ampliando i profili redox e aumentando la reattività superficiale.

I risultati dimostrano che la regolazione della composizione può influenzare le proprietà fisico-chimiche e redox degli ossidi di perovskite.

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Introduction

The development, investigation, and characterization of perovskite-type polycationic oxides have become a focal point in the field of catalysis due to their unique structural properties and versatile functionalities.

This thesis specifically examines lanthanum-based perovskite catalysts, including samples such as La_xFeO_3 , La_xMnO_3 , $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

Perovskite oxides, characterized by their ABO_3 crystal structure, offer a high degree of tunability through compositional modifications. This structural versatility is particularly advantageous for catalytic applications, as it enables the fine-tuning of electronic and structural properties to optimize catalytic performance. Lanthanum-based perovskites, in particular, have shown promise due to their remarkable oxygen mobility and structural adaptability, which are facilitated by doping.

The catalytic activity of perovskite-based materials is underpinned by two pivotal factors: the mobility of oxygen within the surface-subsurface region and their structural adaptability. Processes such as exsolution, vacancy formation, and the presence of minority phases play a crucial role in enhancing catalytic performance. Understanding the intricate interplay between composition, structure, and catalytic activity is essential for tailoring these materials to suit specific reaction requirements.

To unravel the underlying mechanisms and structural intricacies governing heterogeneous catalytic reactions, this study adopts a comprehensive approach. It combines routine characterization techniques such as Raman spectroscopy, Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD), and Brunauer-Emmett-Teller (BET) analysis with advanced methodologies like Temperature-Programmed Reduction (TPR) and Temperature-Programmed Oxidation (TPO). By employing these sophisticated techniques, the aim is to elucidate the fundamental processes occurring at the surface of these catalysts and gain insights into the transient species and intermediates involved during catalytic transformations.

The utilization of mixed oxides based on perovskite structures allows for a high degree of structural versatility and tunability, providing a platform for exploring novel catalytic functionalities. Through a systematic investigation of dopant effects, phase transformations, and surface properties, this research seeks to elucidate the structure-function relationships governing the catalytic behavior of lanthanum-based perovskite oxides.

This thesis is divided into five chapters. The first three chapters are bibliographic and provide a framework for interpreting the results obtained. The last two chapters are experimental, based on tests performed in the laboratory on synthesized samples. The first chapter reviews the state of the art of perovskites. The second chapter explores the synthesis methods, and the third chapter discusses the instrumentation used for analysis. In the fourth chapter, the results from classical characterization techniques are examined, while the fifth chapter analyses the results obtained from advanced methods.

Through this systematic investigation, the goal is to elucidate the structure-function relationships that govern the catalytic performance of lanthanum-based perovskite oxides, thereby contributing to the advancement of knowledge in the field of catalysis and paving the way for future studies aimed at optimizing these materials for industrial applications.

Chapter 1

Perovskites catalysis state of art

Typical perovskite metal oxides are characterized by a structural arrangement known as ABO_3 . In this configuration, “A” represents a metal ion with a relatively large ionic radius, occupying the central position within the cubic structure of the perovskite crystal, and coordinated with 12 oxygen ions. On the other hand, “B” represents a metal ion with a smaller ionic radius situated at the apex angle of the cubic structure, coordinated with 6 oxygen ions. The stability of the perovskite crystal structure is theoretically determined by the structural tolerance factor, denoted as “t” ($0.75 < t < 1$), which is calculated as the ratio of the sum of the ionic radii of A and B to the sum of the ionic radii of B and O.

1.1 Perovskites structure

In the perovskite crystal structure, the length of the B-O bond is equivalent to half of the cubic unit cell, whereas the A-O bond length is $\sqrt{2}$ times the cubic cell parameter. However, practical difficulties encountered during the synthesis process often result in lattice distortions or defects within the perovskite framework. These imperfections, while challenging, are crucial as they contribute to the unique properties of the material and are fundamental to its various applications ^[1].

The structural flexibility of perovskites ($0.75 < t < 1$) accommodates a wide range of elements, making them highly adaptable ^[16,17]. Typically, the A site in the perovskite structure serves as a structural support, while the B site acts as the catalytically active site. Interactions between A and B sites combine mutual influences and constraints, ensuring structural stability and charge balance. The coefficient α that was initially proposed by Goldschmidt in 1926 for the description of the perovskite structure's accommodation capability is now generally denoted as the tolerance factor “t” as shown in the following **Equation (1.1)** ^[4,17].

$$t = \alpha = \frac{1}{\sqrt{2}} \frac{r_A + r_O}{r_B + r_O} \quad (1.1)$$

Elements typically found at the A-site that satisfy these specific characteristics include alkaline earth and/or rare earth metals, such as La, Sr, Ca, or Eu. Meanwhile, the B-site is usually

occupied by 3d, 4d, or 5d transition metals, such as Fe, Mn, or Co. This versatility results in a wide variety of possible perovskite compositions, each with unique properties and potential applications.

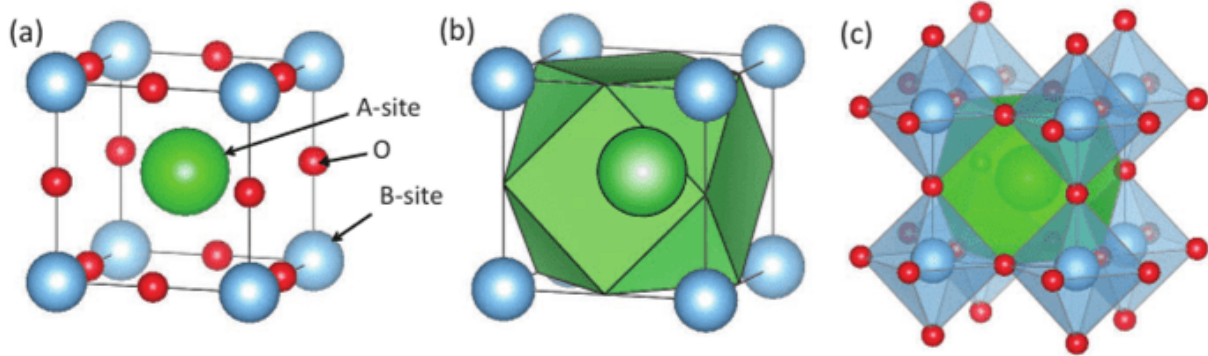


Figure 1.1: An ideal cubic perovskite structure of ABO_3 , (a) Unit cell (the smaller B site is chosen as the origin of the unit cell, while in Figure 1.2a, the larger A site is the origin); (b) the coordination of A-site ion; and (c) the coordination of B-site ion. ^[2]

Partial substitutions within the perovskite structure can lead to a certain degree of cation and anion defects, as explained in [section \[1.3\]](#). These defects are not merely imperfections but play a significant role in determining the material's properties and functionality.

The ideal composition of a perovskite crystal adheres to strict charge balance constraints, typically represented by formulas such as $A^{1+}B^{5+}O_3$, $A^{2+}B^{4+}O_3$, or $A^{3+}B^{3+}O_3$ ^[15]. In this study, the produced perovskites belong to the $A^{3+}B^{3+}O_3$ group, with additional complexity introduced through doping at both the A and B sites.

1.1.1 Detailed Analysis of the Perovskite Structure

(i) Bond Lengths and Lattice Parameters

The perovskite structure, characterized by its ABO_3 formula, consists of a network of corner-sharing BO_6 octahedra with A-site cations situated in the dodecahedral voids formed by these octahedra. The bond lengths and angles within this framework are critical to its stability and properties. The B-O bond length, being half the cubic unit cell parameter, is a fundamental descriptor of the crystal geometry. Similarly, the A-O bond length, which is $\sqrt{2}$ times the cubic cell parameter, influences the overall lattice dynamics and stability ^[4,15].

(ii) Lattice Distortions and Defects

During synthesis, deviations from the ideal structure often occur, leading to lattice distortions or the formation of defects. These can include vacancies, interstitials, or anti-site defects, where atoms occupy non-native lattice positions. Such imperfections are not merely detrimental; they are integral to the functionality of perovskites in various applications, such

as catalysis, photovoltaics, and solid oxide fuel cells. The presence of these defects can enhance ionic conductivity, modify electronic properties, and influence catalytic activity.

1.1.2 Elemental Flexibility and Doping

The perovskite structure's ability to incorporate a wide range of elements at both the A and B sites is a key factor in its versatility and utility across various applications. This elemental flexibility allows for significant compositional tuning, which can be leveraged to tailor the material's properties for specific functions. Doping, the intentional introduction of impurities into a material, plays a crucial role in enhancing the performance of perovskites in areas such as electronics, photonics, and catalysis ^[17].

Doping in perovskites can occur through several mechanisms, each affecting the material's properties differently ^[16,17]:

- ❖ **Substitutional Doping:** This involves replacing a host atom with a dopant atom of equivalent size. For example, substituting a B-site cation with another transition metal can alter the electronic structure and catalytic activity of the perovskite.
- ❖ **Interstitial Doping:** This involves placing dopant atoms in the interstitial sites (the spaces between the regular lattice positions) within the perovskite structure. Interstitial dopants can influence the material's ionic conductivity and overall stability.
- ❖ **Aliovalent Doping:** This type of doping involves substituting a host atom with a dopant of a different valence state. This can create vacancies or interstitial defects to maintain charge neutrality, significantly impacting the material's electrical properties.

The introduction of dopants into the perovskite structure can lead to various changes in its physical and chemical properties ^[16,17]:

- ✓ **Electronic Properties:** Doping can modify the electronic band structure of perovskites, thereby influencing their electrical conductivity and semiconducting behaviour. For instance, incorporating aliovalent dopants can introduce free carriers (electrons or holes), enhancing the material's conductivity. This is particularly beneficial in applications like perovskite solar cells and light-emitting diodes (LEDs), where efficient charge transport is crucial.
- ✓ **Optical Properties:** The optical properties of perovskites, such as bandgap energy and light absorption, can be finely tuned through doping. By selecting appropriate dopants, researchers can adjust the absorption spectrum of perovskites to optimize their performance in photovoltaic cells. This tunability is one of the reasons why perovskite solar cells have achieved high efficiencies.

- ✓ **Magnetic Properties:** Certain dopants can introduce or enhance magnetic properties in perovskites. For example, doping with transition metals like Mn or Co can induce ferromagnetism or antiferromagnetism, making doped perovskites suitable for spintronic devices and magnetic storage applications.
- ✓ **Catalytic Activity:** Doping can significantly enhance the catalytic activity of perovskites by modifying the electronic environment of active sites. For instance, doped perovskites can exhibit improved performance in oxygen evolution reactions (OER) and oxygen reduction reactions (ORR), which are critical for energy conversion and storage technologies like fuel cells and batteries.
- ✓ **Stability and Durability:** The introduction of certain dopants can improve the thermal and chemical stability of perovskites. This is especially important for applications in harsh environments, such as high-temperature catalysis or long-term operation in photovoltaic devices.

In conclusion, the elemental flexibility and doping capability of perovskites are central to their versatility and widespread applicability. Through careful selection and incorporation of dopants, researchers can tailor perovskite properties to meet the demands of various advanced technologies. The ongoing exploration and optimization of doping strategies will continue to unlock new potentials for these remarkable materials.

1.2 Properties and applications of perovskites

Lanthanum-based perovskites have gained significant attention due to their remarkable properties and diverse applications. These materials, characterized by their unique crystal structure, exhibit high stability, electronic conductivity, and catalytic activity, making them ideal for a variety of technological and industrial uses ^[29,30].

- *Catalysis:* One of the primary applications of lanthanum-based perovskites is in catalysis. These materials are highly effective in oxidation reactions and oxygen reduction reactions (ORR). Their ability to facilitate these reactions with high efficiency and stability makes them valuable in energy conversion processes, such as in fuel cells and metal-air batteries. Additionally, they are utilized in traditional heterogeneous catalysis, contributing to industrial chemical processes ^[29,31, 32].
- *Electrode Materials:* Lanthanum-based perovskites are also used as electrode materials in supercapacitors. Their excellent electronic conductivity, thermal stability, and ability to store oxygen make them suitable for this purpose. These materials can enhance the performance of supercapacitors by providing higher capacitance and longer cycle life, which are crucial for energy storage applications ^[30,33].

- *Photocatalysis*: In environmental applications, lanthanum ferrite-based perovskites are employed in photocatalytic processes. These processes are essential for pollutant degradation and hydrogen production. The photocatalytic properties of these perovskites allow them to harness light energy to drive chemical reactions, contributing to cleaner energy production and environmental remediation ^[31,32].
- *Corrosion Analysis*: The robust structural properties of lanthanum-based perovskites make them useful in corrosion analysis and mitigation. They can withstand harsh environments and provide valuable insights into corrosion mechanisms, helping to develop more effective corrosion-resistant materials and coatings. This application is particularly important in industries where materials are exposed to aggressive conditions ^[29,31,33].
- *Microelectronics*: In the field of microelectronics, lanthanum-based perovskites are utilized for their stability and electrical properties. They are employed in the development of advanced sensors and electronic devices. Their ability to maintain performance under varying conditions makes them ideal for use in microelectronic components that require reliable operation over extended period ^[29].
- *Scientific Trends*: Recent scientific advancements have further expanded the applications of lanthanum-based perovskites. Over the past five years, there has been noteworthy progress in understanding and optimizing these materials for various applications. Research has focused on enhancing their catalytic performance, improving their stability, and developing new synthesis methods to tailor their properties for specific uses. This ongoing research is driving innovation in fields such as pharmaceuticals, forensic science, geological studies, and glass manufacturing ^[32, 33].

Lanthanum-based perovskites are versatile materials with a wide range of applications in all these sectors. Their unique properties and the ongoing research into their capabilities continue to unlock new potential uses, making them an important focus in both scientific research and industrial development.

1.2.1 Effect of substitution on A site

The primary substitutions at the A site, which is typically occupied by lanthanum in perovskite structures, are commonly performed using Sr^{2+} (strontium) and Ce^{4+} (cerium) ions. These substitutions have significant impacts on the catalytic properties of the materials ^[44]. For instance, doping with Sr^{2+} has been demonstrated to enhance the catalytic activity for hydrocarbon (HC) oxidation. This enhancement is primarily attributed to charge compensation mechanisms that lead to the partial formation of B^{4+} ions and the generation of oxygen vacancies ^[45,46,47]. These vacancies introduce defects into the crystal structure, thereby enhancing the

mobility of oxygen within the material. Such structural modifications are crucial for improving the catalytic performance [44,48].

However, it is important to notice that not all effects of Sr^{2+} doping is beneficial. Voorhoeve et al. reported a decrease in catalytic activity for CO oxidation in Sr-doped perovskites. This finding suggests that while Sr^{2+} doping can enhance HC oxidation, its impact on CO oxidation can be detrimental. The reasons for this decrease in activity could be multifaceted, including changes in the electronic structure or the nature of the active sites for CO oxidation [47, 48].

In contrast to Sr^{2+} , substitution with Ce^{4+} promotes CO oxidation. Nonetheless, it has been observed that incorporating more than 0.2 molar fractions of Ce^{4+} is problematic. At higher concentrations, Ce^{4+} cannot be stabilized within the perovskite structure, leading to the formation of CeO_2 , a catalytically inactive phase. Despite this, CeO_2 is renowned for its exceptional oxygen storage capacity, which is due to its facile redox cycles. This property makes CeO_2 one of the most effective oxygen storage materials used to date [44, 46, 47, 50].

Additionally, other divalent ions, such as Ca^{2+} (calcium), can be employed to achieve similar effects by inducing unusual oxidation states in B-site ions and/or creating oxygen vacancies. Pecchi et al. investigated the partial substitution of La^{3+} with Ca^{2+} in LaFeO_3 for methane combustion. Their findings indicated that this substitution led to the formation of Fe^{4+} ions, which significantly enhanced the catalytic activity. Barbero et al. reported analogous results for propane oxidation, reinforcing the beneficial effects of Ca^{2+} doping in these systems [45,46].

In another line of research, various substitution patterns of La_2CuO_4 have been explored to boost its catalytic activity. Zhu et al. examined the partial substitution of Sr^{2+} for La^{3+} in La_2CuO_4 for the $\text{NO} + \text{CO}$ reaction. Their study revealed a correlation between the Sr^{2+} content, the molar ratio of $\text{Cu}^{3+}/\text{Cu}^{2+}$, and the amount of non-stoichiometric oxygen. They found that LaSrCuO_4 displayed the highest catalytic activity for this reaction. The increase in oxygen vacancies, denoted as VO, appeared to enhance the adsorption and dissociation of NO on the oxide surface, thus playing a crucial role in the catalytic mechanism. This observation was further confirmed in studies on CH_4 oxidation, where higher surface area oxides exhibited increased catalytic performance. In these studies, the presence of Cu^{3+} species was confirmed using X-ray photoelectron spectroscopy (XPS), providing insights into the oxidation states of copper and their role in the catalytic processes [48, 49, 50].

Overall, the substitution of lanthanum in perovskite structures with various dopants such as Sr^{2+} , Ce^{4+} , and Ca^{2+} offers a versatile approach to tailoring the catalytic properties of these materials. Each dopant introduces unique modifications to the crystal structure and electronic environment, thereby influencing the material's catalytic activity in different reactions. The choice of dopant and its concentration must be carefully optimized to achieve the desired catalytic performance for specific applications [46, 48, 49, 50].

1.2.2 Effect of substitution on B site

The substitution of B-site cations in perovskite structures with non-isovalent cations is a crucial strategy in materials science, as it leads to the formation of oxygen vacancies and B-site cations in unusual oxidation states. This type of substitution can significantly alter the redox behaviour and ion mobility of the perovskite, resulting in enhanced catalytic properties compared to the parent material. These modifications are instrumental in improving the efficiency and performance of perovskite-based catalysts in various chemical reactions ^[51].

One notable example of this phenomenon is the partial substitution of iron (Fe) with copper (Cu) in LaFeO_3 . LaFeO_3 , in its pure form, exhibits moderate catalytic activity in several oxidation and reduction reactions, including the $\text{CO} + \text{NO}$ reaction. However, when Fe is partially replaced with Cu, the catalytic activity is considerably enhanced ^[52]. This improvement is primarily due to the creation of anion vacancies, which facilitate the adsorption of reactants and the dissociation of adsorbed NO molecules. The presence of these vacancies also increases the mobility of oxygen within the perovskite structure, which in turn speeds up the regeneration of active catalytic sites. Furthermore, Cu-substituted LaFeO_3 shows higher selectivity for N_2 during NO reduction, outperforming the non-substituted LaFeO_3 in terms of catalytic efficiency and selectivity.

In addition to iron-based perovskites, manganese-based perovskites also exhibit significant improvements upon partial substitution. Although manganese perovskites are already known for their high activity in oxidation reactions, their performance can be further enhanced by incorporating copper. Mizuno et al. investigated the incorporation of Cu into manganese perovskites and achieved remarkable results ^[53]. Specifically, they measured the rate constants for CO oxidation and the $\text{NO} + \text{CO}$ reaction at 400 °C for $\text{LaMn}_{1-x}\text{Cu}_x\text{O}_3$ (with catalyst masses ranging from 10 to 50 mg, diluted with 250 mg of SiC) at a pressure of 8 kPa with a CO to NO ratio of 1. The rate constants for $\text{LaMn}_{0.6}\text{Cu}_{0.4}\text{O}_3$ were approximately 400 times higher than those for LaMnO_3 and 5000 times higher than those for La_2CuO_4 . Additionally, $\text{LaMn}_{0.6}\text{Cu}_{0.4}\text{O}_3$ exhibited a rate constant that was 100 times higher than that of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$.

These findings indicate that the Cu-substituted manganese perovskite performs on par with $\text{Pt/Al}_2\text{O}_3$, a widely used catalyst. The exceptional performance is attributed to a synergistic effect where copper facilitates CO activation, and manganese enhances the reactivity of lattice oxygen.

Magnesium doping in manganese perovskites has also been explored to improve catalytic performance. Saracco et al. studied the effects of magnesium incorporation in LaMnO_3 and found that for compositions where $0 < x \leq 0.2$ in $\text{LaMn}_{1-x}\text{Mg}_x\text{O}_3$, there was a notable increase in activity for methane combustion ^[54]. This enhancement is attributed not only to the intrinsic properties of magnesium but also to the formation of MgO, which aids in the creation of small perovskite crystals and prevents their agglomeration. The presence of MgO helps maintain a

high surface area and promotes the stability of the perovskite structure, thereby improving its catalytic performance.

In summary, the substitution of B-site cations in perovskites with various dopants such as copper and magnesium demonstrate a powerful strategy for enhancing catalytic performance. Each dopant introduces specific structural and electronic changes that improve the material's activity in different catalytic reactions. Optimizing the type and concentration of dopants is essential for achieving the desired catalytic properties tailored to specific applications. This approach not only enhances the efficiency of existing catalytic materials but also opens new avenues for the development of advanced catalysts with superior performance ^[51-54].

1.3 Complex perovskites

Complex perovskites represent an advanced class of materials that have attracted significant interest due to their versatile properties and wide range of applications. These materials extend the basic perovskite structure, denoted as ABO_3 , by incorporating multiple cations into the A and/or B sites, allowing for a tailored approach to meet specific technological needs ^[34, 36]. This essay explores the structural characteristics, electronic and magnetic properties, and diverse applications of complex perovskites, highlighting their roles in catalysis, energy storage, environmental applications, and microelectronics.

The fundamental perovskite structure is inherently adaptable, accommodating various chemical substitutions. This flexibility enables the formation of complex perovskites, such as double perovskites ($A_2BB'O_6$) and layered perovskites (Ruddlesden-Popper phases). Double perovskites, for example, involve two different cations at the B-site, leading to enhanced magnetic, electronic, and optical properties due to the ordered arrangement of these cations.

Complex perovskites exhibit a range of electronic properties, including superconductivity, colossal magnetoresistance, and ferroelectricity. A notable example is Sr_2FeMoO_6 , a double perovskite that displays half-metallicity and high magnetoresistance, making it suitable for spintronic applications. Another significant example is La_2CuO_4 , a layered perovskite known for its high-temperature superconductivity, which has been pivotal in the development of superconducting materials.

In the realm of catalysis, complex perovskites are valued for their stability and catalytic activity. $La_{0.8}Sr_{0.2}MnO_3$ is a prominent example used as a cathode material in solid oxide fuel cells (SOFCs), owing to its high performance and durability under operational conditions. Additionally, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ is employed in oxygen evolution reactions (OER) for water splitting, demonstrating exceptional efficiency and stability, crucial for renewable energy applications ^[35,36,40].

Complex perovskites have shown great promise in energy storage applications due to their efficient oxygen storage and release capabilities. For instance, $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ is used as a cathode material in lithium-ion batteries, providing high capacity and long cycle life. This material's structure facilitates the easy incorporation and extraction of lithium ions, which is essential for the performance of rechargeable batteries ^[36,37,41].

Environmental applications of complex perovskites include pollutant degradation and gas sensing. $\text{BaTi}_{0.85}\text{Sn}_{0.15}\text{O}_3$ is effective in photocatalytic degradation of organic pollutants under UV light, making it useful for water purification. Furthermore, $\text{SrTi}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ is utilized in gas sensors for detecting gases like CO and NO₂, thanks to its high sensitivity and selectivity. The optical properties of complex perovskites are leveraged in various optoelectronic applications. $\text{Cs}_2\text{AgBiBr}_6$, a lead-free double perovskite, is promising for solar cells due to its excellent light absorption and long carrier diffusion lengths. Additionally, $\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$ is used in nonlinear optical devices because of its high second-harmonic generation efficiency, highlighting the material's potential in advanced photonic applications ^[38,39,40].

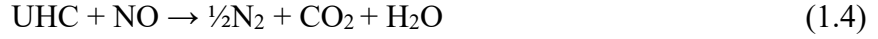
Despite the significant potential of complex perovskites, there are challenges in their synthesis and stability. Achieving precise stoichiometry and desired cation ordering is crucial for optimizing their properties. Future research aims to develop novel synthesis methods and enhance the understanding of structure-property relationships, enabling the tailoring of these materials for specific applications ^[42,43].

It is possible finally to denote that complex perovskites offer a vast playground for material scientists due to their structural flexibility and tenable properties. Their applications span from catalysis and energy storage to environmental remediation and microelectronics, making them indispensable in advancing modern technology ^[39,43]. Ongoing research and development efforts continue to unlock new potential uses for these versatile materials, paving the way for innovative solutions to contemporary scientific and industrial challenges.

1.4 Principle of 3-way catalysis (TWC)

Internal combustion engines produce several harmful gases as part of their exhaust emissions. Chief among these pollutants are unburnt hydrocarbons (UHC), carbon monoxide (CO), and nitrogen oxides (NO_x) ^[55]. To comply with stringent environmental regulations, it is essential to remove these compounds before they are released into the atmosphere. For this purpose, gasoline-powered vehicles are equipped with a Three-Way Catalytic (TWC) converter. This emission control device, comprising a mixture of catalytically active components deposited onto a monolithic honeycomb substrate, facilitates the simultaneous conversion of UHC, CO,

and NO_x into harmless compounds such as CO₂, H₂O, and N₂ ^[56,57] as shown in **Equations (1.2-1.5)**.



The efficiency of TWCs is highest when operated under conditions close to the stoichiometric air-to-fuel ratio (14.7:1 by weight for gasoline vehicles). An oxygen sensor continuously monitors the exhaust composition, and the fuel-control feedback system adjusts the air-to-fuel ratio accordingly. However, there is a slight delay between the analysis and the adjustment, causing minor redox fluctuations around the stoichiometric point ^[58].

Current TWC technology in gasoline vehicles relies on noble metals. Platinum and palladium are used as oxidation catalysts and can also aid in NO_x reduction, although rhodium is significantly more effective for this purpose. The catalytic performance of these metals is enhanced by dispersing them on a high surface area (approximately 100 m²/g) γ -Al₂O₃ support. Additionally, ceria-zirconia, known for its high Oxygen Storage Capacity (OSC), is utilized to minimize air-to-fuel ratio fluctuations in the exhaust ^[59]. Other common additives include BaO (NO_x trap), zeolites (UHC or NO_x adsorbent), La₂O₃ (enhances thermal stability for γ -Al₂O₃), TiO₂, NiO, and SiO₂ ^[60].

Natural gas vehicles (NGVs) emit exhaust with higher concentrations of methane, a major greenhouse gas and the most challenging hydrocarbon to oxidize. Consequently, TWCs for NGVs are predominantly based on palladium, the most active catalyst for methane oxidation, and contain three times the noble metal loading (approximately 3 mg/cm³) compared to their gasoline counterparts (approximately 1 mg/cm³) ^[61].

TWCs are subjected to higher temperatures (up to 1000°C) than diesel oxidation catalysts due to their proximity to the engine and higher fuel load during operation. This thermal exposure can lead to noble metal sintering or diffusion into the alumina support over time, resulting in a loss of catalytic activity. Given the cost and scarcity of noble metals, there is a critical need to enhance TWC technology to limit the quantity of noble metals and increase their tolerance to harsh operating conditions ^[62].

As early as 1971, LaCoO₃ perovskite-type oxide was proposed as an economical alternative to noble metal-based exhaust after-treatment catalysts. Perovskite-type oxides based on cobalt, iron, manganese, and ruthenium have shown promising activity for CO oxidation and NO_x reduction ^[63-67]. For instance, La_{0.8}Sr_{0.2}CoO₃ has been found comparable to 1 wt% Pt/Al₂O₃ for hydrocarbon oxidation. Additionally, the promising oxygen storage capacity of LaMn_{0.976}Rh_{0.024}O_{3+δ} has been highlighted ^[68]. However, high sulphur levels in fuels significantly limited their application in real-world scenarios. Recent studies have demonstrated

the potential of $\text{LaFe}_{0.95}\text{Pd}_{0.05}\text{O}_3$ for gasoline engine exhaust treatment and $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ for diesel vehicle exhaust, reaffirming the viability and renewing interest in this class of catalysts [69-71].

A conventional catalytic converter is a sophisticated system, exemplified in the TWC depicted in **Fig. 1.2**. Typically, a metallic or ceramic (cordierite: $2 \text{MgO} \cdot 2 \text{Al}_2\text{O}_3 \cdot 5 \text{SiO}_2$) monolith is encased in a metal housing, shielded by a ceramic or metal wire mesh mat. This cylindrical monolith has a honeycomb structure with numerous long and narrow channels, allowing for a high surface area for gas exchange. A cell density of 300 to 600 cells per square inch (cpsi) is commonly used in automotive exhaust gas treatment [72]. The monolith is wash coated with a highly porous oxide layer with a high specific surface area (SSA), usually alumina, and includes various additives known as promoters and the catalytically active phase.

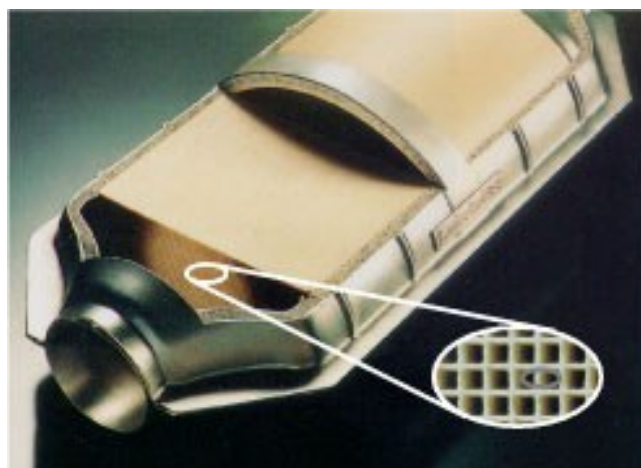


Figure 1.2: Conventional TWC converter.^[73]

Promoters, mainly rare earth metal oxides such as CeO_2 and ZrO_2 , as well as La_2O_3 and BaO , are added to enhance the oxygen storage capacity (OSC) and stabilize stoichiometry by temporarily storing or releasing oxygen. Despite advancements, the air-to-fuel (A/F) ratio does not consistently meet ideal stoichiometry, cycling around it instead. Promoters buffer these fluctuations by balancing the oxygen content, aiding in continuous conversion of all three pollutants [74,75]. La_2O_3 and BaO also improve the thermal stability of alumina, while CeO_2 and ZrO_2 further enhance this stability [76]. Additionally, CeO_2 stabilizes noble metal dispersion and promotes the water-gas shift (WGS) and steam reforming reactions by enhancing catalytic activity at metal-support interfaces and improving CO oxidation using lattice oxygen [77,78].

The active phase is dispersed onto the washcoat as small nanoparticles (approximately 1 to 2 nm for a fresh catalyst) of noble metals from the platinum group (PGM), primarily Pt, Pd, and Rh. Though Ru and Ir have been investigated, they proved unsuitable due to volatility and/or toxicity. Pt and Pd mainly promote oxidation, while Rh enhances reduction, improving NO conversion through enhanced NO dissociation [79,80].

A significant challenge with PGM nanoparticles is their tendency to sinter over time due to high operating temperatures (exceeding 1000°C), reducing catalytic activity due to fewer active sites [72,74]. Despite extensive optimization over decades, the TWC system remains costly, primarily due to the expensive PGMs used as the active phase. Recent price increases for rare earths, driven by export restrictions from China, have exacerbated this issue. However, following a World Trade Organization (WTO) ruling against China after a dispute initiated by the European Union (EU), Japan, and the United States, these restrictions are expected to be lifted [81-83].

Over the past several years, continuous efforts have been made to understand and improve the catalytic properties of perovskite-type oxides for automotive applications. This review aims to summarize the redox properties and relevant mechanisms involved in the oxidation and reduction reactions characteristic of TWC operation. Given our particular interest in catalytic converters for NGV applications, the review will focus on the practical aspects of using structured perovskite-type oxide catalysts, with a special emphasis on TWCs.

The advantages and limitations of perovskite-type oxide catalysts will be discussed to identify the most suitable types for automotive applications. The goal is to enhance the durability and efficiency of these catalysts under the demanding conditions of vehicle exhaust systems, ultimately reducing reliance on scarce and expensive noble metals while maintaining stringent emission standards.

In conclusion, the development and optimization of TWC technology, particularly through the use of perovskite-type oxides, holds significant promise for improving the efficiency and sustainability of automotive exhaust treatment. By addressing the challenges of thermal aging and material scarcity, future advancements in this field can contribute to more environmentally friendly and cost-effective solutions for controlling vehicle emissions [81].

1.5 Perovskites in heterogeneous catalysis

Perovskites have garnered substantial attention in the field of heterogeneous catalysis. Their unique crystal structure, which can accommodate a variety of elements, allows for significant tunability of their chemical and physical properties, making them promising candidates for catalytic applications.

The perovskite structure is notable for its ability to host a wide range of cations in the A and B sites, which can be chosen from distinct groups in the periodic table. This flexibility allows researchers to tailor the electronic and ionic properties of perovskites to optimize their catalytic performance. For instance, doping with transition metals or rare earth elements can introduce desirable redox properties and enhance catalytic activity.

The surface properties of perovskites, such as surface area, porosity, and the nature of active sites, play a crucial role in their catalytic efficiency. High surface area and porosity increase the availability of active sites for reactants, thereby enhancing catalytic reactions. Additionally, the

presence of oxygen vacancies on the surface of perovskites can significantly influence their catalytic behaviour. These vacancies act as active sites for reactions involving oxygen, such as oxidation and reduction processes.

1.5.1 Heterogeneous catalysis

Heterogeneous catalysis is a crucial process in the field of chemical engineering and industrial chemistry, playing a pivotal role in numerous reactions essential for manufacturing and environmental processes. This type of catalysis uses a catalyst that is in a different phase from the reactants, typically a solid catalyst with gaseous or liquid reactants. The fundamental principles governing heterogeneous catalysis encompass adsorption, reaction, and desorption, which collectively facilitate the transformation of reactants into desired products.

The first stage in heterogeneous catalysis involves the reactants being adsorbed onto the surface of the catalyst. This adsorption can be either physisorption, involving weak van der Waals forces, or chemisorption, which entails the formation of stronger chemical bonds. The nature of adsorption significantly influences the activation energy of the reaction. According to a study by Somorjai and Li (2010), the catalyst surface provides active sites where reactants are temporarily bonded, allowing them to interact more readily than in their free state. Once adsorbed, the reactants undergo a series of surface reactions. These reactions often include dissociation, rearrangement, and formation of intermediates. The catalyst facilitates these reactions by providing an alternative pathway with a lower activation energy compared to the uncatalyzed reaction. This aspect is particularly evident in processes such as the Haber-Bosch process for ammonia synthesis, where the presence of an iron catalyst significantly reduces the energy barrier, thus increasing the reaction rate.

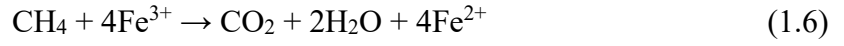
The ultimate step in the catalytic cycle is desorption, where the products of the reaction are released from the catalyst surface. Desorption is crucial as it regenerates the active sites on the catalyst, making them available for subsequent cycles of the reaction. The efficiency of desorption directly impacts the catalyst's turnover frequency, which is a measure of how many reactant molecules a single catalytic site can convert per unit time. The effectiveness of a heterogeneous catalyst is inherently linked to its surface characteristics. Factors such as surface area, pore size, and the nature of active sites play a significant role in determining the catalyst's performance. Advanced catalyst design often involves tailoring these properties to optimize activity, selectivity, and stability. For instance, nanoparticle catalysts have garnered attention due to their high surface-to-volume ratio, providing more active sites for reactions ^[45,47,52].

1.5.2 Redox properties on perovskites

Perovskites exhibit remarkable redox properties, which are essential for various catalytic processes. The ability to undergo reversible changes in oxidation states allows perovskites to

participate actively in redox reactions. For example, LaFeO_3 perovskites have shown excellent activity in methane oxidation due to the facile redox cycling between Fe^{3+} and Fe^{2+} . This property is crucial for applications such as automotive exhaust treatment, where efficient oxidation of pollutants is required.

A key advantage of perovskites is their ability to participate in redox cycling, a process where the material alternates between different oxidation states during the catalytic reaction. This cycling is crucial for maintaining continuous catalytic activity. As said previously, in the catalytic oxidation of methane, LaFeO_3 perovskites demonstrate efficient redox cycling between Fe^{3+} and Fe^{2+} . The iron cations can readily accept and donate electrons, facilitating the activation and subsequent oxidation of methane molecules. The reaction can be summarized as follows:



This dual functionality enables perovskites to serve as both oxygen storage and oxygen release materials, making them highly effective in catalytic processes that involve oxidation and reduction reactions.

Oxygen vacancies in perovskite structures play a significant role in enhancing their redox properties. These vacancies, which are sites where oxygen atoms are missing, create localized regions of charge imbalance that can act as active sites for catalytic reactions. The presence of oxygen vacancies facilitates the dissociation of molecular oxygen (O_2) into reactive oxygen species, which are essential for oxidation reactions.

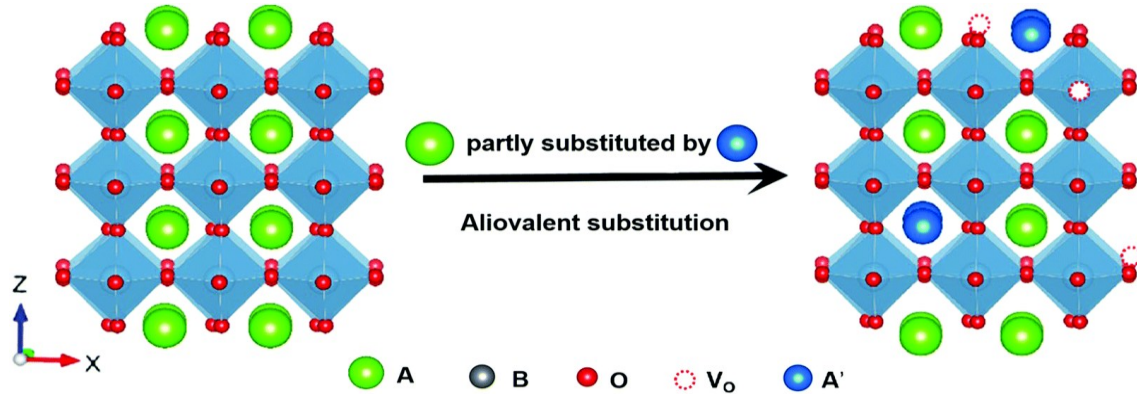


Figure 1.3: The role of oxygen vacancies of ABO_3 perovskite oxides in the oxygen reduction

For instance, in the case of perovskites like LaMnO_3 , the creation of oxygen vacancies can be represented by the following defect reaction **Equation (1.8)**:



Where O represents an oxygen ion in its lattice position, $V_o^{\bullet\bullet}$ is an oxygen vacancy, and e^- denotes an electron. The generation of oxygen vacancies enhances the catalytic performance of perovskites in oxidation reactions such as the catalytic oxidation of volatile organic compounds (VOCs) and carbon monoxide (CO).

1.5.3 Perovskites in TWC

Perovskites were first identified as being active in three-way-catalysis as early as the 1950s. For example, compounds such as LaFeO_3 or $\text{La}_{0.55}\text{Sr}_{0.35}\text{MnO}_3$ were noted for their catalytic properties in CO oxidation. However, the significance of their catalytic properties became more prominent in the 1970s following Meadowcraft's documentation of the electrocatalytic activity in oxygen reduction of a cobaltite. Subsequent reports further elucidated the gas-phase reactivity of LaCoO_3 and LaMnO_3 , which were found to be catalytically active in CO oxidation, NO removal, and various other reactions, including the hydrogenation and hydrogenolysis of cis-2-butene.

In the late 1980s, Nitadori et al. conducted studies on the influence of A- and B-site cations in perovskites on heterogeneous catalysis. Variations based on the A-site cation manifest in thermal stability under reductive atmospheres, as previously noted. La-containing perovskites are the most stable among the lanthanide series and exhibit marginally higher catalytic activities than Sm- and Gd- containing perovskites.

The primary objective of this study is to investigate LaFeO_3 and LaMnO_3 perovskites. Occasional references to LaCoO_3 or other perovskite materials will be made, given that LaCoO_3 is among the most extensively studied systems. It is important to acknowledge that partial substitutions at the A- and B -sites, as discussed in the **subsections [1.2.1 and 1.2.2]**, can enhance the catalytic activity of various perovskites. In addition to compositional effects, other parameters determined by the catalyst preparation method, discussed in the following chapter such as specific surface area (SSA), redox behaviour, and oxygen mobility, may also significantly influence the catalytic activity of perovskites.

In the past years, a lot of studies were conducted, and the main aim of the research was to develop perovskite-based catalysts for three-way catalysis, reducing the use of precious metals. Results of characterization of perovskite-based catalysts showed that lanthanum-deficient synthesis and replacement of iron with copper significantly improved catalytic activity, particularly for CO and propene oxidation. The orthorhombic structure was confirmed for all solids, and the decrease in lanthanum content in the bulk reduced the excess lanthanum observed on the surface. In addition, increased activity for NO reduction under stoichiometric conditions was shown by doping with Rh.

The main observation regarding NO conversion during the first Stoic1 temperature cycle was that NO conversion was almost zero. However, a significant gain in NO conversion was noted during the first Stoic1 temperature cycle, suggesting an improvement in the surface properties of the catalyst. Heat treatment positively affects NO conversion during stoichiometric temperature cycles, as NO conversion increases significantly during the second Stoic2 cycle compared to the first Stoic1 cycle. This improvement is attributed to the metal oxidation state of the rhodium particles, which stabilizes the surface properties of the catalyst. In addition, the heat treatment promotes higher catalytic activity, especially under stoichiometric conditions. Incorporation of Rh into $\text{La}_{0.67}\text{Fe}_{0.83}\text{Cu}_{0.17}\text{O}_3$ accelerates the complete reduction of oxidic copper species to metallic copper, thus improving catalytic performance. However, the addition of 0.1 wt.% Rh did not show a significant effect on NO conversion during the Stoic1 cycle. In general, the presence of Rh helps to optimize the surface properties of the catalyst, increasing the activity for reduction and oxidation reactions. Temperature-programmed reduction (TPR) experiments on the $\text{La}_{0.67}\text{Fe}_{0.83}\text{Cu}_{0.17}\text{O}_3$ solids show an H_2 consumption profile indicating a significant reduction in copper species, while the Rh/ $\text{La}_{0.67}\text{Fe}_{0.83}\text{Cu}_{0.17}\text{O}_3$ sample exhibits an accelerated reduction in oxidic copper species. In addition, the Rh sample shows a reduction peak at lower temperatures than the sample without Rh, suggesting greater reactivity. These results highlight the importance of Rh in improving the reducibility and catalytic activity of the system ^[85].

Lanthanum-deficient synthesis improves catalyst reactivity because it reduces the excess lanthanum typically present on the surface of perovskite-based materials. This deficiency leads to increased availability of active sites and improved interaction between catalyst components, increasing the activity for CO and propene oxidation reactions. In addition, the decreased lanthanum content in the bulk contributes to a more active and reactive perovskite structure ^[85].

1.5.4 Non-stoichiometry behaviour of La based perovskites

Research on catalysts $\text{La}_{1-x}\text{FeO}_{3-1.5x}$ has led to significant discoveries regarding their synthesis, structure, and catalytic activity. These catalysts were synthesized through a low-temperature thermal decomposition process, resulting in an orthorhombic structure for the value of $x=0$. The unit cell dimensions for this configuration were determined as follows: $a_0 = 5.57 \text{ \AA}$, $b_0 = 7.85 \text{ \AA}$ and $c_0 = 5.55 \text{ \AA}$.

As the value of x increased, the structure showed a transition to pseudo cubic symmetry for values of $0 < x \leq 0.3$. The catalytic activity of the materials was tested for methane oxidation, revealing that the highest yield is obtained for $x = 0.1$. However, activity decreases for values of $x = 0.2$ and 0.3 , suggesting that excess oxygen may adversely affect catalytic performance. Several analytical techniques were used to characterize the catalysts, including DTA analysis, XRD, BET, SEM and Mössbauer spectroscopy. These techniques provided detailed

information on the structure and morphology of the catalysts, highlighting the presence of coordinatively unmet FeO₆ layers. This feature has been identified as a key factor in catalytic activity, as it appears to promote the chemical reactions required for methane oxidation.

In summary, the study of La_{1-x}FeO_{3-1.5x} catalysts has highlighted the importance of composition and structure in their catalytic activity, paving the way for further research to optimize the performance of these materials in industrial applications. Results obtained from the study of the catalytic properties of perovskites include:

- High catalytic activity: The perovskites showed excellent performance in the total oxidation of methane, with peak activity for specific compositions, such as La_{1-x}FeO_{3-1.5x} with x=0.1.
- Thermal stability: The catalysts showed good thermal stability during reactions, maintaining their activity even at elevated temperatures.
- Monophasic structure: Analysis revealed that the catalysts are monophasic and that their crystal structure varies according to composition, directly affecting catalytic activity.
- Effect of non-stoichiometry: Non-stoichiometry showed a significant impact on crystallite size and catalytic activity, with a decrease in activity for values of or greater than 0.1.

These results highlight the potential of perovskites as effective catalysts for industrial applications, particularly in hydrocarbon oxidation [86].

Another example can be done with the perovskite with Manganese, considering that the La/Mn molar ratio significantly affects the catalytic activity of LaMnO₃ perovskites. Mn-rich samples (x < 1) show higher activity for CO and propane oxidation, while La-rich samples (x > 1) show lower activity than stoichiometric LaMnO₃. The enhanced activity is attributed to the increased presence of Mn⁴⁺ cations and the formation of Lewis acid sites. The nonstoichiometric strategy improves the activity of perovskite LaMnO₃, as the use of different La/Mn molar ratios allows optimization of catalytic properties. For example, LaMn_{0.9}O₃ with excess La cations shows higher activity for total methane oxidation than stoichiometric LaMnO₃. In addition, the presence of Mn⁴⁺ cations and the formation of Lewis acid sites are key factors contributing to this enhanced activity. The apparent activation energy (E_a) for the LaMnO₃ catalyst is 45.3 kJ mol⁻¹. This value indicates the energy required to initiate the CO oxidation process. Compared with other catalysts, La_{0.84}MnO₃ has a lower E_a of 38.7 kJ mol⁻¹, suggesting higher reactivity. XRD measurements of La_xMnO₃ samples show that the main diffraction peaks correspond to the hexagonal perovskite phase, without the presence of Mn- or La-related species. The results indicate that the crystal size increases with calcination temperature, confirming the purity of the perovskite phase. In addition, N₂ adsorption measurements reveal that the samples have similar surface areas, suggesting a uniform pore size distribution [87].

There are different studies that focus on analysing the catalysis of nitrogen monoxide (NO) oxidation using LaMnO_3 based perovskites, particularly the nonstoichiometric samples. The importance of Non stoichiometry can be highlighted by the results, which revealed that nonstoichiometric perovskites exhibit specific structural properties, such as variations in the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio, active oxygen mobility, and cation vacancy defects. In particular, the $\text{La}_{0.9}\text{MnO}_3$ sample showed promising catalytic activity for NO oxidation, suggesting that a lower amount of La in the A site induces a transformation of Mn^{3+} to Mn^{4+} to balance the charge and maintain structural stability.

The role of Mn^{4+} and Active Oxygen was discovered by the study that showed that oxygen-associated Mn^{4+} plays a crucial role in the oxidation process of NO. Through reduction experiments at different temperatures, it was observed that the amount of Mn^{4+} and associated oxygen species decreases with increasing reduction temperature. Notably, the sample reduced at 200 °C maintained its catalytic activity, suggesting that surface oxygen species are not critical to the NO oxidation process. However, reductions to higher temperatures (330 °C and 500 °C) resulted in a significant decrease in catalytic performance, indicating that Mn^{4+} and associated oxygen species are essential for catalytic activity.

Catalytic activity in LaMnO_3 perovskites changes significantly as a function of nonstoichiometric ratios, particularly the ratio of Mn^{4+} to Mn^{3+} .

Here are some key points on how these ratios affect catalytic activity:

- $\text{Mn}^{4+}/\text{Mn}^{3+}$ Ratio: An increase in the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio is associated with increased catalytic activity. This is because Mn^{4+} is able to complex oxygen, forming active oxygen species that are crucial for oxidation reactions, such as oxidation of NO.
- Structural Stability: In nonstoichiometric perovskites, less La at the A site leads to more Mn^{4+} formation to balance the charge and maintain structural stability. This stability is critical for maintaining catalytic activity over time.
- Active Oxygen: The presence of active oxygen associated with Mn^{4+} is essential for NO oxidation. Samples with a higher ratio of Mn^{4+} tend to show a greater ability to generate active oxygen, thus improving the efficiency of the reaction.
- Effect of Reduction: Reduction of samples at different temperatures affects the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio. For example, reductions at higher temperatures can lead to a decrease in the amount of Mn^{4+} and oxygen species, thus reducing catalytic activity. Conversely, reductions at lower temperatures may preserve catalytic activity.
- Oxygen Regeneration: In some cases, surface oxygen can be regenerated during oxidation conditions, which can help maintain catalytic activity even after reduction treatments. In summary, nonstoichiometric ratios in LaMnO_3 perovskites directly influence catalytic activity through changes in the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio, structural stability, and availability of active oxygen species. Optimizing these ratios is crucial for improving catalytic performance in applications such as NO oxidation [88].

In recent years, manganese-based materials, particularly LaMnO_3 compounds, have attracted attention for their potential as catalysts in the oxygen reduction reaction (ORR). Their electrocatalytic activity is known to depend on several factors, including the crystalline phases and the concentration of active species on the surface. In this study, $\text{La}_{1-x}\text{MnO}_x$ materials were synthesized using a sol-gel method by varying the ratio of lanthanum to manganese. This variation led to the formation of different crystalline phases and changed the surface concentration of manganese, thus affecting the electrochemical properties of the materials. The results showed that the presence of a cubic perovskite phase is associated with better electrocatalytic performance in ORR. In particular, the $\text{La}_{0.6}\text{MnO}_x$ /Vulcan sample showed the best electrocatalytic response due to a high ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ and the presence of oxygen vacancies. These factors help to increase electrical conductivity and promote metal-oxygen bond covalency, making the material more effective in catalysing the oxygen reduction reaction. In addition, it has been observed that crystallite size varies depending on the crystalline phase present, with the cubic perovskite phase having smaller crystallite sizes than the rhombohedral phase. This suggests that the crystallite size and material structure can be optimized to further improve electrocatalytic performance. In conclusion, optimizing the composition and structure of manganese-based materials, particularly through manipulation of the La/Mn ratio, can lead to significant improvements in their energy applications, making them promising candidates for use in fuel cells and other sustainable energy technologies ^[89].

Chapter 2

Perovskites synthesis methods

Various synthesis methods have been developed over the years to prepare perovskites, driven by the need to enhance their textural properties, such as specific surface area (SSA) and porosity, to make catalytically active components more accessible. The primary motivation in the field of catalysis has been to optimize these properties for better performance.

Numerous perovskite preparation routes have been proposed, ranging from traditional solid-state reactions and co-precipitation to more advanced techniques like reverse micelles microemulsion and microwave-assisted synthesis. Each method offers unique advantages and challenges. For instance, solid-state reactions are straightforward but often result in low SSA, while methods like reverse micelles microemulsion can produce materials with higher SSA and controlled porosity.

Synthesizing perovskite compounds with controlled properties is crucial for optimizing their performance in various applications. This review explores several commonly employed synthesis techniques, emphasizing their principles, benefits, and the characteristics of the materials they produce. Understanding these synthesis strategies is essential for tailoring perovskite materials to meet specific application requirements and advancing their technological impact.

By mastering these methods, researchers can significantly enhance the functionality and applicability of perovskite-based materials in various fields.

2.1 General synthesis methods

In the following section, all the general synthesis method are going to be discussed.

2.1.1 *Classical synthesis*

The historical synthesis methods for perovskites revolve around ceramic and coprecipitation techniques. The ceramic method involves a straightforward thermal process where metal cation precursors are ground, mixed, and repeatedly calcined at temperatures exceeding 1000°C. This process ensures the decomposition of precursors, solid-solid ion diffusion, and the complete transformation of simple oxide phases into perovskite ^[3]. However, due to the elevated

temperatures involved, resulting materials typically consist of large crystal grains with low surface areas, generally less than $5 \text{ m}^2 \cdot \text{g}^{-1}$.

The coprecipitation method allows perovskite crystallization at lower temperatures, typically ranging from 700°C to 900°C , depending on the desired phase.

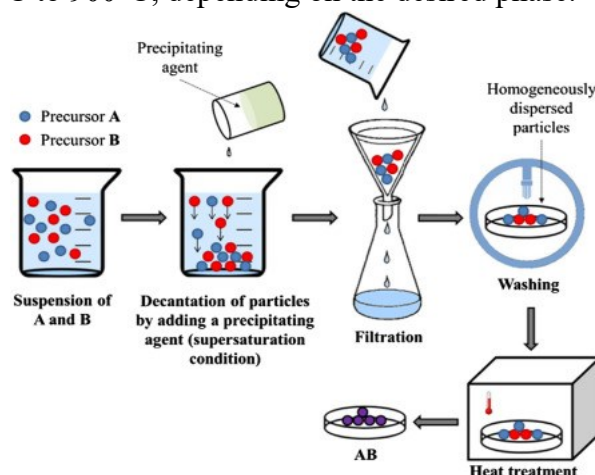


Figure 2.1: Schematic view of the elementary steps of a perovskite preparation using the coprecipitation approach ^[3].

Starting with an aqueous solution of A and B cation precursors, coprecipitation in a basic medium lead to the formation of an amorphous mixed A and B hydroxide. The distribution of cations within the amorphous solid is more uniform, promoting a quicker conversion into the crystalline perovskite phase compared to the ceramic method. Consequently, smaller crystal sizes are achieved, resulting in higher surface areas that can reach up to $15 \text{ m}^2 \cdot \text{g}^{-1}$. The precipitation of metal salts is a common technique for synthesizing simple oxides. This process begins by adding a chemical reagent that reduces the solubility limit, causing the metal salts to precipitate. Co-precipitation occurs when multiple cations in a solution precipitate at the same time. To achieve uniform precipitation of all cations and produce homogeneous products, it is crucial to manage the temperature, concentration, pH, and homogeneity of the solution. Common reagents used in this method include ammonia, ammonium oxalate, urea, and ammonium carbonate. The formation of insoluble oxide compounds happens through the thermal decomposition of hydroxides, organic salts, or carbonate salts ^[90].

2.1.1.1 Solid-state reactions

In solid-state reactions, both the starting materials and the final products are solid, which allows reagents such as carbonates, nitrates, and oxides to be mixed in stoichiometric ratios. Perovskites can be synthesized through these reactions by combining oxides or carbonates of B-site and A-site metal ions according to the perovskite formula ABO_3 . This mixture needs to

be heated to temperatures above 2/3 of the melting point for up to ten hours to achieve the desired composition.

All the ingredients are thoroughly mixed using ball milling in a medium of isopropanol or acetone. The resultant mixture is then dried at 100°C and calcined in air at 600°C for 4–8 hours with alternating temperature rates of 2°C per minute (warming and cooling). After this, the samples are ground, sieved, and then re-calcined at 1300–1600°C for 5–15 hours under the same alternating temperature conditions to ensure the formation of a single-phase perovskite. Finally, the samples are ground and sieved again ^[90].

2.1.1.2 Hydrothermal synthesis

The principle of hydrothermal synthesis involves carrying out reactions in an aqueous solution or suspending precursors at elevated temperature and pressure. This method allows for the production of crystalline powders without the need for calcination. Initially used to synthesize and verify the thermodynamic stability of BaTiO₃ and other perovskites, this technique now also enables control over particle size and shape by adjusting reaction temperature, pH, time, and reactant concentration.

Recently, BaTiO₃ has been synthesized at low temperatures using this method with the application of an electric field in a hydrothermal cell at specific temperatures (100 and 200°C). Researchers have further managed to reduce the hydrothermal synthesis temperature even more by employing an electric field ^[90].

2.1.1.3 Gas phase preparation

Gas phase reactions or transport reactions are utilized to create perovskite films with specific thicknesses and structures. This process can be categorized into three types of deposition: at crystallization temperature under a suitable atmosphere, at an intermediate temperature of 873–1073 K followed by post-annealing, and at a low substrate temperature followed by high-temperature post-annealing.

Yttrium barium copper oxide, specifically YBa₂Cu₃O_{7-x} films, can be produced through the co-evaporation of Y, Cu, and BaF₂, followed by high-temperature curing in an O₂ atmosphere. The process is further enhanced by the addition of water vapor to reduce curing time and improve the substrate interface. Techniques such as magnetron sputtering, laser ablation, molecular beam epitaxy, thermal evaporation, DC sputtering, and electron beam evaporation have been developed for gas phase deposition ^[90].

2.1.1.4 Microwave synthesis

Microwaves are increasingly being utilized as a novel method in Solid State Chemistry. The use of microwave irradiation presents a promising alternative heat source for synthesizing

perovskite oxides. This approach offers considerable time savings and energy efficiency compared to traditional ceramic synthesis methods. Microwave synthesis of perovskite oxides can be accomplished through various techniques such as combining microwave heating with other synthetic methods like sol-gel or combustion, irradiating a solution in an autoclave, or directly irradiating a mixture of solid reactants.

There are two main techniques for microwave synthesis: microwave-assisted hydrothermal synthesis and solid-state microwave synthesis. Solid-state microwave synthesis is typically limited to "simple" compositions, whereas combining microwaves with other methods such as combustion, hydrothermal synthesis, or sol-gel allows for better stoichiometric control of complex doped phases.

Integrating solvothermal synthesis with microwave heating results in new morphologies and metastable phases. The properties of perovskite oxide materials, such as their superconducting, dielectric, ferromagnetic, ferroelectric, and multiferroic characteristics, play a crucial role in their synthesis using microwave techniques. The simplicity and speed of microwave synthesis make it particularly appealing for Pb-containing perovskites, as it minimizes Pb-loss ^[90].

2.1.2 Pechini sol-gel method

The Sol-Gel method is a cost-effective, well-established, and versatile synthetic technique for creating a wide variety of micro- and nanostructures. Small adjustments in pH, temperature, precursors, time, pressure, and atmosphere can produce a diverse array of compounds with similar molecular structures. In this section, is presented an extensive review of the synthesis of LaMnO₃, SrTiO₃, BaTiO₃ perovskites, and zinc vanadium oxide nanostructures via the Sol-Gel method and it is explored how minor variations in synthesis parameters can influence the morphology, shape, size, homogeneity, and aggregation of the resulting products. Additionally, there will be the examination of the different precursors, solvents, working temperatures, and reaction times employed throughout the synthesis process.

In the initial step, called hydrolysis, metal alkoxide (MA) precursors are combined with solvents. During this step, oxygen from water initiates a nucleophilic attack on the MA, leading to the removal of the alkoxide functional group and the formation of an alcohol functional group (M – OH). The process of hydrolysis and subsequent condensation reactions are greatly influenced by parameters such as the nature of the R-group, steric hindrance of the alkoxy functional group, temperature, pH, the use of aqueous or non-aqueous media, organic solvents like alcohols, the ratio of solvent to MA, acetylacetonates as precursors, and the concentration of catalysts (acidic or basic). These variables add complexity to the synthetic control through this route. The gel structure that forms varies greatly depending on the catalyst, influenced by

the relative speeds of the hydrolysis and condensation reactions. Typically, the hydrolysis step is slower in acidic conditions and faster in basic conditions.

The condensation or polycondensation step involves forming a polymer network made of metal oxide linkages by eliminating solvents (water or alcohol) to form a sol. As the polymer network expands, the solution's viscosity increases, creating a porous structure within the liquid phase (Gel). The general chemical reactions for hydrolysis and condensation are as follows:



where M represents a metal, and X is either hydrogen or an alkyl group ($\text{C}_n\text{H}_{2n+1}\text{C}_n\text{H}_{2n+1}$). During the aging step, polycondensation continues, accompanied by the precipitation of the gel network, which reduces porosity and increases thickness between colloidal particles. Another significant factor is the physical treatment of the sol or gel. For instance, the evaporation rate during gelation can substantially impact the gel structure. Removing the liquid from the gel can lead to significant changes in the network structure. If the structure remains intact, an aerogel is produced; if it collapses, a xerogel is formed. When the liquid is removed at low temperatures, the resulting material is called cryogels. Aerogels have high pore volume and surface area, whereas xerogels possess lower surface area and pore volume. Heat treatment is essential for drying gels, eliminating surface hydroxyl groups, densifying the material to form a ceramic monolith, or transforming it into a crystalline substance^[91].

The alkoxide, alkoxide-salt, and Pechini methods are among the most popular Sol-Gel techniques for synthesizing perovskites. The Sol-Gel Pechini method (chelat polyesterification) is particularly valued for its versatility in preparing perovskite membranes, depositing dielectric films for capacitors, and producing multicomponent oxide materials. One of the main advantages of this method is its simplicity and the low-temperature handling of precursors, which leads to nanopowders of high purity and uniformity, as well as precise control over the final material composition.

The Pechini method is particularly popular for synthesizing various mixed oxides because it can combine chemicals such as lactic, glycolic, citric, and EDTA acids to form polybasic acid chelates with dissolved cations. Chelating agents are used to prevent partial metal segregation in the final compound, which can result from interactions between metal ions in solution. When a polyhydroxy alcohol is added to the solution and heated, creating a cross-linked chain of metal atoms connected to organic radicals, polyesterification of chelates occurs. When two chelating agents are used together to complex all metal ions, a precursor solution is formed where all metal ions are fully bound, resulting in a more stable chelate complex. The polymerization is further enhanced by adding ethylene glycol, which improves uniformity and reduces metal segregation during decomposition under heat treatment conditions.

In the synthesis process and subsequent heat treatment, maintaining a high ratio of metal precursors to chelating agents is crucial. This ensures that all metal ions are tightly bound and prevents precipitates from forming in the solution.

The Sol-Gel Pechini method offers superb control over the perovskite structure, resulting in highly homogeneous solutions.. At temperatures near 1000°C, this approach results in the formation of pure crystalline perovskite structures ^[91].

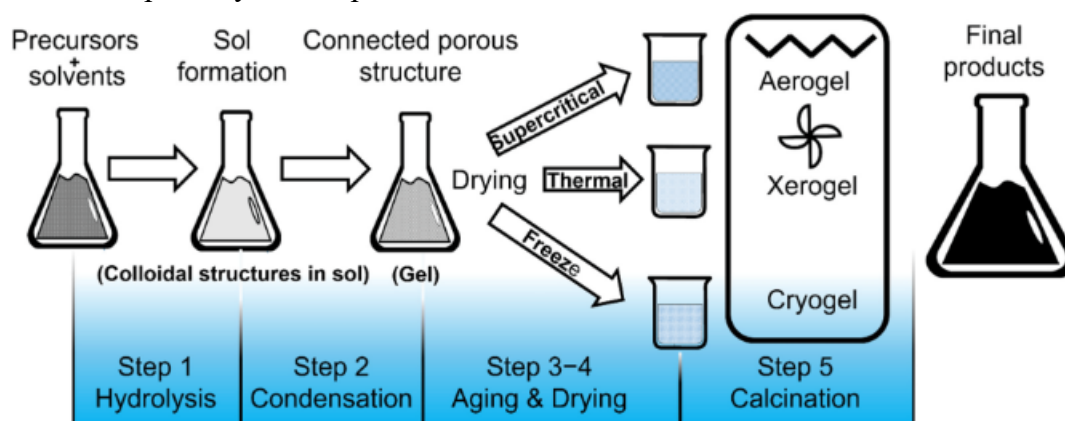


Figure 2.2: Schematic view of the elementary steps of a perovskite preparation using the sol-gel method ^[91].

2.2 Synthesis procedure adopted: Auto-combustion

Auto-combustion synthesis is a straightforward and efficient technique for preparing various advanced ceramics, catalysts, and nanomaterials. This method relies on a thermally induced redox reaction between an oxidant and a fuel, based on propellant chemistry principles. There are multiple types of combustion synthesis, differing mainly in the physical state of the reactants or the combustion modality. Combustion-based methods enable the production of monophasic nanopowders with uniform microstructures at lower temperatures or shorter reaction times compared to traditional methods like solid-state synthesis or nitrate methods.

2.2.1 Synthesis method

Combustion synthesis methods are inspired by Pechini's approach, where citric acid and ethylene glycol are added to an aqueous solution containing suitable metal salts or oxides in precise proportions. During solvent evaporation, gelation occurs due to the poly-condensation of citric acid and ethylene glycol. This process immobilizes the metal citrate complexes within the gel, preventing the precipitation of cations and ensuring that chemical homogeneity is maintained throughout the drying process. After the gel has dried, it is fired at high temperatures to produce finely dispersed powders of metal oxides and/or metal carbonates. After calcination at an appropriate temperature, a phase-pure ceramic powder is produced.

The synthesis typically involves four key steps:

- (i) formation of organometallic complexes in solution,
- (ii) solvent evaporation and gel formation,
- (iii) auto-combustion (pyrolysis), followed by
- (iv) heat treatment of the obtained powder.

Among the various chelating agents, ethylene-diamine-tetraacetic acid (EDTA) and citric acid (CA) are the most frequently used. EDTA has a higher chelating power, allowing it to form complexes with a broader range of cations compared to CA. However, CA, with its three carboxyl groups and one hydroxyl group, possesses a stronger gelation ability.

Despite its advantages, using CA alone as a chelating agent can result in a highly exothermic and non-uniform combustion reaction, which can adversely affect the morphology of the powder. Therefore, CA and EDTA are often used together as combined chelating agents to optimize the synthesis process. Polyesterification of chelates happens when a polyhydroxy alcohol is added to the solution and heated, creating a cross-linked chain of metal atoms attached to organic radicals. When two chelating agents collaborate to complex all metal ions, a precursor solution is formed with all metal ions fully bound. This leads to a more stable chelate complex system, and the subsequent addition of ethylene glycol enhances uniformity, aiding in the polymerization process.

This method tends to reduce metal segregation after decomposition under heat treatment conditions. The ratio of metal precursors to chelating agents is crucial during the synthesis process and the subsequent heat treatment. This ratio must be high enough to ensure that all metal ions are tightly bound within their structures, preventing precipitates in the solution.

The Sol-Gel Pechini method provides excellent control over the perovskite structure, producing highly homogeneous solutions. At temperatures approaching 1000°C, this approach results in

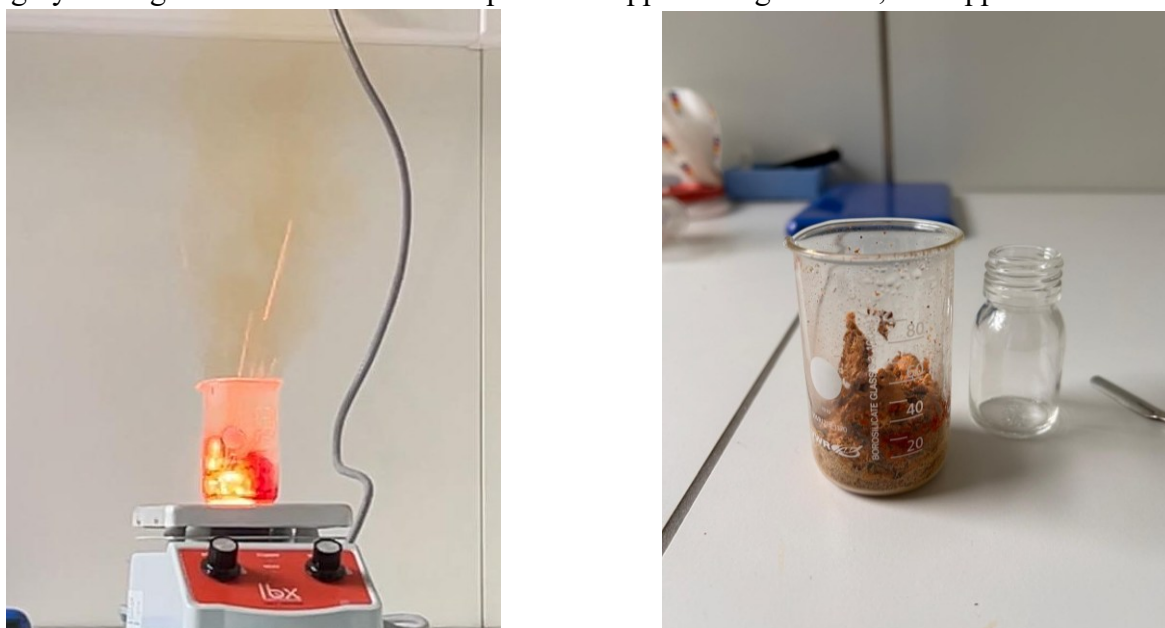


Figure 2.3-2.4: Representation of what happened in an Auto-Combustion reaction.

the formation of pure crystalline perovskite structures. The ability to achieve such uniform and pure products makes the Pechini method highly valuable for various advanced materials applications.

Traditionally, the composition of a combustion reaction mixture is described using the oxidizer-to-fuel ratio, ϕ , known as the equivalence ratio. However, this concept becomes less useful when fuel molecules contain oxidizer elements or oxidizer molecules contain fuel elements. Combustion reactions are redox reactions, and therefore, oxidation numbers can be employed to identify which elements in the reactant mixture serve as oxidizers and which function as fuels (reductors).



Figure 2.5: Powder product of the Auto-Combustion reaction.

2.2.2 La_xFeO_3 and La_xMnO_3 via Auto-combustion method

Lanthanum orthoferrite (LaFeO_3) is a significant perovskite-type oxide with the formula ABO_3 , where A represents a rare earth element and B is a 3d transition metal. The unit cell of LaFeO_3 includes four formula units, with Fe^{3+} ions coordinated by six O^{2-} ions, forming an octahedral structure. This results in an orthorhombic structure with a Pbnm space group. LaFeO_3 's mixed ionic-electronic conductivity makes it an attractive material for various advanced technological applications, such as solid oxide fuel cells, oxygen sensors, and photocatalysts.

The FeO_6 octahedral units in LaFeO_3 consist of two interpenetrating pseudocubic face-centered sublattices. The collinear arrangement of Fe^{3+} ions in these sublattices leads to antiferromagnetic interactions. Bulk LaFeO_3 exhibits antiferromagnetic behaviour, characterized by a high Néel temperature of 740 K and an exceedingly small spontaneous

magnetization of 0.044 $\mu\text{B}/\text{Fe}$. Interestingly, antiferromagnetic nanoparticles often show an increase in net magnetization due to the presence of uncompensated surface spins. Consequently, controlling the size, morphology, and crystallinity of LaFeO_3 , factors highly dependent on the preparation method, can enhance its ferromagnetic behaviour.

Improving the synthesis of LaFeO_3 has attracted significant interest from researchers. Traditional physical methods like solid-state reactions and ball-milling are now less favoured due to their drawbacks, such as affecting the size and purity of the products. Consequently, various wet chemical methods, including hydrothermal, thermal decomposition, micro-emulsion, microwave plasma, electrospinning, polymer pyrolysis, co-precipitation, and hot soap methods, have been explored.

However, wet chemical approaches have their own challenges, including the use of expensive reagents, small-scale production, continuous monitoring of pH and reactant composition, the need for high-temperature calcination over extended periods, and environmental impacts. Recently, sol-gel auto-combustion routes have been developed to synthesize such materials, resulting in highly active, stoichiometric, and homogeneous yields. These methods are simple, cost-effective, environmentally friendly, and efficient. Moreover, no further calcination is required since the heat generated during the reaction is sufficient for the complete formation of the products.

Most auto-combustion processes for preparing LaFeO_3 use citric acid or glycine as fuel. Recently, other effective fuels like egg whites, gelatine, chitosan, urea, and sucrose have been successfully utilized for efficient ferrite synthesis. These fuels offer an environmentally friendly, fast, and economical alternative for material preparation. Different synthetic routes have been shown to influence the structural, electrical, and magnetic properties of the materials. This study focuses on preparing LaFeO_3 perovskite nanocrystals through simple, economical, and environmentally friendly sol-gel auto-combustion routes using various fuels, including egg whites, gelatine, citric acid, urea, chitosan, and sucrose. The auto-combustion and ferrite formation processes were analysed using DTA-TG, XRD, FT-IR, and TEM measurements. The magnetic and dielectric properties, as well as the AC-conductivity, were measured to study the effect of different preparation routes on these properties and to propose suitable applications.

The Synthesis begins with the precise weighting of the reagents. The primary reagents used are Lanthanum Oxide (La_2O_3), Iron Nitrate Nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Manganese Nitrate Nonahydrate ($\text{Mn}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and Citric Acid. The quantities of these reagents are carefully measured based on the stoichiometric requirements of the reaction. The exact amounts used are determined by the degree of sub-stoichiometry required for the specific synthesis.

- La_xFeO_3 : As already mentioned, the precursor and the complexant are going to be weighted considering of the product that is desired. An excel file was made and in the case of La_xFeO_3 the following table refers to the La_1FeO_3 .

Precursors			Complexant	
Formula	La_2O_3	$\text{Mn}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Formula	Citric Acid
MM (g/mol)	325,8092	240,95	MM (g/mol)	$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$
n (mol) of cation in the precursor	2	1	n (mol)	210,14
m (g) to be weighed	1,5741	3,8805	m (g) to be weighed	0,0470
				9,8686

PRODOTTO		3+	3+/2+	2-
Formula	La_xFeO_3	La	Fe	O
MM (g/mol)	242,7487	138,9055	55,845	15,9994
n (mol) of cations in the product	0,0124	1,00	1,00	3,00
m (g) required	3,00	/	/	/

- La_xMnO_3 : Also in this case, the precursor and the complexant are going to be weighted considering of the product that is desired. A different excel file was made and in the case of La_xMnO_3 the following table refers to the $\text{La}_{0,6}\text{MnO}_3$.

Precursors			Complexant	
Formula	La_2O_3	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Formula	Citric Acid
MM (g/mol)	325,8092	404,00	MM (g/mol)	$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$
n (mol) of cation in the precursor	2	1	n (mol)	210,14
m (g) to be weighed	1,5665	6,4748	m (g) to be weighed	0,0490
				10,2882

PRODOTTO		3+	3+/2+	2-
Formula	La_xMnO_3	La	Mn	O
MM (g/mol)	186,2795	138,9055	54,938	15,9994
n (mol) of cations in the product	0,0161	0,60	1,00	3,00
m (g) required	3,00	/	/	/

The Citric Acid acts as a chelating agent, facilitating the formation of a homogeneous precursor solution and promoting the auto-combustion process.



Figure 2.6: Solutions with reagents and water.

The weighted reagents are thoroughly mixed under controlled temperature with water to form a homogeneous precursor solution for about 6 hours. This step is crucial to ensure uniform distribution of the components and to promote a consistent reaction.

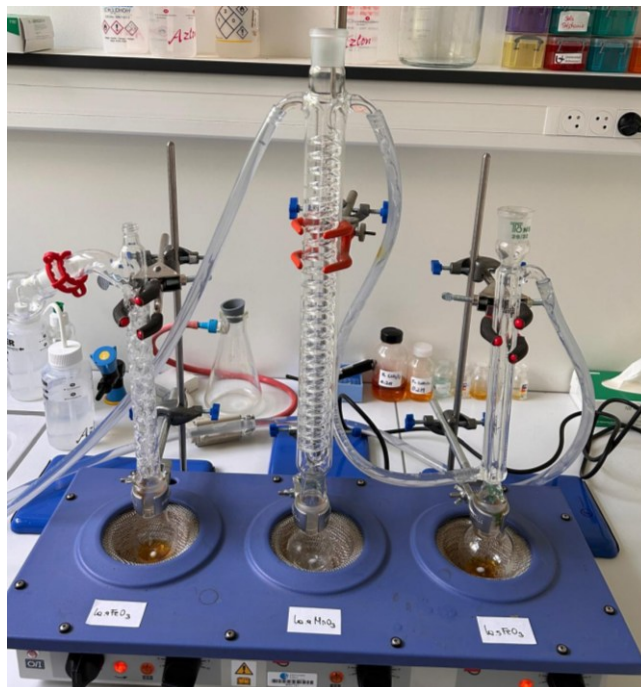


Figure 2.7: System made for mixing and heating the solutions.

After the six hours mixing period, the solution is transferred to a beaker and placed on a heat source without mixing. The heat source facilitates the evaporation of water from the solution. As the water evaporates, the solution becomes more concentrated, leading to the initiation of the auto-combustion reaction.

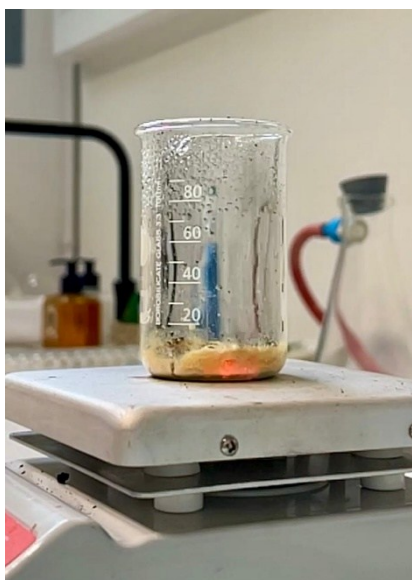


Figure 2.8: Auto-Combustion reaction, ignition of the flame.

Figure 2.9: Final solid product of the synthesis.

Once the water has completely evaporated, the auto-combustion reaction occurs. This self-sustaining exothermic reaction rapidly converts the precursor solution into the desired perovskite phase. The reaction is characterized by the release of heat and the formation of a dried perovskite product, which is ready for the calcination and then for catalytic tests.



Figure 2.10: Some of the perovskites that were synthesized in the UCCS laboratory, as it is possible to notice there is no water thanks to the reaction.

Chapter 3

Techniques of analysis and instrumentation

Analysing perovskite materials is essential for understanding their structural, compositional, and functional properties, which are crucial for optimizing their performance in various applications. Perovskites exhibit a wide range of fascinating properties, including electronic, optical, magnetic, and catalytic behaviour, making them highly attractive for applications such as solar cells, sensors, catalysts, and more. To fully harness the potential of perovskites, it is essential to employ advanced analytical techniques capable of providing detailed insights into their properties at the atomic and molecular levels. This review discusses various analytical techniques commonly used for the characterization of perovskite materials: Raman spectroscopy, X-ray Diffraction, Thermogravimetric analysis, Temperature-Programmed Reduction/Oxidation, X-ray Photoelectron Spectroscopy and BET analysis.

3.1 Raman spectroscopy

Spectroscopy examines how electromagnetic radiation interacts with matter. Various spectroscopic methods, such as emission, absorption, fluorescence, or scattering, are employed. Raman spectroscopy, named after its inventor C.V. Raman, is particularly noteworthy. Alongside K.S. Krishnan, Raman published the first paper on this technique. Raman spectroscopy (RS) is highly adaptable and overcomes many limitations of other spectroscopic methods. It is adept at both qualitative and quantitative analysis, with qualitative assessments based on scattered radiation frequency and quantitative assessments based on scattered radiation intensity. Infrared spectroscopy is often discussed alongside Raman spectroscopy to provide a comprehensive analytical approach ^[5,6,7].

3.1.1 Instrumentation for the analysis

In Raman spectroscopy, a monochromatic laser beam illuminates the sample, interacting with its molecules to generate scattered light. The resulting scattered light, with a frequency different from that of the incident light (inelastic scattering), is used to generate a Raman spectrum. These

spectra originate from the inelastic collision between incident monochromatic radiation and the sample's molecules [6,8].

Upon striking the sample, the monochromatic radiation scatters in various directions following its interaction with the sample molecules. Most of this scattered radiation shares the frequency of the incident radiation, constituting Rayleigh scattering. However, a small fraction exhibits a frequency distinct from that of the incident radiation, constituting Raman scattering. In Raman spectra, Stokes lines appear when the frequency of incident radiation exceeds that of scattered radiation. Conversely, anti-Stokes lines emerge when the frequency of incident radiation is lower than that of scattered radiation. Typically, scattered radiation is measured at a right angle to the incident radiation [7,9,10].

A Raman spectrum is typically presented as a plot of intensity against wavelength shift. These spectra are often recorded within a range of $4000\text{--}10\text{ cm}^{-1}$. However, the Raman-active normal modes of vibration for organic molecules typically occur within the range of $4000\text{--}400\text{ cm}^{-1}$. Depending on the design and optical components of the spectrophotometer, typical Raman spectra cover a wavenumber region between $400\text{--}5\text{ cm}^{-1}$ and $4000\text{--}3800\text{ cm}^{-1}$.

Compared to their Infrared (IR) counterparts, Raman spectra are notably simpler due to the rarity of overtones, combination, and difference bands in normal Raman spectra [6].

Raman spectrophotometers can be categorized as dispersive or non-dispersive. Dispersive Raman spectrophotometers utilize prisms or gratings, while non-dispersive ones employ interferometers such as the Michelson interferometer in Fourier Transform Raman spectrophotometers.

In the early days, mercury arc lamps were commonly used as light sources in Raman spectrophotometers, with the 435.8 nm line of coiled low-pressure mercury arc lamps being prevalent until the 1960s [6,7]. However, laser sources, which became available in the late 1960s, completely replaced mercury lamps. Laser sources offer stable and intense radiation beams. Various lasers such as Argon ion, Krypton ion, Helium-Neon (He-Ne), Near Infrared (IR) diode lasers, Neodymium-Yttrium Aluminium Garnet (Nd:YAG), and Neodymium-Yttrium Ortho-Vanadate (Nd:YVO4) can be utilized as light sources in Raman spectrophotometers [8]. While short-wavelength sources like argon ion and krypton ion lasers may produce significant fluorescence and photodecomposition of the sample, long-wavelength sources such as diode or Nd:YAG lasers can operate at higher power without causing sample photodecomposition and can eliminate or reduce fluorescence in most cases [7].

To isolate a single laser beam, band-pass filters are employed. Dispersive instruments commonly use a combination of notch filters and high-quality grating monochromators. Additionally, double, or triple grating monochromators, super notch filters, rejection filters, holographic notch or edge filters, and holographic filters are utilized to separate relatively weak Raman lines from intense Rayleigh scattered radiation [6,7,11,12].

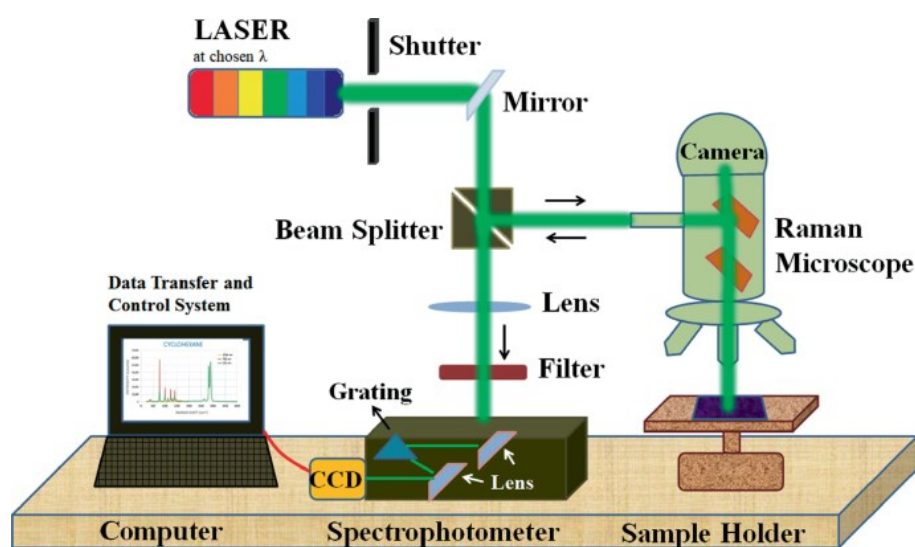


Figure 3.1: Schematic drawing of the main mechanisms used to explain the Raman spectroscopy. [13,14]

3.2 X-ray diffraction XRD

X-ray diffraction (XRD) is a powerful non-destructive technique used to analyse the structure of materials at the atomic or molecular level. It is particularly effective for crystalline and partially crystalline substances, but it can also be applied to non-crystalline materials. XRD provides detailed information on structures, phases, preferred crystal orientations (texture), and other structural parameters such as average grain size, crystallinity, strain, and crystal defects. XRD operates on the principle that X-rays, which are a form of light with nanometre-scale wavelengths, scatter when they encounter a material with a corresponding structural scale. This scattering leads to interference patterns with varying intensities, similar to the colourful patterns seen in soap bubbles. The constructive interference of a monochromatic X-ray beam, scattered at specific angles by the lattice planes in the sample, produces diffraction peaks. The distribution of atoms within the lattice determines the intensities of these peaks, making the diffraction pattern a unique fingerprint of the material's atomic arrangement [26,27].

Unlike X-ray radiography or tomography, which rely on the differential absorption of X-rays by various materials to produce direct images of internal structures (useful in medical diagnostics and materials science), XRD produces a diffraction pattern that indirectly reveals the internal structure on a scale ranging from 0.1 to 100 nm.

A simplified XRD experiment involves directing an X-ray beam at a sample and measuring the scattered intensity as a function of the outgoing direction. The angle between the incoming and outgoing beam directions is known as 2θ . According to Bragg's Law, constructive interference, resulting in higher scattered intensity, occurs when [26]:

$$n\lambda = 2d\sin\theta \quad (3.1)$$

Where: n is an integer, λ represents the wavelength of the X-ray beam, and θ is half the scattering angle 2θ . For more complex materials, there is a relationship between the interparticle distances in the sample and the angles at which the scattered intensity peaks. Larger distances d correspond to smaller scattering angles 2θ .

This review highlights the rapid advancements in X-ray diffraction techniques over the past five years, with significant applications in pharmaceuticals, forensic science, geological studies, microelectronics, glass manufacturing, and corrosion analysis [26,27]. These developments have enhanced our ability to characterize and understand the intricate structures of various materials, making XRD an invaluable tool in both scientific research and industrial applications.

3.2.1 Instrumentation for the analysis

The X-ray source generates X-rays that illuminate the sample, which then diffracts these rays. The diffracted rays are captured by the detector. To measure intensity and record diffraction data, the tube or sample and detector are adjusted to change the diffraction angle (2θ , which is the angle between the incident and diffracted beams). Depending on the diffractometer's design and the type of sample, the angle between the incident beam and the sample can be either fixed or adjustable, and it is typically coordinated with the angle of the diffracted beam.

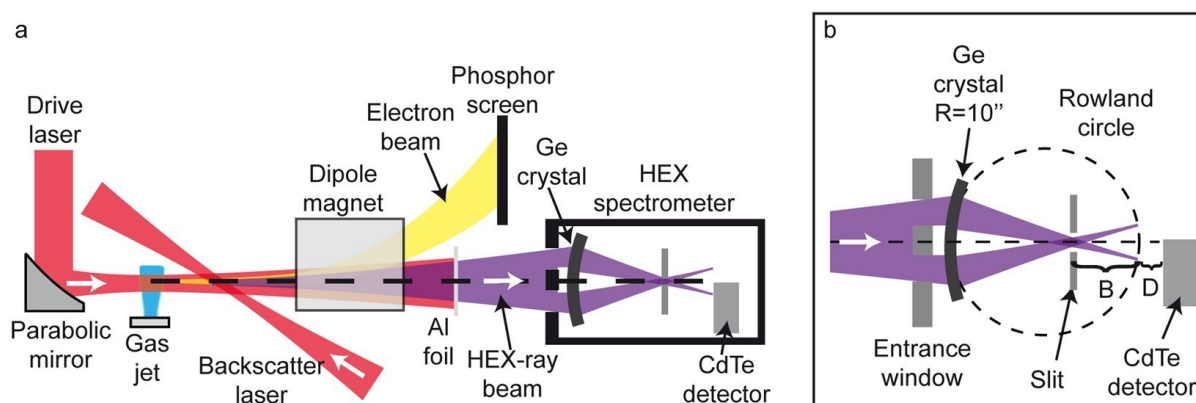


Figure 3.2: Schematic drawing of the main mechanisms used to explain the X-ray diffraction. [28]

3.3 Thermogravimetric Analysis TGA

The thermogravimeter [18] is a specialized instrument that measures the weight change of a material when heated, resulting from decomposition due to the evolution of gaseous products. Thermogravimetry is a traditional technique used for quantitative thermal analysis of a sample by measuring weight loss at specific temperatures, without identifying the nature of the components. This analysis produces graphs (mass vs. temperature) known as thermogravimetric curves.

In thermogravimetric analysis (TGA), a sample is continuously weighed while being heated in an inert gas atmosphere. Many solids undergo reactions that release gaseous byproducts, which are removed in TGA, and changes in the remaining sample mass are recorded. Three common variations are employed:

1. **Dynamic TGA:** The temperature increases over time while mass is recorded, allowing simultaneous identification of the amount of gas removed and the temperature at which it occurs.
2. **Static TGA:** The temperature is held constant while the mass is measured, providing detailed information on decompositions at specific temperatures or assessing a material's ability to withstand a given temperature.
3. **Quasistatic TGA:** The sample is heated in multiple temperature intervals and held at these intervals until the mass stabilizes. This method is ideal for investigating substances that decompose differently at various temperatures and for better characterizing their decomposition behaviour.

3.3.1 Instrumentation for the analysis

The instrumentation is conceptually simple, but practically very delicate and precise and requires periodic checking and calibration: in essence, it is an extremely precise balance in which the sample is progressively heated from room temperature to over 1000 °C with programmable ramps of ascent in programmable temperature ramps. The different components are ^[19,22,23]:

- Sensitive analytical balance (capacity between 5 and 20mg);
- Furnace (temperature from 25 to 1500 °C);
- Purge gas system ensuring an inert atmosphere and heat diffusion at every point;
- Computer for instrument control, data acquisition and display.

The core component of the instrument is the thermobalance, which comprises a dual-armed balance. One of these arms, where the sample under analysis is placed, is situated within a furnace. This furnace is capable of varying its temperature according to programmed scans within a controlled atmosphere ^[20,24]. Depending on the geometrical configuration of the furnace relative to the balance arm, the thermobalance can be designed with either a horizontal or vertical orientation. In the thermobalance with vertical geometry, the support arm is typically positioned outside the furnace, and the sample is suspended within the furnace either from above or below. The primary advantages of this type of geometry are related to the absence of expansion phenomena in the support arm, which can lead to measurement drift. However, a notable disadvantage is the increased difficulty in evacuating gases evolved during the analysis, as the hot gases tend to rise due to convective movements, creating a chimney effect.

The primary advantage of instruments with horizontal geometry is the capability to couple Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC) measurements with thermogravimetric analysis. This coupling allows for the detection of thermal transitions that occur without weight loss and/or the verification of whether the reaction or transition associated with weight loss is exothermic or endothermic.

Furthermore, based on the mechanism for measuring weight variation, the thermobalance can be classified as follows ^[18,19,20]:

- **Null point mechanism balance:** This type employs a sensor to determine the deviation from the equilibrium position (null point) of the sample and activates a servomechanism to correct this deviation. It is the most commonly used mechanism as it allows the sample to remain in the same position within the furnace regardless of weight variation.
- **Deflection mechanism balance:** This type includes rod, cantilever, torsion, or spring mechanisms. In this case, the deflection from the equilibrium point due to weight variation is measured using different mechanisms.

In both cases, calibration with certified weights is necessary to correlate the position variation or the force required to nullify it with the weight variation. Sample holder crucibles can be made of aluminium, quartz, ceramic, or platinum, depending on the temperatures to be reached and the type of atmosphere in which the measurement is conducted.

Within the furnace, typically made of refractory material, a thermocouple is positioned to record the real-time temperature profile of the sample. This thermocouple, generally made of chromel/alumel alloy, is calibrated using standard samples with well-defined Curie points (variation in magnetic properties) for vertical geometry thermobalances, and samples of metals or pure compounds with well-defined melting points for horizontal geometry thermobalances with DTA sensors. The purge gas system allows for the management and programming of the type of gas (inert, such as nitrogen or argon, or reactive, such as oxygen or air) and its flow rate. Operating with a gas flow, rather than in a static atmosphere, has the advantage of reducing the condensation of decomposition products on the cooler parts of the thermobalance. Additionally, it facilitates the removal of any corrosive gases and minimizes the likelihood of secondary reactions ^[21,22,25].

Despite the apparent simplicity of the technique, various sources of error can arise in thermogravimetry. A primary source of error is buoyancy, caused by changes in the viscosity and density of the purge gas during the temperature scan; this typically results in a drift of the signal, which has been almost entirely, but not completely, corrected in modern instrumentation. Other sources of error may include:

- External vibrations leading to unexpected weight variations (the thermobalance typically measures in micrograms or tenths of micrograms);

- The positioning of the thermocouple relative to the sample, causing a substantial difference between the temperature read by the system and the actual temperature of the sample;
- Highly exothermic reactions with rapid heat evolution.

It is important to emphasize that the thermogram resulting from a thermogravimetric measurement strongly depends on the analytical conditions set, particularly: the weight and shape of the sample, the temperature scan rate, the type and flow rate of the purge gas, and/or the system pressure conditions ^[24,25].

For all the aforementioned reasons, it may be advisable to perform the determination in duplicate or triplicate (weighing quantities of the sample as similar as possible for repeated measurements) and to express the result as the average of the data, especially in the case of analyses of samples characterized by low homogeneity (mixtures, composites) ^[25].

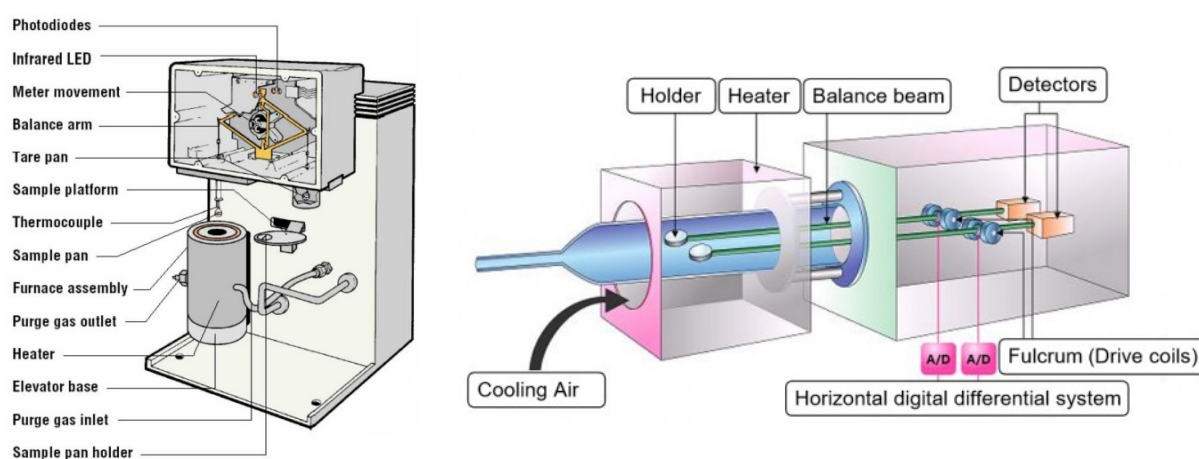


Figure 3.3-3.4: Vertical and horizontal instrumentation for the TGA. ^[18,22,25]

3.4 Temperature-Programmed Reduction/Oxidation TPR / TPO

Temperature programmed reduction (TPR) is a material characterization technique commonly used in catalysis studies to analyse the surface chemistry of metals and metal oxides under varying thermal conditions. This method utilizes TPR-enabled mass spectrometry equipment to provide both quantitative and qualitative data about the reducing gas mixtures passed over metallic samples. TPR is significant for offering precise insights into the reducibility of catalysts and the reaction rates on metal surfaces, which are essential for evaluating catalyst performance and ensuring reproducibility. This information helps establish benchmarks or reduction profiles that ideal manufactured catalysts should meet, aiding in quality control.

Temperature programmed oxidation (TPO) is another analytical technique used to characterize catalysts, playing a crucial role in research and development. TPO requires a furnace or microreactor capable of increasing the temperature of a catalyst in precise increments, such as 1-20°C per minute, up to 1000°C. An integrated mass spectrometer allows for continuous real-

time analysis of catalytic activity throughout a thermal reaction, where a gas mixture flows over a catalyst during an incrementally programmed temperature rise. Various reactions occur between the gas and the catalyst in the microreactor during the temperature ramp. For instance, coke build-up on the catalyst, which blocks reaction sites and reduces efficiency during pyrolysis reactions, can be investigated using an oxygen flow and TPO experiments. The coke can be characterized by measuring carbon monoxide, carbon dioxide, and hydrocarbon species at the reactor outlet. TPO is typically used to provide insights into various catalytic reactions with numerous applications, including research and development of alternative energy fuels and increased energy efficiency in chemical manufacturing.

Hydrogen-based fuel cells have emerged as a highly efficient, low-pollutant energy source, gradually being introduced in fuel cell electric vehicles (FCEVs) with a positive yet potentially superficial impact on greenhouse gas emissions. However, the primary method of hydrogen production is natural gas reformation. Steam-hydro carbonation reforming reacts a natural hydrocarbon, such as methane (CH_4), with high-pressure steam at up to 1000°C in the presence of a catalyst. This produces hydrogen for use in various industries, including greener energy sources.

Despite this, the process has remarkably high energy demands, significantly reducing the environmental benefits of the end product. TPO is used to characterize coke during this reaction.

3.4.1 *Instrumentation for the analysis*

In a typical TPR experiment, a metal oxide like nickel oxide (NiO) is dispersed on a surface and assessed in a fixed bed reactor. A reducing gas mixture, such as hydrogen (H_2), is then passed over the catalyst while the temperature is gradually increased. This controlled heating allows the reduction rate to be correlated with the temperature. An overly sensitive detector continuously monitors the changes in atmospheric concentration at the outlet, providing an accurate depiction of the catalyst's maximum or peak reduction rate. The TPR profiles generated through this method are vital for determining a metal oxide's potential as a commercial or industrial catalytic material.

However, TPR methods alone cannot provide all the necessary physiochemical catalytic data. Therefore, these linear heating experiments are typically conducted alongside spectrometric equipment to obtain a comprehensive analysis. TPR-enabled mass spectrometers combine a microreactor chamber with a mass spectrometer system, allowing for various types of data acquisition from catalytic reaction experiments. A prime example of this technology is the modular CATLAB-PCS system, which offers a broad range of operating modes for various experimental methods in catalysis and reaction studies.

The CATLAB-PCS system is equipped with a sensitive thermocouple embedded in the reactor bed, allowing for direct measurement of the catalyst's temperature. This is crucial for capturing

precise linear heating and reduction values, which are recorded by the system's intuitive software. The software also facilitates data acquisition from the mass spectrometer, providing comprehensive insights into the catalytic reactions.

One of the standouts features of the CATLAB-PCS system is its template-driven software, which allows for precise and automated control over gas composition and flow rates. Users can manually operate the system or program it to follow established templates, accommodating heating rates of up to 1000°C in increments ranging from 1 to 20°C per minute. This level of control ensures that experiments can be tailored to specific requirements, enhancing the accuracy and reliability of the results.

With the ability to finely tune both mass spectrometer parameters and heating rates, the CATLAB-PCS system is indispensable for modern catalysis studies. It enables researchers to conduct detailed and varied experiments, leading to a better understanding of catalytic processes and the development of more efficient catalysts.

The TPO process involves a furnace or microreactor that can gradually increase the temperature of a catalyst in precise increments, ranging from 1-20°C per minute, up to extreme temperatures of 1000°C. During this process, an integrated mass spectrometer continuously monitors and analyses the catalytic activity in real-time as a gas mixture flows over the catalyst, which is being heated incrementally.

As the temperature ramps up during the experiment, various reactions occur between the gas and the catalyst within the microreactor. For instance, one application of TPO is to study coke build-up on catalysts during pyrolysis reactions. Coke build-up can block reaction sites and reduce the efficiency of the catalyst. By using an oxygen flow in TPO experiments, the presence of coke can be detected and characterized by measuring the carbon monoxide, carbon dioxide, and hydrocarbon species at the reactor's outlet.

TPO provides valuable insights into various catalytic reactions and has a wide range of applications. A notable application is in the research and development of alternative energy fuels and the improvement of energy efficiency in chemical manufacturing.

For example, hydrogen-based fuel cells are emerging as a highly efficient, low-pollutant energy source, increasingly being implemented in fuel cell electric vehicles (FCEVs). Although these vehicles have the potential to positively impact greenhouse gas emissions, the primary method of hydrogen production—natural gas reformation—poses challenges. This method, known as steam-hydro carbon reforming, involves reacting a natural hydrocarbon like methane (CH_4) with high-pressure steam at temperatures up to 1000°C in the presence of a catalyst. While this process produces hydrogen for various industries, including greener energy sources, it also demands significant energy, which can reduce the overall environmental benefits.

During the steam-hydro carbon reforming process, coke formation can occur, which can negatively impact the efficiency and longevity of the catalyst. TPO is used to characterize this coke formation, helping researchers to better understand and mitigate this issue.

Although TPO is a powerful tool for characterizing catalysts, it is often used in conjunction with other analytical techniques to obtain comprehensive physiochemical data. For instance, combining TPO with infrared spectroscopy or X-ray diffraction can provide deeper insights into the structural and chemical changes occurring within the catalyst. This integrated approach ensures a more thorough understanding of the catalytic processes, aiding in the development and optimization of more efficient and effective catalysts for various industrial applications.

Overall, TPO is an indispensable technique for advancing the field of catalysis, offering critical insights that drive innovation and improve the sustainability and efficiency of industrial processes.

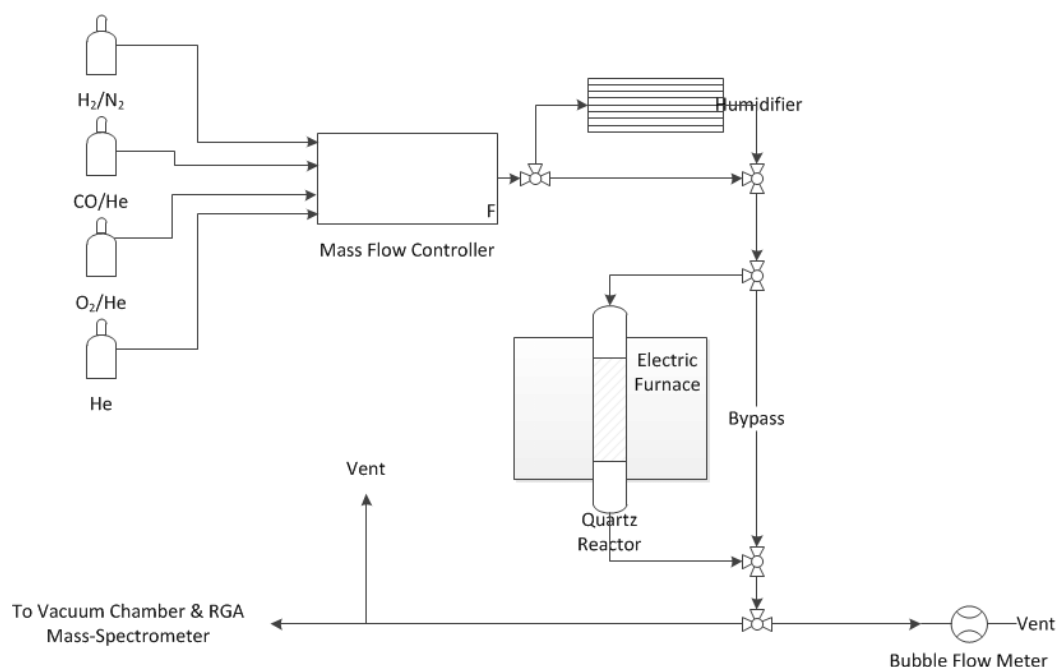


Figure 3.5: Schematic diagram of the custom made TPR-TPD-TPO Instrument.

3.5 X-ray Photoelectron Spectroscopy XPS

X-ray Photoelectron Spectroscopy (XPS), also called Electron Spectroscopy for Chemical Analysis (ESCA) is a powerful technique which analyses the composition, the element constituting the surface and the chemical bonding state by irradiating x-rays on the sample surface. Everything is done measuring the kinetic energy of the photoelectrons emitted. The fundamental principle behind XPS lies in the photoelectric effect, a phenomenon where electrons are ejected from a material upon exposure to X-ray. When X-rays with a specific energy interact with the atoms on the material's surface, they transfer their energy to the core-level electrons, causing these electrons overcome the binding energy that holds within the atom. The kinetic energy of the emitted photoelectrons is then measured, and this energy is directly related to the

binding energy of the electrons in their original atomic orbitals. The binding energy of the photoelectrons is characteristic of the element and their chemical states, allowing researchers to identify and quantify the elements present on the surface of the material. Moreover, the chemical shift in the binding energies provide valuable information about the oxidation states and chemical environments of the elements ^[92,93].

An advantage of the usage of XPS is that the change in bond energy, also known as chemical shift, caused by the electron state surrounding the atoms to be analysed, tend to be greater than the chemical shift observed in other technique, like AES (Atomic Emission Spectroscopy). Traditional XPS is sensitive to detect the elements on the surface with 2-10 nm depth ^[94].

3.5.1 Instrumentation for the analysis

The instrumentation for X-ray Photoelectron Spectroscopy is designed to precisely generate, detect and analyse photoelectron emitted from the material's surface. A typical XPS system consist of several key components, including X-ray source, the electron energy analyser, the vacuum system, and the detection system.

1. **X-ray Source:** The X-ray source is critical for generating the primary X-rays used to excite the core-level electrons in the sample. Two common types of X-ray sources are Al K α (1486.6 eV) and Mg K α (1253.6 eV) anodes. The sources typically consist of an X-ray where high-energy electrons strike the anode, producing X-rays that are collimated and directed onto the sample surface. These monochromatic X-rays ensure high spectral resolution and minimize background noise.
2. **Sample preparation and Stage:** The sample is typically mounted on a stage within the ultra-high vacuum (UHV) chamber. The stage can be adjusted in multiple axes (X, Y, Z and rotational) to precisely position the sample in the X-ray beam. Sample preparation is crucial to ensure a clean, contaminant-free surface, and it often involves methods like sputter cleaning, solvent washing and drying.
3. **Electron Energy Analyzer:** The electron energy analyser is a sophisticated device that measures the kinetic energy distribution of the emitted photoelectrons. The most common type of energy analyser is the hemispherical analyser, which consists of two hemispherical electrodes that create an electric field. Photoelectrons pass through a small entrance slit and travel along a curved path between the electrodes. Only electrons with specific kinetic energies reach the detector, while others are deflected away. This mechanism enables the precise determination of electron binding energies.
4. **Detection System:** The detection system in XPS includes an array of detectors such as channeltrons, microchannel plates or multichannel plate detectors. These detectors are highly sensitive and capable of detecting low-intensity electron signals. When photoelectrons reach the detector, they generate a cascade of secondary electrons,

resulting in a measurable electric signal. The signal intensity is then recorded as a function of electron binding energy, creating the XPS spectrum.

5. **Vacuum System:** The entire XPS analysis is conducted in an ultra-high vacuum (UHV) environment, typically maintained at pressure around 10^{-9} to 10^{-10} torr. The UHV condition is essential to prevent photoelectron scattering by air molecules, ensuring accurate and high-resolution measurements. The vacuum system consists of various pumps, such as turbomolecular pumps, ion pumps and cryopumps, which work together to achieve and maintain the required vacuum levels.
6. **Data Acquisition and Processing:** Modern XPS system are equipped with advanced data acquisition and processing software that controls the instrumentation, collects data, and analyses the XPS spectra. The software allows for the identification of peaks corresponding to different elements and chemical states, as well as quantification of the elemental composition on the sample surface. It also facilitates background subtraction, peak fitting, and data interpretation.

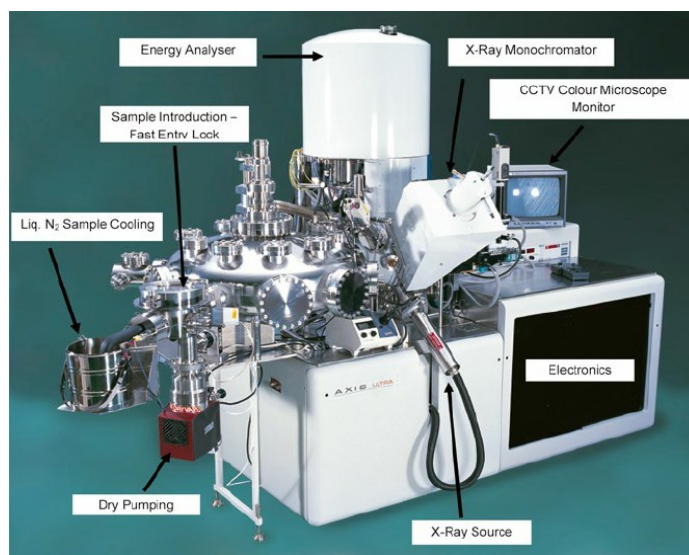


Figure 3.6: An example of a commercial XPS instrument—the

Through the combination of these components, XPS instrumentation enables detailed and accurate analysis of surface chemistry, aiding the understanding and development of new materials and technologies [94, 95].

3.6 BET analysis

Brunauer-Emmett-Teller (BET) analysis are used to determine the specific surface area of solid materials based on gas adsorption measurements. This method is suitable for analysing a wide range of solid matrices from catalyst powders to monolithic materials.

Gas adsorption is a powerful technique for determining critical information about the structure of solid materials.

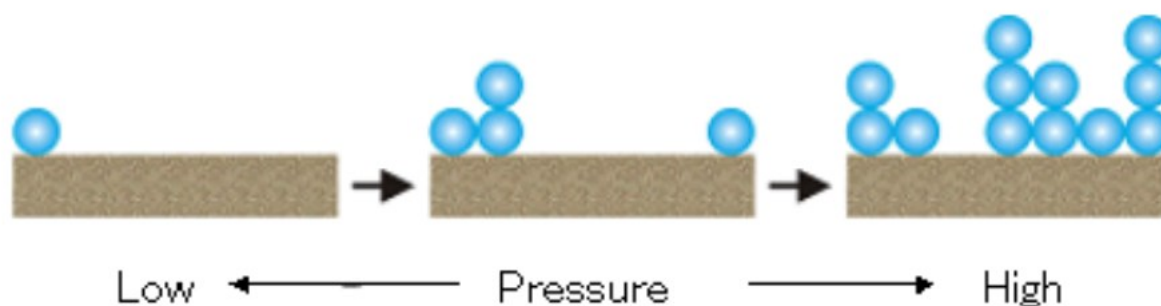


Figure 3.7: Compact scheme of the BET principle with respect of pressure.

The BET theory states that the adsorbent first begins to adsorb on the strongest energy points on the surface, and later, with increasing pressure, adsorption can also be observed on the points with the next lower energy levels. The model also considers the adsorption of the 2nd, 3rd and upper layers and the application of BET include the design catalysts for chemical reactions, developing adsorbent for gas storage and separation technologies.

The specific surface area of a material influences its catalytic activity, adsorption capacity, chemical reactivity, among other properties.

3.6.1 Instrumentation for the analysis

Instruments designed for BET (Brunauer-Emmet-Teller), as previously said, analysis play a pivotal role in characterizing the specific surface area and porosity of materials through gas adsorption techniques. These instruments are indispensable in fields such as material science and catalysis where surface properties significantly influence functionality.

A typical BET system works as follows:

- 1- **Degassing System:** Eliminates contaminants like water vapor and organic residues that may interfere with accurate measurement. Degassing is typically conducted under vacuum conditions or by flowing inert gas while applying controlled heat to desorb unwanted molecules adhered to the sample's surface.
- 2- **Gas Flow and Adsorption Chamber:** It is thermally controlled environment where the sample is exposed to an inert gas, often nitrogen or krypton. The instrument uses precision gas flow controllers to ensure consistent gas delivery to the sample, providing data critical for constructing isotherms and subsequent analysis.
- 3- **Pressure and Temperature Measurements Units:** High-precision pressure transducer and thermocouples monitor key parameters of pressure and temperature during the analysis. Accurate monitoring is essential, as these data determine the shape and reliability of the adsorption isotherm, the foundation of surface area calculation.

- 4- **Gas Dosing and Quantification System:** Advanced gas dosing system, using volumetric or gravimetric approaches, are integral to determining the amount of gas adsorbent by the sample. Volumetric methods rely on precise pressure changes, while gravimetric methods monitor mass changes resulting from gas adsorption. Both techniques are compatible with the BET theory for multilayer adsorption.
- 5- **Data Processing and Analysis Software:** Modern BET instruments integrate sophisticated software for processing experimental data. The software applies the BET equation to adsorption isotherms to calculate parameters such as specific surface area, monolayer gas volume, and pore size distribution. Additionally, the software outputs comprehensive graphical reports, including adsorption-desorption isotherms.
- 6- **Automatic and Safety Features:** Automated features such as programmable degassing sequences, gas flow adjustments, and safety interlocks reduce human error and enhance repeatability. These features streamline the workflow, ensuring both the accuracy and reliability of the analysis.

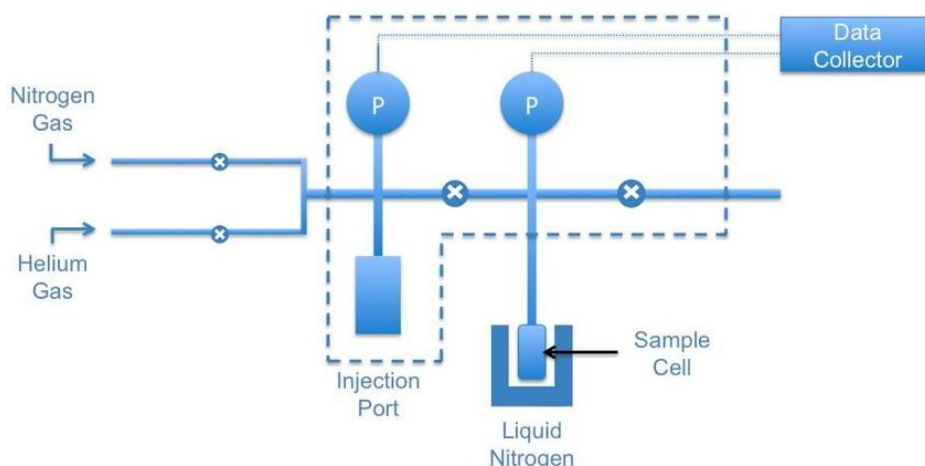


Figure 3.8: Schematic of BET surface analyser.

BET analysers continue to evolve, incorporating advancements in automation, precision, and analytical capabilities, thus expanding their applicability across diverse scientific domain [96, 97].

Chapter 4

Experimental results of structural analysis

The results presented in this chapter are expected to provide significant insights into the molecular structure and composition of powder samples.

As specified in previous bibliographical chapters, these tests help to identify the structure of the catalyst, which will be very useful in identifying its catalytic properties and activity in more complex reaction.

4.1 Raman spectroscopy

The Raman spectra were developed using the Raman Imaging Microscope in the laboratory of the UCCS (Lille).

The primary objective of these analyses was to gain a comprehensive understanding of the structural and compositional characteristics of the powder samples. To achieve this, each sample underwent a meticulous examination under a microscope prior to the Raman spectroscopy analysis.

The microscopic examination was crucial in providing a preliminary visual assessment of the powder's morphology. This step involved capturing high-resolution images of the samples at various magnification, especially at 10x and 50x. These magnifications were chosen to offer a detailed view of the microstructural features and to identify any heterogeneities or anomalies present in the samples. The images obtained were then subjected to a thorough analysis to interpret the structural attributes and to correlate these observations with the subsequent Raman spectra results.

Following the microscopic examination, the Raman spectroscopy analyses were performed using a laser with a wavelength of 532 nm. This wavelength was selected due to its efficacy in exciting the vibrational modes of the molecule within the samples, thereby providing detailed spectral information. The Raman spectra were recorded at various laser intensities, ranging from 0.01% to 100% (in particular 0.01%, 0.1%, 1%, 10%, 25%, 50% and 100%). This range of intensities was employed to ensure that the spectral data captured was comprehensive and to observe the effects of varying laser power on the Raman signal.

4.1.1 La_xFeO_3 perovskite's structure

The detailed structural analysis of La_xFeO_3 will be presented in this section, where the stoichiometric coefficient x varies from 0,5 to 1. The primary objective of this analysis is to investigate the morphological and crystallographic characteristics of the synthesized perovskites and to understand the influence of varying lanthanum content on their structural properties. The analysis was conducted using images captured at 10x and 50x magnification as mentioned before, to provide detailed insights into the microstructural characteristics of the materials.

The most significant images captured at 10x magnification for the La_xFeO_3 are shown in Figures 4.1, 4.2, 4.3 and 4.4.

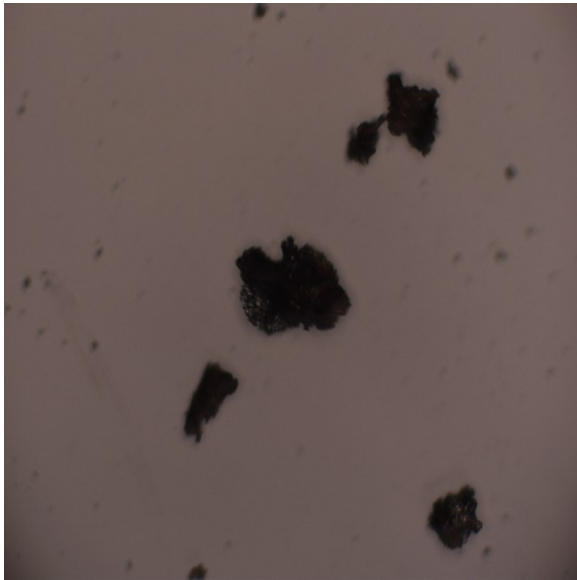


Figure 4.1: $\text{La}_{0.5}\text{FeO}_3$ structure at 10x.

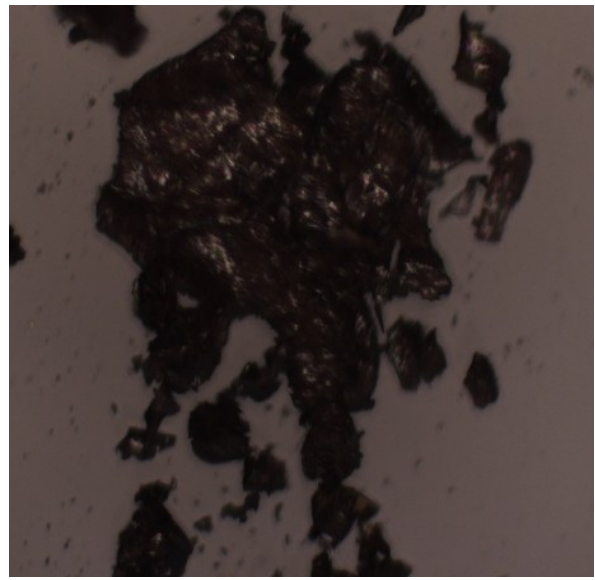


Figure 4.2: $\text{La}_{0.6}\text{FeO}_3$ structure at 10x.



Figure 4.3: $\text{La}_{0.8}\text{FeO}_3$ structure at 10x.

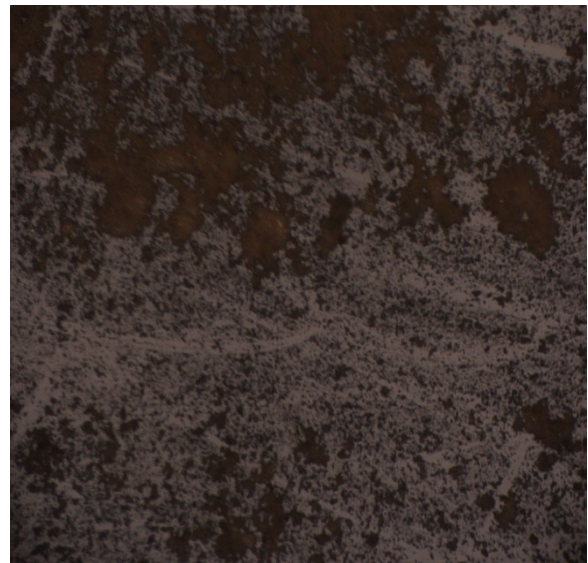


Figure 4.4: LaFeO_3 structure at 10x.

At this magnification, the overall morphology of the samples exhibits a relatively uniform distribution of particles, with no significant agglomeration or clustering. However, differences in the crystallinity of the samples are evident. For the sample with $x = 0,5$ the structure appears less crystalline, with a more amorphous and irregular morphology. As the lanthanum content increases to $x = 0,6$ and $0,7$ the crystallinity improves, and the particles appear more defined and structured. The samples with $x = 0,8$ and $0,9$ exhibit the highest degree of crystallinity, with more ordered structures. The sample with $x = 1$ exhibits the higher degree of crystallinity, with well-defined and uniformly distributed particles.

These observations suggest that higher lanthanum content leads to improved crystallinity and a more ordered structure.

The most significant images captured at 50x magnification for the La_xFeO_3 are shown in Figures 4.5, 4.6, 4.7 and 4.8.

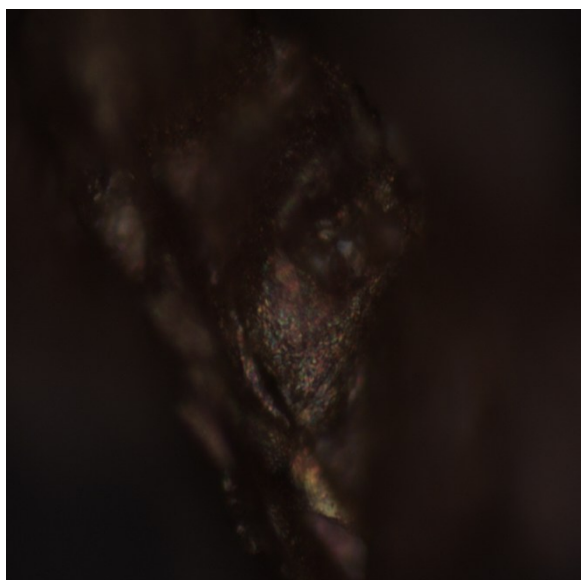


Figure 4.5: $\text{La}_{0.5}\text{FeO}_3$ structure at 50x.

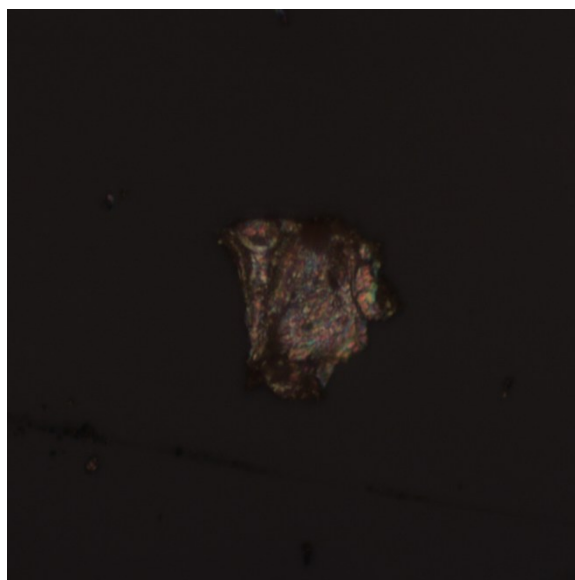


Figure 4.6: $\text{La}_{0.7}\text{FeO}_3$ structure at 50x.

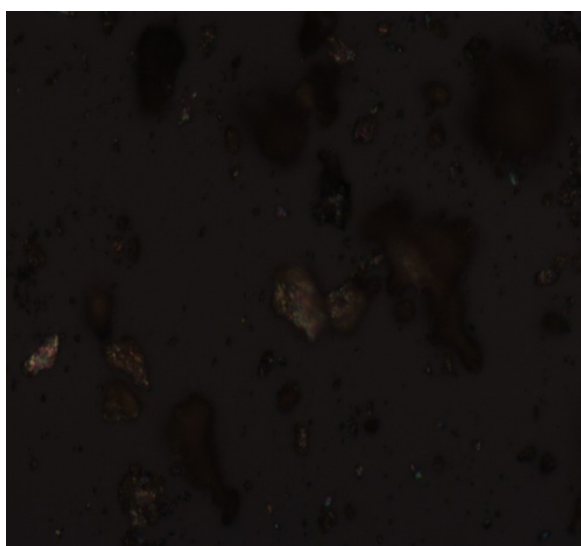


Figure 4.7: $\text{La}_{0.9}\text{FeO}_3$ structure at 50x.

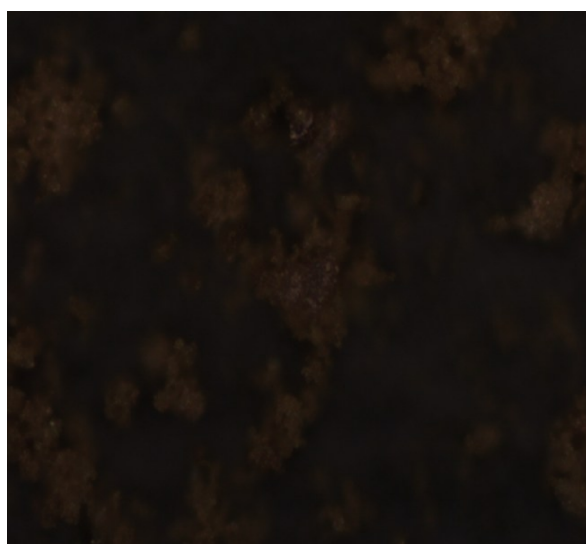


Figure 4.8: LaFeO_3 structure at 50x.

At this higher magnification, the finer details of the microstructure can be observed. The images reveal significant differences in the surface in the surface morphology and in the particle size distribution among samples.

For the sample with $x = 0,5$ the particles appear irregular and poorly defined, indicating a lower degree of crystallinity. The surface morphology is rough, and the particle size distribution is broad, with a mixture of small and large particles. As the lanthanum content increases to $x = 0,6$ and $0,7$ the particles become more uniform in size and shape, and the surface morphology becomes smoother. The samples with $x = 0,8$ and $0,9$ exhibit further improvements in particle uniformity and surface smoothness as mentioned above.

The sample with $x = 1$ exhibits the most uniform and well-defined particles, with a narrow particle size distribution and a smooth surface morphology.

These observations suggest further confirm that higher lanthanum content leads to improved crystallinity and a more ordered structure.

The comparison of the images captured at 10x and 50x magnification provides valuable insights into the structural characteristics of La_xFeO_3 samples. The images at 10x magnification offer a broad overview of the overall morphology, while the images at 50x magnification reveal the finer details of the microstructure. The differences in crystallinity and particle size distribution observed at both magnifications highlight the impact of lanthanum content on the structural properties of the samples.

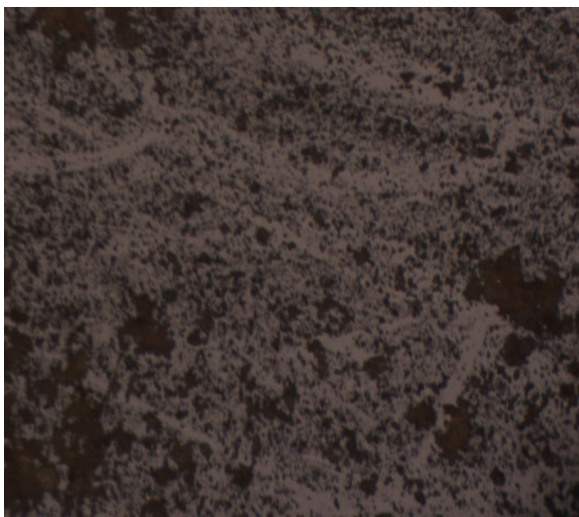


Figure 4.10: LaFeO_3 structure at 10x.

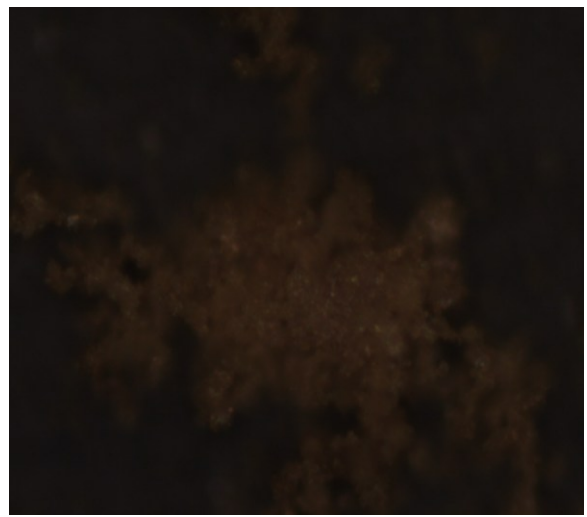


Figure 4.11: LaFeO_3 structure at 50x.

For all values of x , the images at 50x magnification provide a clearer and more detailed view of the microstructure, allowing for a more accurate assessment of the crystallinity and particle size distribution. The improvement in crystallinity and more ordered structure observed in the samples with higher lanthanum content are consistent across both magnifications, reinforcing the conclusion that in this case the perovskite's structure leads to better structural properties.

4.1.2 La_xMnO_3 perovskite's structure

This section presents an in-depth structural analysis of La_xMnO_3 perovskites, specifically focusing on the sample's stoichiometric coefficients $x = 0,5$ and $x = 1$. The primary objective of this analysis is to investigate the morphological and crystallographic characteristics of these synthesized perovskites and to understand the influence of varying lanthanum content on their structural properties. The analysis was conducted using images captured at 10x and 50x magnification prior to performing Raman spectroscopy using high-resolution optical microscope.

The images captured at 10x magnification for the $\text{La}_{0,5}\text{MnO}_3$ and LaMnO_3 samples are shown in Figures 4.12 and 4.13, respectively.

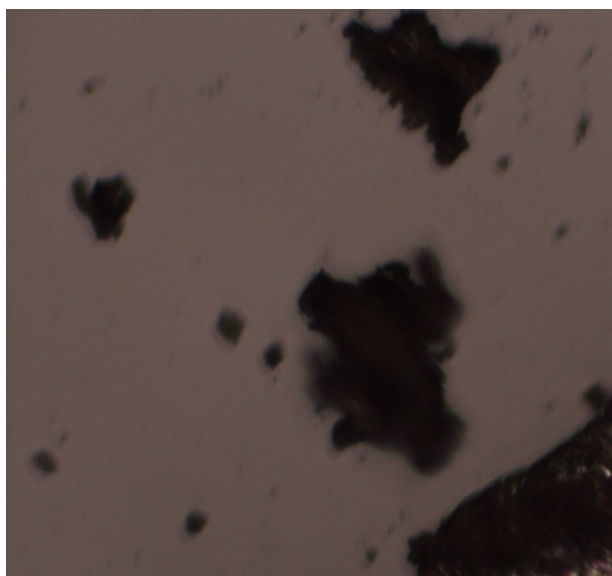


Figure 4.12: $\text{La}_{0,5}\text{MnO}_3$ structure at 10x.

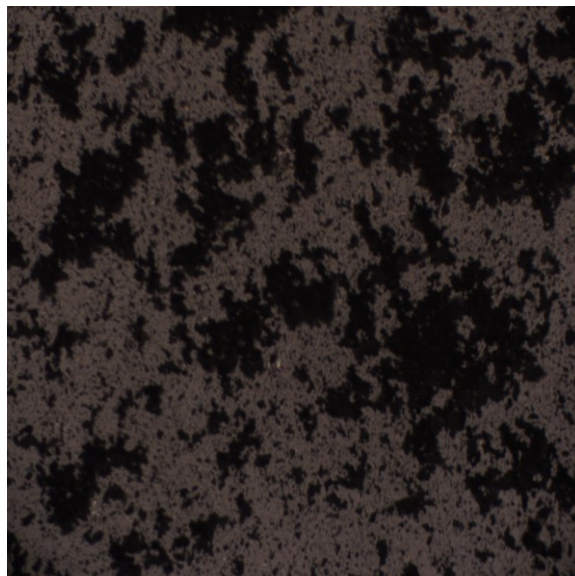


Figure 4.13: LaMnO_3 structure at 10x.

At this magnification, the overall morphology of the samples can be observed. The images reveal that both samples exhibit a relatively uniform distribution of particles, with no significant agglomeration or clustering. However, differences in the crystallinity of the samples are evident.

For the $\text{La}_{0,5}\text{MnO}_3$, the structure appears less crystalline, with a more amorphous and irregular morphology. The particles are loosely packed and exhibit a rough surface texture. In contrast, the LaMnO_3 sample shows improved crystallinity, with more defined and structured particles. The surface morphology is smoother, and the particles are more uniformly distributed.

These observations suggest that higher lanthanum content leads to improved crystallinity and a more ordered structure.

The images captured at 50x magnification for the $\text{La}_{0.5}\text{MnO}_3$ and LaMnO_3 samples are shown in Figures 4.14 and 4.15, respectively.



Figure 4.14: $\text{La}_{0.5}\text{MnO}_3$ structure at 50x.



Figure 4.15: LaMnO_3 structure at 50x.

At this higher magnification, the finer details of the microstructure can be observed. The images reveal significant differences in the surface morphology and particle size distribution between the two samples.

For the $\text{La}_{0.5}\text{MnO}_3$ sample, the particles appear irregular and poorly defined, indicating a lower degree of crystallinity. The surface morphology is uneven, and the particle size distribution is broad, with a mixture of small and large particles. As the magnification increases, the irregularities in the particle shapes become more apparent. In contrast, the LaMnO_3 sample exhibits more uniform and well-defined particles, with narrow particle size distribution and a smooth surface morphology. The particles are more compact and with a higher degree of crystallinity. These observations further confirm that higher lanthanum content leads to improved crystallinity and a more ordered microstructure.

The structural analysis of La_xMnO_3 perovskites using images captured at 10x and 50x magnification has provided valuable insight into the influence of lanthanum content on their crystallographic and morphological properties. The results have demonstrated that higher lanthanum content leads to improved crystallinity and a more ordered microstructure. These findings are significant for several reasons.

Firstly, the enhanced crystallinity observed in the LaMnO_3 sample suggests that the material's structural integrity is more robust when the lanthanum content is maximized. This improved crystallinity is likely to contribute to better performance in applications where structural stability is crucial. The uniform particle size distribution and smooth surface morphology in the LaMnO_3 perovskites further support its potential for high-performance applications. Secondly,

the comparison between the $\text{La}_{0,5}\text{MnO}_3$ and LaMnO_3 perovskites highlights the impact of lanthanum content on the microstructural characteristics of the perovskites. As mentioned above, the $\text{La}_{0,5}\text{MnO}_3$ sample with its irregular and poorly defined particles, this suggest that reducing the lanthanum content may compromise the material's structural properties, potentially limiting its effectiveness in certain applications.

Moreover, the detailed microscopic examination at both 10x and 50x magnifications has provided a comprehensive understanding of the surface and particle size distribution of the samples.

4.1.3 Raman spectra

This section presents the detailed analysis of Raman spectra obtained from Lanthanum based perovskites. The primary objective of this analysis is to investigate the vibrational modes and structural characteristics of these synthesized perovskites. It is important to note that Raman spectroscopy was not completely performed on the La_xMnO_3 samples due to their dark coloration, which hindered the detection of the Raman signals. This limitation will be discussed in detail in subsequent section.

The samples were synthesized using the auto-combustion method, as described in previous chapter. The Raman spectra were recorded using a high-resolution spectrometer with a laser excitation wavelength of 532nm. The measurements were performed at room temperature.

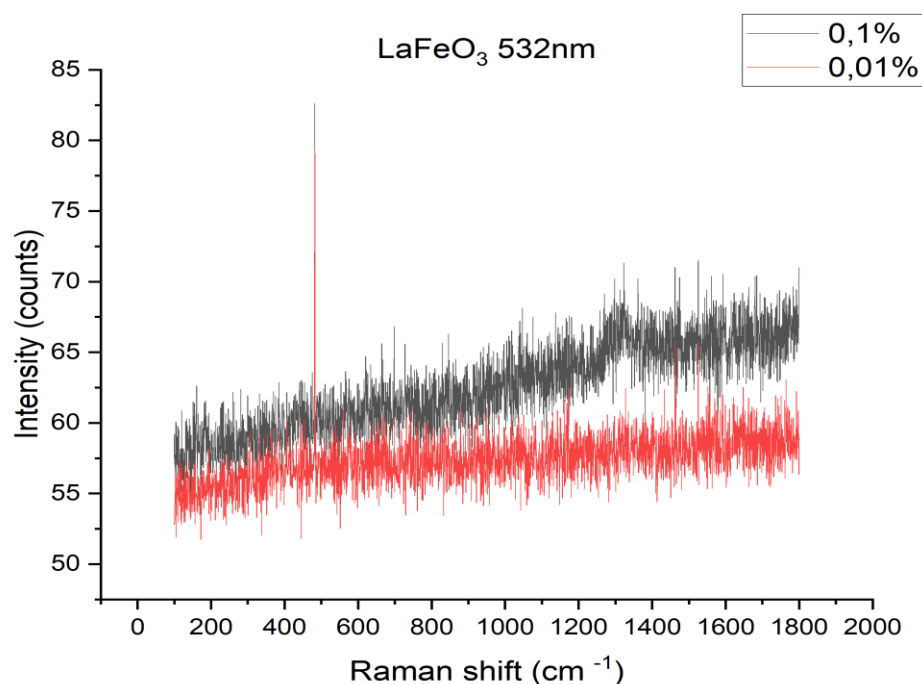


Figure 4.16: LaFeO_3 spectra, 532nm with a laser intensity of 0.01% and 0,1%.

The spectra for LaFeO_3 at 532nm comparing intensity of 0,01% and 0,1% are shown in Figure 4.16 and provides further insights into the material properties. The x-axis represents the Raman shift in cm^{-1} , ranging from 0 to 2000 cm^{-1} , while the y-axis indicates the intensity in counts, ranging from 20 to 85 counts. The data set with a 0,1% laser intensity, represented by the black line, shows higher intensity peaks compared to the red line, which corresponds to a 0,01% laser intensity. The black line exhibits distinct peaks at various Raman shift, indicating stronger Raman scattering at these points, in particular it is possible to observe a modest peak around 300 cm^{-1} and 500 cm^{-1} ; although the peaks are not as pronounced as those seen at higher intensities and the presence of these peaks suggest that even at low laser power, certain vibration modes of LaFeO_3 can be excited, albeit with lower efficiency. In contrast, the red line remains relatively flat, suggesting weaker Raman activity at the lower laser intensity. These results reinforce the observation that higher intensity leads to more produce Raman scattering. The increased intensity at higher laser intensities can be attributed to greater interaction between the laser and the sample.

The spectra for LaFeO_3 at 532nm comparing intensity of 1% and 10% are shown in Figure 4.17.

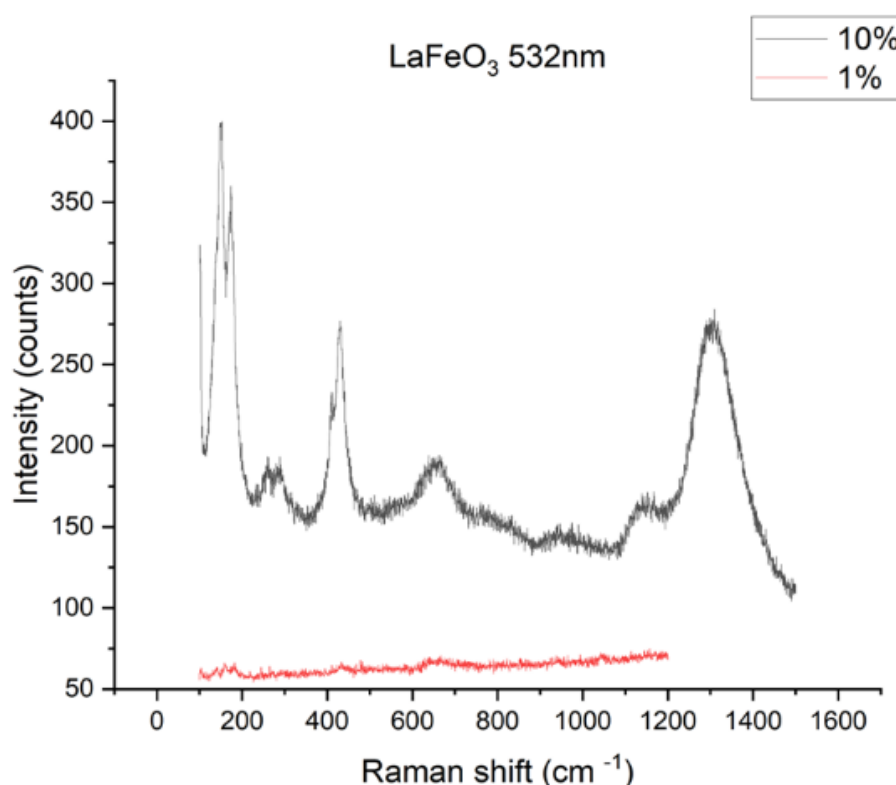


Figure 4.17: *LaFeO₃ spectra, 532nm with a laser intensity of 1% and 10%.*

In this case, the x-axis represents the Raman shift in cm^{-1} , ranging from 0 to 1600 cm^{-1} , while the y-axis indicates the intensity in counts, ranging from 50 to 400 counts. The 1% laser

intensity, represented by the red line, shows a much flatter profile with significantly lower intensity peaks. This indicates again that the lower laser power is insufficient to induce strong Raman scattering, resulting in weaker signals. The reduced intensity suggests that fewer phonons are being excited, leading to less produced Raman activity. At 10% laser intensity, represented by the black line, several prominent peaks are observed, particularly around 200 cm^{-1} , 400 cm^{-1} and 600 cm^{-1} . These peaks indicate strong Raman scattering, suggesting that the laser energy is sufficient to effectively excite the vibrational modes of the perovskite lattice. The higher intensity peaks at these specific Raman shift can be attributed to the resonance enhancement effect, where the laser frequency is close to the electronic transition of the material.

The spectra for LaFeO_3 at 532nm comparing intensity of 25% and 50% are shown in Figure 4.18.

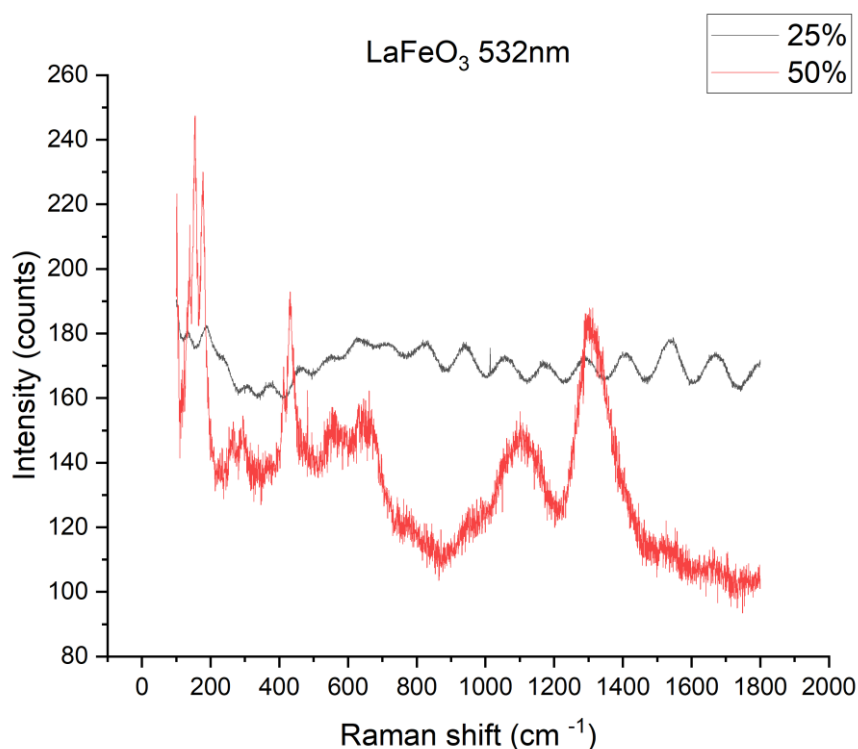


Figure 4.18: *LaFeO₃ spectra, 532nm with a laser intensity of 25% and 50%.*

The Raman spectroscopy plot for LaFeO_3 at 532 nm, comparing laser intensities of 25% and 50%, highlights the impact of moderate to high laser powers on Raman scattering. The x-axis ranges from 0 to 2000 cm^{-1} , and the y-axis ranges from 0 to 260 counts.

At 25% laser intensity, represented by the black line, several distinct peaks are observed, particularly around 200 cm^{-1} , 400 cm^{-1} and 600 cm^{-1} . These peaks are indicative of strong Raman scattering, suggesting that the laser power is sufficient to excite multiple vibrational

modes of the LaFeO_3 lattice. The intensity of these peaks reflects the efficiency of the Raman process at this laser power. At 50% laser intensity, represented by the red line, the peaks are even more pronounced, with higher intensity values. This indicates that the increased laser power enhances the Raman scattering process, resulting in stronger signals. The higher intensity peaks suggest that more phonons are being excited, leading to more pronounced Raman activity. This demonstrates the direct correlation between laser power and Raman signal strength.

The spectra for LaFeO_3 at 532nm with an intensity of 100% is shown in Figure 4.19.

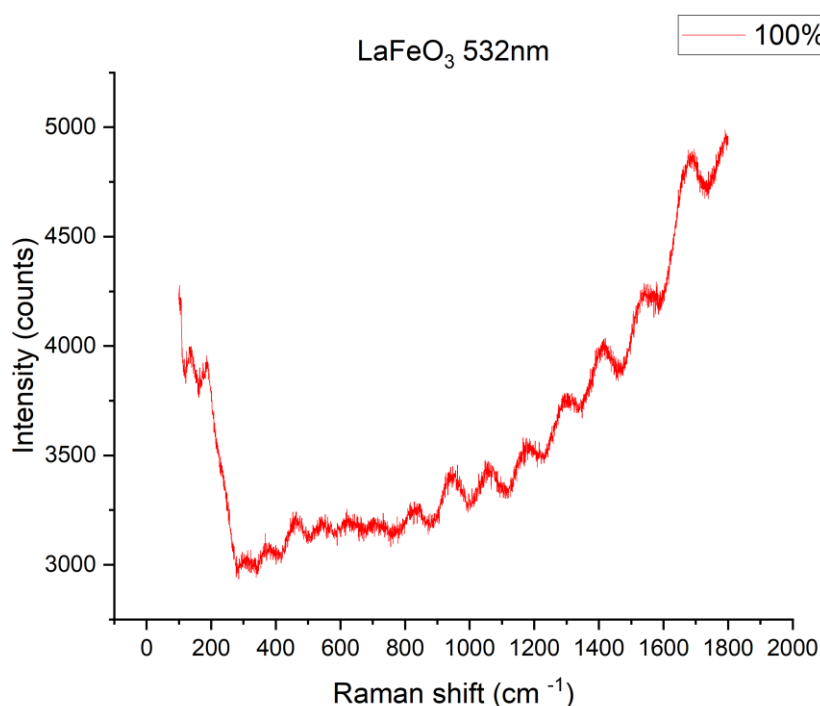


Figure 4.19: *LaFeO₃ spectra, 532nm with a laser intensity of 100%.*

The Raman spectroscopy plot for LaFeO_3 at 532 nm, representing a laser intensity of 100%, provides insights into the effects of maximum laser power on Raman scattering. The x-axis ranges from 0 to 2000 cm^{-1} , and the y-axis ranges from 0 to 5000 counts. At 100% laser intensity, represented by the red line, very high intensity peaks are observed at various Raman shift values, particularly around 200 cm^{-1} , 400 cm^{-1} , and 600 cm^{-1} . These peaks indicate extremely strong Raman scattering, suggesting that the laser power is maximized to effectively excite the vibrational modes of the LaFeO_3 lattice. The significant increase in intensity compared to lower laser powers suggests that the interaction between the laser and the sample is at its peak, resulting in pronounced Raman activity.

The high intensity peaks at 100% laser power demonstrate the efficiency of Raman spectroscopy in studying the material properties of LaFeO_3 .

The spectra for LaMnO_3 at 532nm comparing intensity of 0,001% and 0,01% are shown in Figure 4.20.

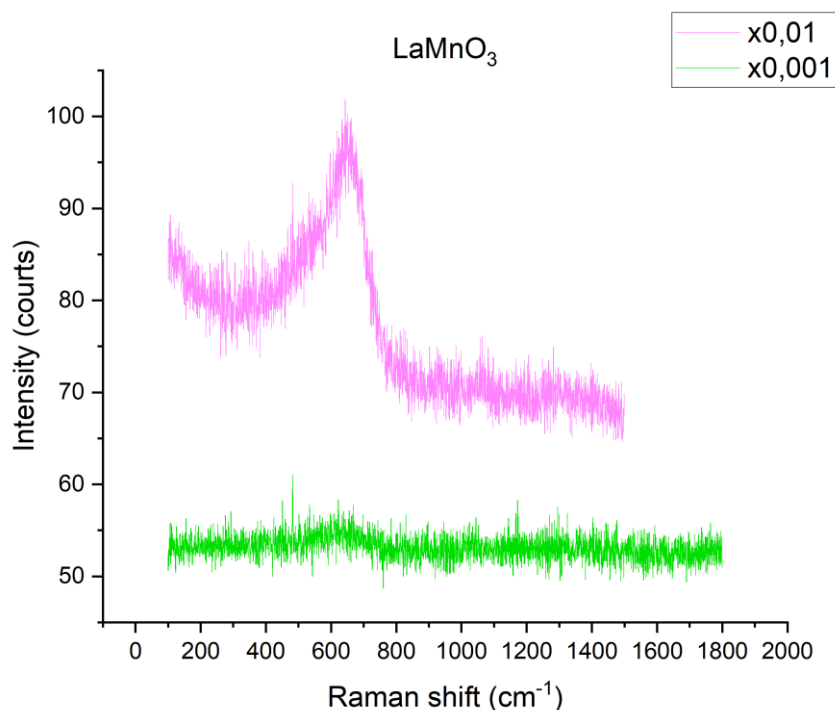


Figure 4.20: LaMnO_3 spectra, 532nm with a laser intensity of 0,001% and 0,01%.

The Raman spectroscopy plot for LaMnO_3 reveals significant insights into the material's properties and behavior under varying laser intensities. The x-axis represents the Raman shift in cm^{-1} , ranging from 0 to 2000 cm^{-1} , while the y-axis indicates the intensity in counts, ranging from 50 to 100 counts.

The pink data set, representing a higher laser intensity (0,01%), shows a distinct peak around 600 cm^{-1} . This peak indicates higher Raman scattering intensity at this specific Raman shift, suggesting that the laser energy is sufficient to excite the vibrational modes of the LaMnO_3 lattice effectively. The presence of this peak can be attributed to the resonance enhancement effect, where the laser frequency is close to the electronic transition of the material.

In contrast, the green data set, representing a lower laser intensity (0,001%), remains relatively flat across the range. This indicates that the lower laser power is insufficient to induce strong Raman scattering, resulting in weaker signals. The reduced intensity suggests that fewer phonons are being excited, leading to less pronounced Raman activity.

As mentioned at the beginning, LaMnO_3 samples are known to exhibit instability, particularly due to their dark coloration. This instability can be attributed to several factors:

1. **Jahn-Teller Distortion:** LaMnO_3 is subject to Jahn-Teller distortion, which involves geometric deformation of the local ionic lattice to lower the overall energy of the system

by removing electron degeneracy from partially occupied orbitals. This distortion can lead to structural instability, affecting the Raman spectra and resulting in broader linewidths and variations in intensity.

2. **Oxygen Stoichiometry:** The oxygen content in LaMnO_3 plays a crucial role in its structural and electronic properties. Variations in oxygen stoichiometry can lead to changes in unit cell volume and reduction in Jahn-Teller distortion. These changes can affect the stability of the material and its Raman scattering behavior.
3. **Phase Transition:** Under certain conditions, such as increased laser power, LaMnO_3 can undergo phase transitions. These transitions can result in significant changes in the Raman spectra, indicating instability in the material's structure.
4. **Photocatalytic Activity:** LaMnO_3 is known for its photocatalytic properties, particularly in the degradation of organic pollutants. The dark coloration of the material can enhance its absorption of visible light, leading to increased photocatalytic activity. However, this can also contribute to instability, as the material undergoes various chemical reactions under light exposure.

These factors collectively contribute to the instability observed in LaMnO_3 samples, particularly those with dark coloration. ^[98]

The spectra for LaMnO_3 at 532nm with an intensity of 100% is shown in Figure 4.21.

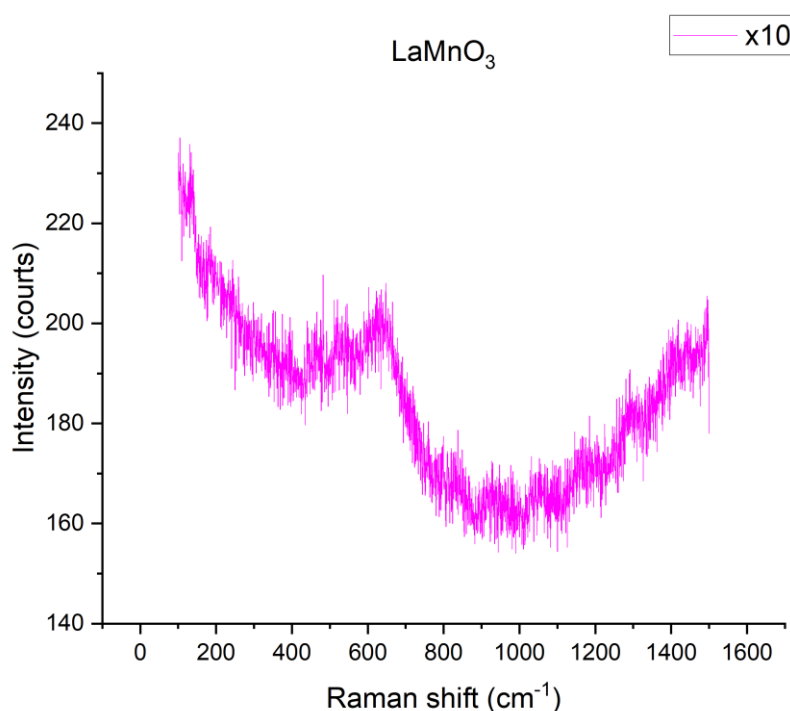


Figure 4.21: LaMnO_3 spectra, 532nm with a laser intensity of 10%.

The Raman spectroscopy data for LaMnO_3 provides significant insights into the material's properties under specific conditions. The x-axis represents the Raman shift in cm^{-1} , ranging from 0 to 1600 cm^{-1} , while the y-axis indicates the intensity in counts, ranging from 140 to 240 counts. The data is represented by a magenta line, indicating the laser intensity used was 10%.

The magenta line exhibits several peaks at specific Raman shift values, with notable peaks around 200 cm^{-1} , 400 cm^{-1} , and 600 cm^{-1} . These peaks correspond to the vibrational modes of the LaMnO_3 lattice, indicating strong Raman scattering at these points. The peak around 600 cm^{-1} is particularly prominent, suggesting a significant interaction between the laser and the material. As mentioned above, the instability of LaMnO_3 particularly due to its dark coloration, is evident in the Raman spectra. The dark coloration enhances the absorption of laser light, leading to increased local heating and potential structural changes in the material. This can result in variations in peak intensity and position, as observed in the plot.

The laser intensity plays a crucial role in the Raman scattering process. Higher laser intensities can lead to more pronounced peaks, as seen in previous analyses. However, excessive laser power can also cause local heating and potential damage to the sample, affecting the stability and Raman spectra. The Jahn-Teller distortion and variations in oxygen stoichiometry continue to influence the Raman spectra of LaMnO_3 . These structural factors can lead to broadening of peaks and variations in intensity, reflecting the material's instability.

LaMnO_3 is known for its phase transitions and photocatalytic properties. These factors can contribute to the observed instability in the Raman spectra. The dark coloration enhances the material's photocatalytic activity, leading to various chemical reactions under light exposure. These reactions can affect the Raman scattering behavior, resulting in changes in peak intensity and position.

4.2 Thermogravimetric analysis (TGA)

In the present chapter, the results of the thermogravimetric analysis (TGA) performed on those complex samples synthesized by Siavash Mohammadelizadeh, used for the article presented in Geneva in July 2024, are meticulously detailed. The primary aim was to explore the thermal stability and composition properties of synthesized materials under controlled conditions, and to rationally adjust the calcination temperature.

The samples were only dried. The TGA experiments were conducted up to a maximum temperature of 900°C , under air atmosphere conditions, with a heating ramp of 5°C per minute. This specific ramp was selected to ensure gradual and controlled increase in temperature, thereby allowing for precise monitoring of the weight changes in the samples as a function of temperature.

The samples synthesized by Siavash are characterized by their complexity and incorporation of various dopants and modifications on both A and B sites, were analysed to reveal critical information regarding their thermal stability, oxidation resistance, and the effects of different synthesis parameter on their behavior.

The data obtained from the TGA experiments were meticulously analysed to interpret the weight loss patterns and to correlate these findings with the structural and compositional characteristics of the samples.

4.2.1 Plot of the TGA

The samples analysed are shown in the following table:

SAMPLES FOR THE ANALYSIS
$\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$
$\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$
$\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$
$\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$
$\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$
$\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$

The perovskite oxide $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ is a complex material where the A site is occupied by lanthanum (La) and strontium (Sr), and the B site is occupied by iron (Fe) and nickel (Ni). This specific composition is designed to explore the effects of varying dopants and concentrations on the material's properties. The subsequent samples will differ in terms of dopants and their concentrations, allowing for a systematic investigation into how these variations influence the thermal and structural characteristics of the material.

The TGA plot $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (Figure 4.22) provides a comprehensive view of the thermal stability and decomposition behavior of the material. The analysis can be broken down into several key temperature regions:

1. Room Temperature to 200°C:
 - Weight Percentage (Black Curve): There is a slight decrease in weight, which can be attributed to the loss of adsorbed moisture and other volatile components.
 - Derivative Weight Percentage (Blue Curve): A small peak indicates the rate of weight loss due to the evaporation of surface-bound water.
 - Heat Flow (Red Curve): An endothermic peak corresponds to the energy absorbed during the evaporation process.
2. 200°C to 400°C:
 - Weight Percentage: A more pronounced weight loss occurs, likely due to the decomposition of organic residues or the release of lattice oxygen.

- Derivative Weight Percentage: A significant peak in this region indicates a rapid decomposition phase.
 - Heat Flow: An endothermic peak suggests energy absorption associated with the decomposition reactions.
3. 400°C to 600°C:
- Weight Percentage: The weight loss continues but at a slower rate, indicating the decomposition of more stable components.
 - Derivative Weight Percentage: Peaks in this region may correspond to the breakdown of intermediate compounds.
 - Heat Flow: Both endothermic and exothermic peaks may be observed, indicating complex reactions involving both energy absorption and release.
4. 600°C to 1000°C:
- Weight Percentage: The weight stabilizes, suggesting the completion of major decomposition processes.
 - Derivative Weight Percentage: Minimal activity in this region indicates that the material has reached a stable state.
 - Heat Flow: Exothermic peaks may indicate crystallization or phase transitions occurring within the material.

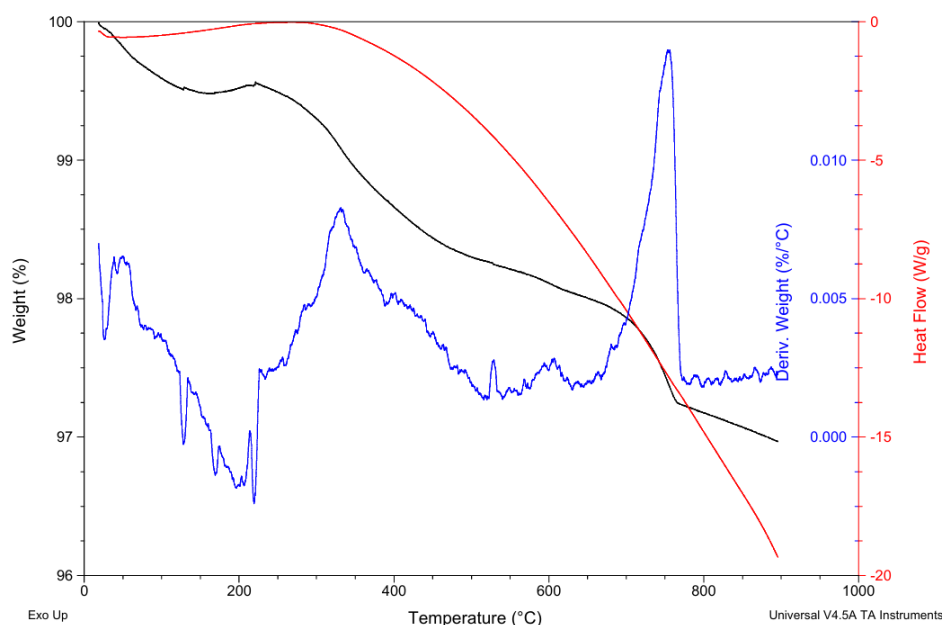


Figure 4.22: TGA plot of $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

Overall, the TGA plot demonstrates the thermal stability and decomposition behavior of $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, which is crucial for understanding its performance in various applications.

The TGA plot for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (Figure 4.23) provides insights into the thermal stability and decomposition behavior of the material. The analysis can be broken down into several key temperature regions:

1. 50°C to 200°C:

- Weight Percentage (Black Curve): There is a slight decrease in weight, which can be attributed to the loss of adsorbed moisture and other volatile components.
- Derivative Weight Percentage (Blue Curve): A small peak indicates the rate of weight loss due to the evaporation of surface-bound water.
- Heat Flow (Red Curve): An endothermic peak corresponds to the energy absorbed during the evaporation process.

2. 200°C to 400°C:

- Weight Percentage: A more pronounced weight loss occurs, likely due to the decomposition of organic residues or the release of lattice oxygen.
- Derivative Weight Percentage: A significant peak in this region indicates a rapid decomposition phase.
- Heat Flow: An endothermic peak suggests energy absorption associated with the decomposition reactions.

3. 400°C to 600°C:

- Weight Percentage: The weight loss continues but at a slower rate, indicating the decomposition of more stable components.
- Derivative Weight Percentage: Peaks in this region may correspond to the breakdown of intermediate compounds.
- Heat Flow: Both endothermic and exothermic peaks may be observed, indicating complex reactions involving both energy absorption and release.

4. 600°C to 1000°C:

- Weight Percentage: The weight stabilizes, suggesting the completion of major decomposition processes.
- Derivative Weight Percentage: Minimal activity in this region indicates that the material has reached a stable state.
- Heat Flow: Exothermic peaks may indicate crystallization or phase transitions occurring within the material.

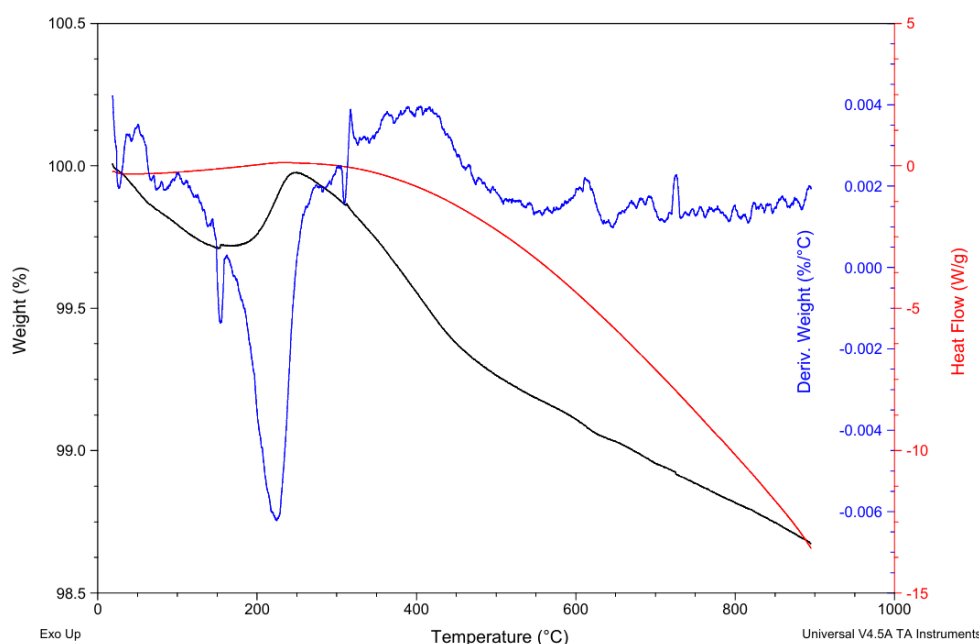


Figure 4.23: TGA plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TGA plot reveals that $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ undergoes several thermal events, including moisture loss, decomposition of organic and inorganic components, and potential phase transitions. The detailed analysis of the weight percentage, derivative weight percentage, and heat flow curves provides valuable insights into the thermal stability and decomposition mechanisms of the material.

The TGA plot for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (Figure 4.24) provides valuable insights into the thermal stability and decomposition behavior of the material. The analysis can be divided into several key temperature regions:

1. 0°C to 200°C:
 - Weight Percentage (Black Curve): A slight decrease in weight is observed, which can be attributed to the loss of adsorbed moisture and other volatile components.
 - Derivative Weight Percentage (Blue Curve): A small peak indicates the rate of weight loss due to the evaporation of surface-bound water.
 - Heat Flow (Red Curve): An endothermic peak corresponds to the energy absorbed during the evaporation process.
2. 200°C to 400°C:
 - Weight Percentage: A more pronounced weight loss occurs, likely due to the decomposition of organic residues or the release of lattice oxygen.

- Derivative Weight Percentage: A significant peak in this region indicates a rapid decomposition phase.
 - Heat Flow: An endothermic peak suggests energy absorption associated with the decomposition reactions.
3. 400°C to 600°C:
- Weight Percentage: The weight loss continues but at a slower rate, indicating the decomposition of more stable components.
 - Derivative Weight Percentage: Peaks in this region may correspond to the breakdown of intermediate compounds.
 - Heat Flow: Both endothermic and exothermic peaks may be observed, indicating complex reactions involving both energy absorption and release.
4. 600°C to 800°C:
- Weight Percentage: The weight stabilizes, suggesting the completion of major decomposition processes.
 - Derivative Weight Percentage: Minimal activity in this region indicates that the material has reached a stable state.
 - Heat Flow: Exothermic peaks may indicate crystallization or phase transitions occurring within the material.

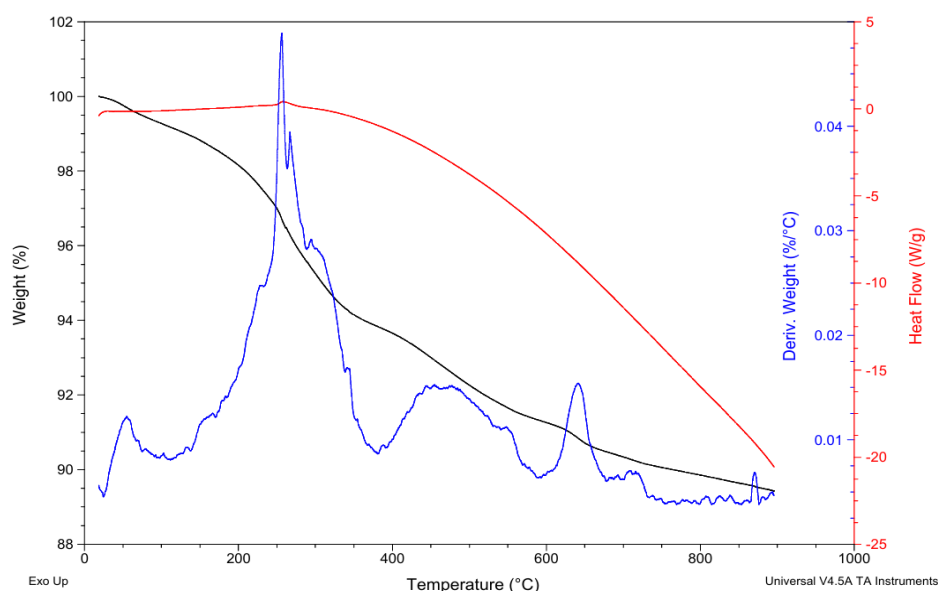


Figure 4.24: TGA plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TGA plot reveals that $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ undergoes several thermal events, including moisture loss, decomposition of organic and inorganic components, and potential phase transitions. The detailed analysis of the weight percentage, derivative weight percentage, and heat flow curves provides valuable insights into the thermal stability and decomposition mechanisms of the material.

The TGA plot for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$ (Figure 4.25) provides valuable insights into the thermal stability and decomposition behavior of the material. The analysis can be divided into several key temperature regions:

1. 0°C to 200°C:

- Weight Percentage (Black Curve): A slight decrease in weight is observed, which can be attributed to the loss of adsorbed moisture and other volatile components.
- Derivative Weight Percentage (Blue Curve): A small peak indicates the rate of weight loss due to the evaporation of surface-bound water.
- Heat Flow (Red Curve): An endothermic peak corresponds to the energy absorbed during the evaporation process.

2. 200°C to 400°C:

- Weight Percentage: A more pronounced weight loss occurs, likely due to the decomposition of organic residues or the release of lattice oxygen.
- Derivative Weight Percentage: A significant peak in this region indicates a rapid decomposition phase.
- Heat Flow: An endothermic peak suggests energy absorption associated with the decomposition reactions.

3. 400°C to 600°C:

- Weight Percentage: The weight loss continues but at a slower rate, indicating the decomposition of more stable components.
- Derivative Weight Percentage: Peaks in this region may correspond to the breakdown of intermediate compounds.
- Heat Flow: Both endothermic and exothermic peaks may be observed, indicating complex reactions involving both energy absorption and release.

4. 600°C to 800°C:

- Weight Percentage: The weight stabilizes, suggesting the completion of major decomposition processes.
- Derivative Weight Percentage: Minimal activity in this region indicates that the material has reached a stable state.
- Heat Flow: Exothermic peaks may indicate crystallization or phase transitions occurring within the material.

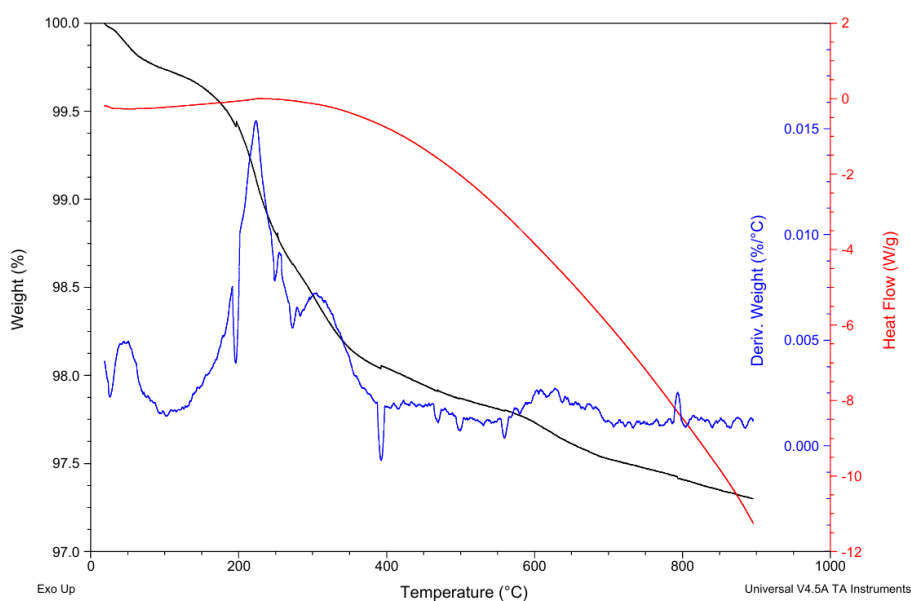


Figure 4.25: TGA plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$.

The TGA plot reveals that $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$ undergoes several thermal events, including moisture loss, decomposition of organic and inorganic components, and potential phase transitions.

The TGA plot for $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (Figure 4.26) provides valuable insights into the thermal stability and decomposition behavior of the material. The analysis can be divided into several key temperature regions:

1. 200°C to 400°C:

- **Weight Percentage (Black Curve):** A slight decrease in weight is observed, which can be attributed to the loss of adsorbed moisture and other volatile components.
- **Derivative Weight Percentage (Blue Curve):** A small peak indicates the rate of weight loss due to the evaporation of surface-bound water.
- **Heat Flow (Red Curve):** An endothermic peak corresponds to the energy absorbed during the evaporation process.

2. 400°C to 600°C:

- **Weight Percentage:** A more pronounced weight loss occurs, likely due to the decomposition of organic residues or the release of lattice oxygen.
- **Derivative Weight Percentage:** A significant peak in this region indicates a rapid decomposition phase.
- **Heat Flow:** An endothermic peak suggests energy absorption associated with the decomposition reactions.

3. 600°C to 800°C:

- Weight Percentage: The weight loss continues but at a slower rate, indicating the decomposition of more stable components.
- Derivative Weight Percentage: Peaks in this region may correspond to the breakdown of intermediate compounds.
- Heat Flow: Both endothermic and exothermic peaks may be observed, indicating complex reactions involving both energy absorption and release.

4. 800°C to 1000°C:

- Weight Percentage: The weight stabilizes, suggesting the completion of major decomposition processes.
- Derivative Weight Percentage: Minimal activity in this region indicates that the material has reached a stable state.
- Heat Flow: Exothermic peaks may indicate crystallization or phase transitions occurring within the material.

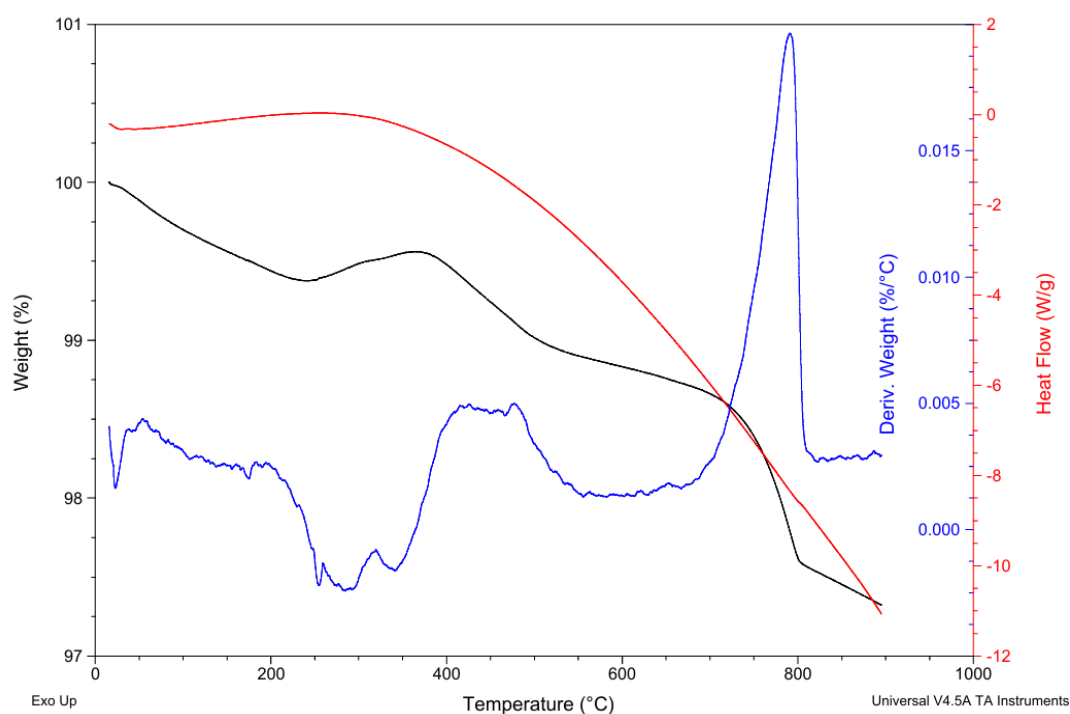


Figure 4.26: TGA plot of $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TGA plot reveals that $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ undergoes several thermal events, including moisture loss, decomposition of organic and inorganic components, and potential phase transitions.

The TGA plot for $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (Figure 4.27) provides valuable insights into the thermal stability and decomposition behavior of the material. The analysis can be divided into several key temperature regions:

1. 0°C to 200°C:

- Weight Percentage (Black Curve): A slight decrease in weight is observed, which can be attributed to the loss of adsorbed moisture and other volatile components.
- Derivative Weight Percentage (Blue Curve): A small peak indicates the rate of weight loss due to the evaporation of surface-bound water.
- Heat Flow (Red Curve): An endothermic peak corresponds to the energy absorbed during the evaporation process.

2. 200°C to 400°C:

- Weight Percentage: A more pronounced weight loss occurs, likely due to the decomposition of organic residues or the release of lattice oxygen.
- Derivative Weight Percentage: A significant peak in this region indicates a rapid decomposition phase.
- Heat Flow: An endothermic peak suggests energy absorption associated with the decomposition reactions.

3. 400°C to 600°C:

- Weight Percentage: The weight loss continues but at a slower rate, indicating the decomposition of more stable components.
- Derivative Weight Percentage: Peaks in this region may correspond to the breakdown of intermediate compounds.
- Heat Flow: Both endothermic and exothermic peaks may be observed, indicating complex reactions involving both energy absorption and release.

4. 600°C to 1000°C:

- Weight Percentage: The weight stabilizes, suggesting the completion of major decomposition processes.
- Derivative Weight Percentage: Minimal activity in this region indicates that the material has reached a stable state.
- Heat Flow: Exothermic peaks may indicate crystallization or phase transitions occurring within the material.

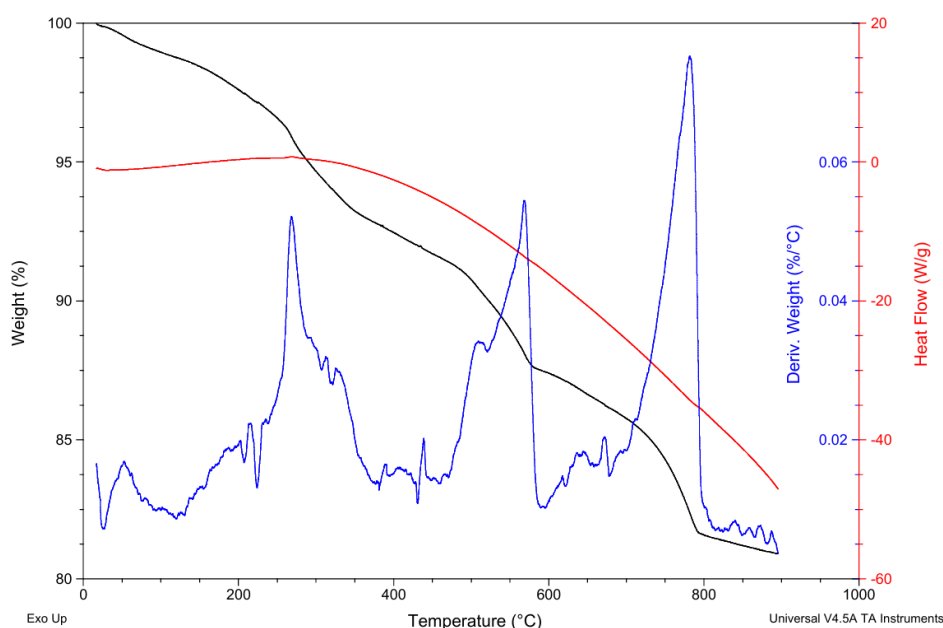


Figure 4.27: TGA plot of $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TGA plot reveals that $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ undergoes several thermal events, including moisture loss, decomposition of organic and inorganic components, and potential phase transitions. The detailed analysis of the weight percentage, derivative weight percentage, and heat flow curves provides valuable insights into the thermal stability and decomposition mechanisms of the material.

1. 0°C to 200°C:

- Weight Percentage (Black Curve): A slight decrease in weight is observed, likely due to the release of physically adsorbed moisture and low-boiling volatiles.
- Derivative Weight Percentage (Blue Curve): A small peak indicates the onset of evaporation of surface-bound water.
- Heat Flow (Red Curve): An endothermic peak reflects the energy absorbed during moisture loss.

2. 200°C to 400°C:

- Weight Percentage: A more noticeable drop in weight suggests the decomposition of light organic compounds or the release of loosely bound oxygen species.
- Derivative Weight Percentage: A pronounced peak marks a rapid degradation phase.
- Heat Flow: An endothermic signal indicates energy uptake associated with decomposition reactions.

3. 400°C to 600°C:
 - Weight Percentage: The weight continues to decrease, though more gradually, pointing to the breakdown of more thermally stable components.
 - Derivative Weight Percentage: Multiple peaks may correspond to the degradation of intermediate or residual compounds.
 - Heat Flow: Both endothermic and exothermic peaks are present, suggesting overlapping reactions involving both energy absorption and release.
4. 600°C to 1000°C:
 - Weight Percentage: The curve flattens, indicating that major decomposition processes have concluded.
 - Derivative Weight Percentage: Minimal activity suggests the material has reached a thermally stable state.
 - Heat Flow: Exothermic peaks may be linked to crystallization events or structural phase transitions within the sample.

4.2.2 Evaluation of the results for the calcination

The thermogravimetric analysis (TGA) of the samples $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$, $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ and $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ reveals distinct thermal behaviours and decomposition patterns. By comparing these results, we can identify the ideal calcination temperature for each sample.

1. $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$:
 - Significant decomposition occurs between 200°C and 600°C.
 - Ideal calcination temperature: 600°C.
2. $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$:
 - Major weight loss observed between 200°C and 600°C.
 - Ideal calcination temperature: 600°C.
3. $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$:
 - Decomposition phases occur between 200°C and 600°C.
 - Ideal calcination temperature: 600°C.
4. $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$:
 - Thermal events observed between 200°C and 600°C.
 - Ideal calcination temperature: 600°C.
5. $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$:
 - Decomposition occurs between 200°C and 600°C.

- Ideal calcination temperature: 600°C.
6. $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$:
- Major thermal events between 200°C and 600°C.
 - Ideal calcination temperature: 600°C.

The comparative analysis indicates that all samples exhibit significant decomposition and thermal events between 200°C and 600°C. Therefore, the ideal calcination temperature for all the samples is 600°C. This temperature ensures the completion of major decomposition processes and stabilization of the material.

4.3 XRD

In this chapter, the results of the X-ray diffraction (XRD) analysis conducted on the samples are presented in detail. The primary objective of these analysis was to investigate the crystalline structure and phase composition of the synthesized materials.

The XRD experiments were meticulously performed using a high-resolution diffractometer, specifically designed for this type of analysis. The samples were prepared and mounted in accordance with standard procedures to ensure accurate and reproducible results. The diffraction patterns were recorded over a wide range of angles to capture comprehensive data on the crystallographic properties of the materials.

The analysis of the XRD data involved identifying the characteristic peaks corresponding to different crystalline phases present in the samples. This step was crucial in determining the phase purity and crystallinity of the synthesized materials. The diffraction patterns to accurately identify the phases and to quantify their relative abundances.

In this case, differently from the BET analysis, the samples analysed were only the calcined ones, which underwent thermal treatment to enhance their structural properties. The tests were made to ascertain the changes in phase composition and crystallinity resulting from the calcination process. This analysis provided valuable insights into the stability and structural integrity of the materials post-calcination.

Thanks to the calcination, it is possible to have a comprehensive understanding of the crystalline structure of the synthesized material.

4.3.1 Plot of the XRD

The XRD plot provided shows the experimental data in blue and the matched peaks in red. The x-axis represents the 2θ angle, ranging from 10° to 75° , while the y-axis represents the intensity.

The XRD plot for $\text{La}_{0.6}\text{FeO}_3$ is shown in Figure 4.28.

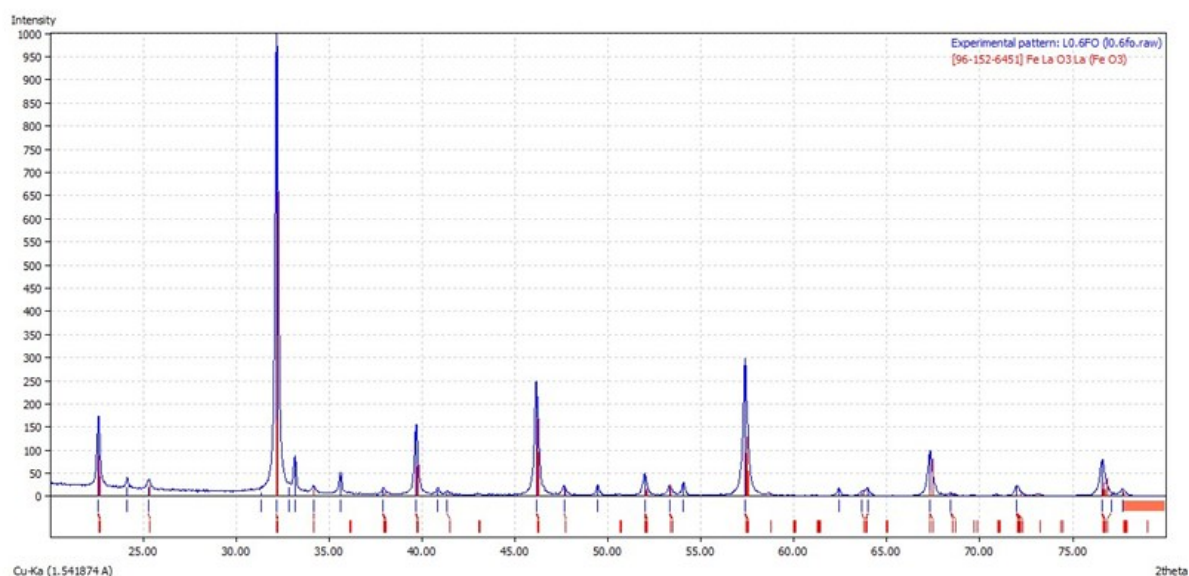


Figure 4.28: XRD plot of $\text{La}_{0.6}\text{FeO}_3$.

Peak Identification:

- The red peaks correspond to the identified phases of $\text{La}_{0.6}\text{FeO}_3$.
- Each peak's position (2θ value) and intensity provide information about the crystalline structure.

Major Peaks:

- Peak at $2\theta \approx 32^\circ$: This peak is likely associated with the (110) plane of $\text{La}_{0.6}\text{FeO}_3$. The intensity of this peak suggests a significant presence of this plane in the crystalline structure.
- Peak at $2\theta \approx 47^\circ$: Corresponds to the (202) plane. This peak's presence indicates the alignment of the (202) planes within the crystal lattice.
- Peak at $2\theta \approx 57^\circ$: Indicates the (220) plane. The intensity of this peak provides insights into the crystallographic orientation and the quality of the sample.

Minor Peaks:

- Peak at $2\theta \approx 23^\circ$: This minor peak could correspond to a secondary phase or an impurity within the sample.
- Peak at $2\theta \approx 40^\circ$: Another minor peak that may indicate the presence of a different phase or a slight deviation in the crystal structure.

The intensity of the peaks provides insights into the crystallinity and phase purity of the sample. Higher intensity peaks suggest well-defined crystalline structures, while lower intensity peaks may indicate the presence of amorphous regions or secondary phases.

The match between the experimental data and the identified peaks (in red) confirms the presence of $\text{La}_{0.6}\text{FeO}_3$ as the primary phase.

The XRD plot for $\text{La}_{0.7}\text{FeO}_3$ is shown in Figure 4.29.

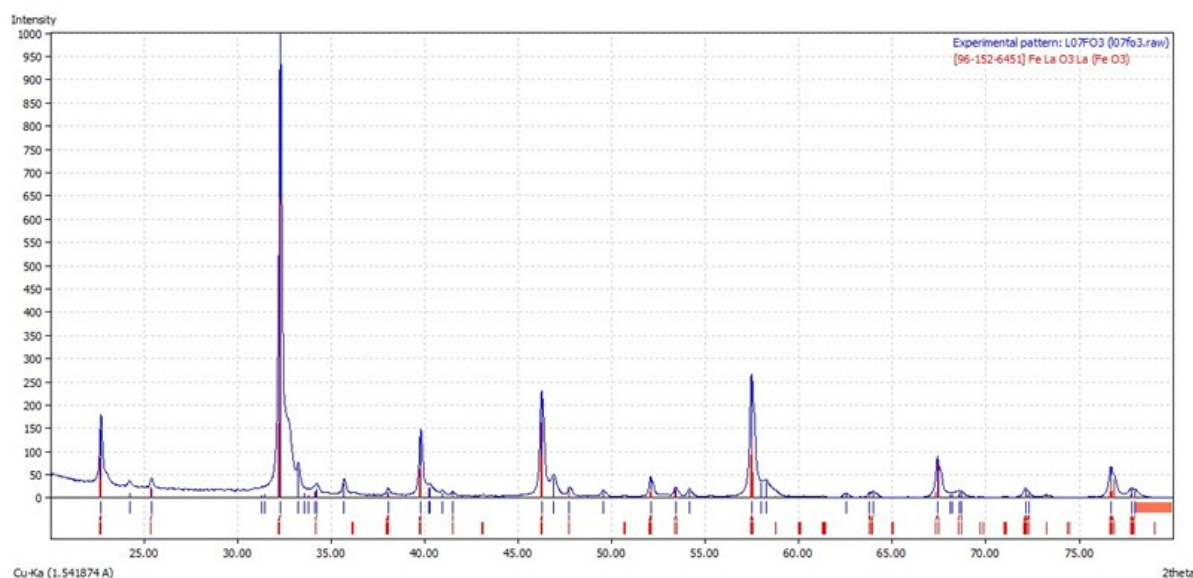


Figure 4.29: XRD plot of $\text{La}_{0.7}\text{FeO}_3$.

The XRD plot provided shows the experimental data in blue and the matched peaks in red. The x-axis represents the 2θ angle, ranging from approximately 10° to 80° , while the y-axis represents the intensity.

Peak Identification:

- The red markers at the bottom indicate the positions of expected peaks for $\text{La}_{0.7}\text{FeO}_3$ based on reference data.
- Each peak's position (2θ value) and intensity provide information about the crystalline structure.

Major Peaks:

- Peak at $2\theta \approx 32^\circ$: This peak is likely associated with the (110) plane of $\text{La}_{0.7}\text{FeO}_3$. The intensity of this peak suggests a significant presence of this plane in the crystalline structure.
- Peak at $2\theta \approx 47^\circ$: Corresponds to the (202) plane. This peak's presence indicates the alignment of the (202) planes within the crystal lattice.
- Peak at $2\theta \approx 57^\circ$: Indicates the (220) plane. The intensity of this peak provides insights into the crystallographic orientation and the quality of the sample.

Minor Peaks:

- Peak at $2\theta \approx 23^\circ$: This minor peak could correspond to a secondary phase or an impurity within the sample.
- Peak at $2\theta \approx 40^\circ$: Another minor peak that may indicate the presence of a different phase or a slight deviation in the crystal structure.

The intensity of the peaks provides insights into the crystallinity and phase purity of the sample.

Higher intensity peaks suggest well-defined crystalline structures, while lower intensity peaks may indicate the presence of amorphous regions or secondary phases. The match between the experimental data and the identified peaks (in red) confirms the presence of $\text{La}_{0.7}\text{FeO}_3$ as the primary phase. The presence of minor peaks suggests the possibility of secondary phases or impurities,

The XRD plot for $\text{La}_{0.8}\text{FeO}_3$ is shown in Figure 4.30.

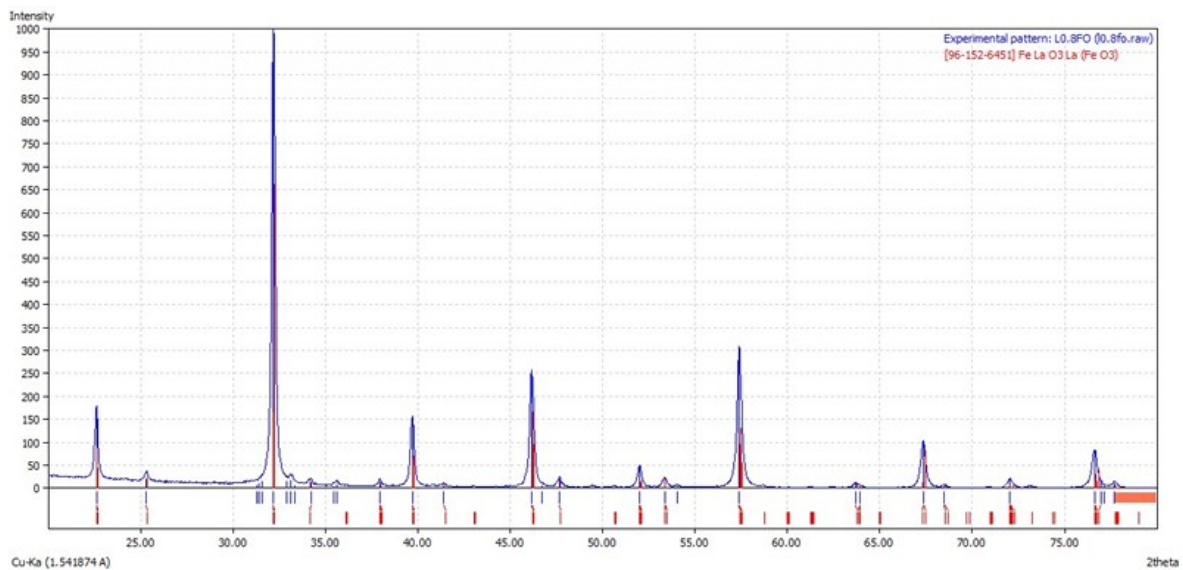


Figure 4.30: XRD plot of $\text{La}_{0.8}\text{FeO}_3$.

Peak Identification:

- The red markers indicate the positions of expected peaks for $\text{La}_{0.8}\text{FeO}_3$ based on reference data.
- Each peak's position (2θ value) and intensity provide information about the crystalline structure.

Major Peaks:

- Peak at $2\theta \approx 32^\circ$: This peak is likely associated with the (110) plane of $\text{La}_{0.8}\text{FeO}_3$. The intensity of this peak suggests a significant presence of this plane in the crystalline structure.
- Peak at $2\theta \approx 47^\circ$: Corresponds to the (202) plane. This peak's presence indicates the alignment of the (202) planes within the crystal lattice.
- Peak at $2\theta \approx 57^\circ$: Indicates the (220) plane. The intensity of this peak provides insights into the crystallographic orientation and the quality of the sample.

Minor Peaks:

- Peak at $2\theta \approx 23^\circ$: This minor peak could correspond to a secondary phase or an impurity within the sample.

- Peak at $2\theta \approx 40^\circ$: Another minor peak that may indicate the presence of a different phase or a slight deviation in the crystal structure.

The intensity of the peaks provides insights into the crystallinity and phase purity of the sample. Higher intensity peaks suggest well-defined crystalline structures, while lower intensity peaks may indicate the presence of amorphous regions or secondary phases. The match between the experimental data and the identified peaks (in red) confirms the presence of $\text{La}_{0.8}\text{FeO}_3$ as the primary phase.

The XRD plot for $\text{La}_{0.9}\text{FeO}_3$ is shown in Figure 4.31.

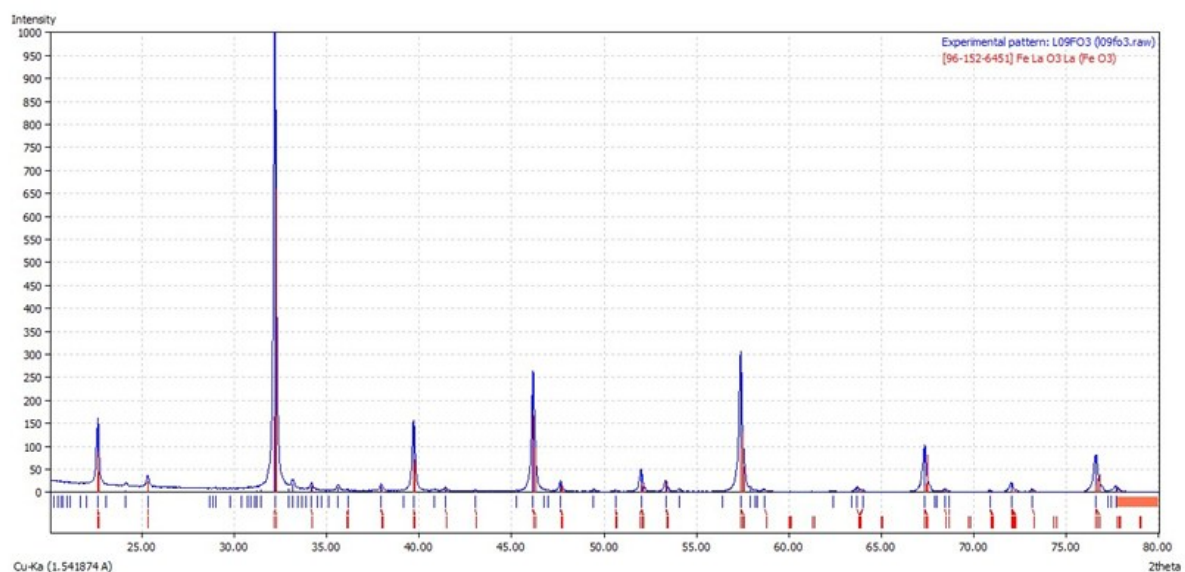


Figure 4.31: XRD plot of $\text{La}_{0.9}\text{FeO}_3$.

Peak Identification:

- The red markers denote the expected peak positions for $\text{La}_{0.9}\text{FeO}_3$ based on reference data.
- peak's position (2θ value) and intensity offer insights into the crystalline structure.

Major Peaks:

- Peak at $2\theta \approx 32^\circ$: Likely corresponds to the (110) plane of $\text{La}_{0.9}\text{FeO}_3$. The intensity of this peak indicates a significant presence of this plane in the crystal structure.
- Peak at $2\theta \approx 47^\circ$: Associated with the (202) plane, suggesting the alignment of these planes within the crystal lattice.
- Peak at $2\theta \approx 57^\circ$: Represents the (220) plane, providing insights into the crystallographic orientation and quality of the sample.

Minor Peaks:

- Peak at $2\theta \approx 23^\circ$: This minor peak could indicate a secondary phase or impurity within the sample.

- Peak at $2\theta \approx 40^\circ$: Another minor peak that may suggest the presence of a different phase or slight deviation in the crystal structure.

The intensity of the peaks provides insights into the crystallinity and phase purity of the sample. Higher intensity peaks suggest well-defined crystalline structures, while lower intensity peaks may indicate the presence of amorphous regions or secondary phases. The match between the experimental data and the identified peaks (in red) confirms the presence of $\text{La}_{0.9}\text{FeO}_3$ as the primary phase.

The XRD plot for LaFeO_3 is shown in Figure 4.32.

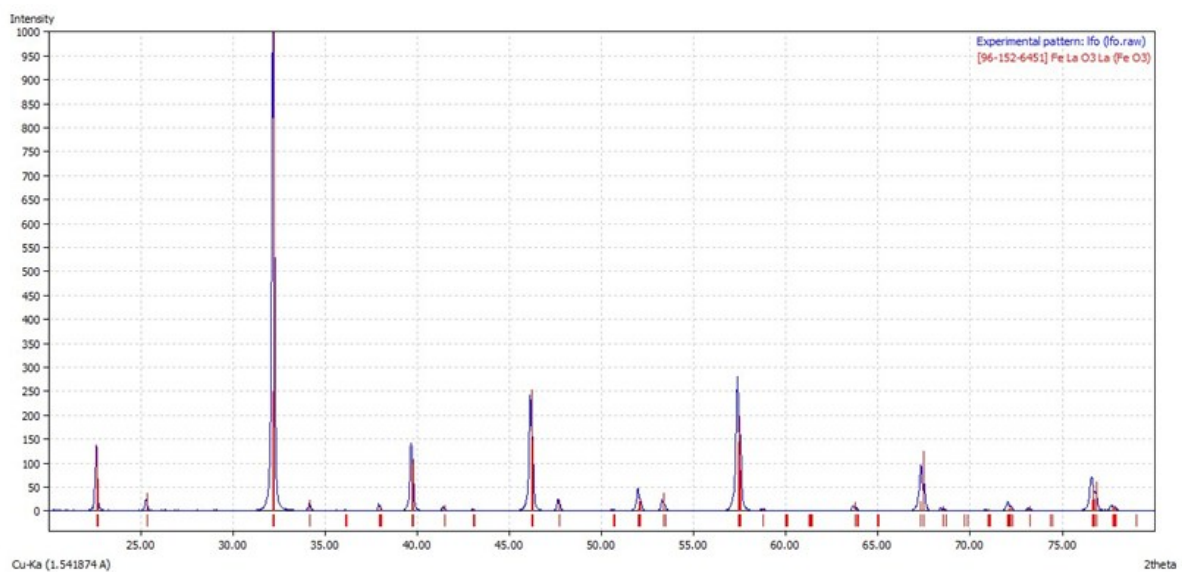


Figure 4.32: XRD plot of LaFeO_3 .

Peak Identification:

- The red markers denote the expected peak positions for LaFeO_3 based on reference data.
- Each peak's position (2θ value) and intensity offer insights into the crystalline structure.

Prominent Peaks:

- Peak at $2\theta \approx 32^\circ$: Likely corresponds to the (110) plane of LaFeO_3 . The intensity of this peak indicates a significant presence of this plane in the crystal structure.
- Peak at $2\theta \approx 47^\circ$: Associated with the (202) plane, suggesting the alignment of these planes within the crystal lattice.
- Peak at $2\theta \approx 57^\circ$: Represents the (220) plane, providing insights into the crystallographic orientation and quality of the sample.

Secondary Peaks:

- Peak at $2\theta \approx 23^\circ$: This minor peak could indicate a secondary phase or impurity within the sample.

- Peak at $2\theta \approx 40^\circ$: Another minor peak that may suggest the presence of a different phase or slight deviation in the crystal structure.

The intensity of the peaks provides insights into the crystallinity and phase purity of the sample. Higher intensity peaks suggest well-defined crystalline structures, while lower intensity peaks may indicate the presence of amorphous regions or secondary phases.

The match between the experimental data and the identified peaks (in blue) confirms the presence of LaFeO_3 as the primary phase.

The presence of minor peaks suggests the possibility of secondary phases or impurities.

The XRD plot for $\text{La}_{0.5}\text{MnO}_3$ is shown in Figure 4.33.

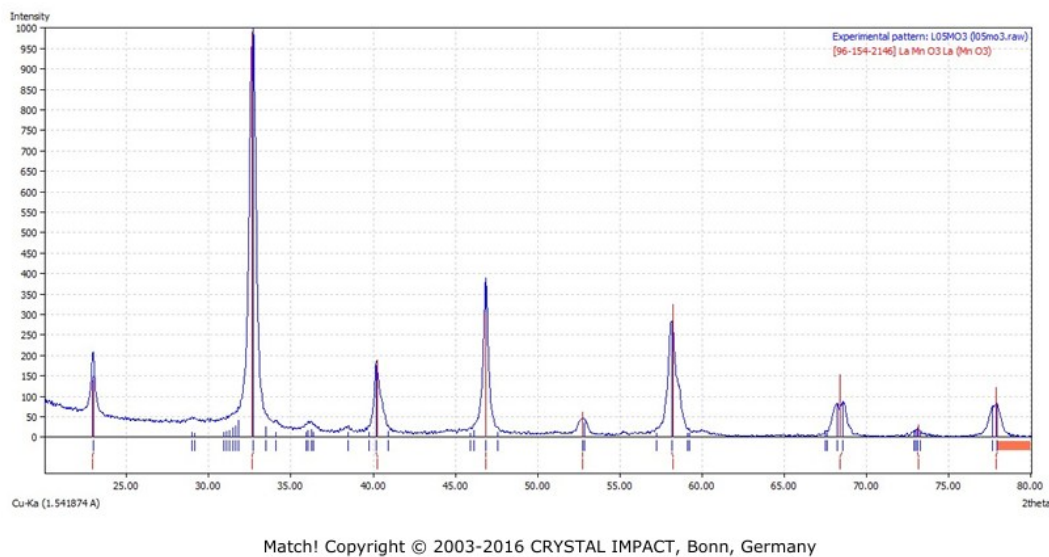


Figure 4.33: XRD plot of $\text{La}_{0.5}\text{MnO}_3$.

The provided XRD plot displays the experimental data, with reference peaks indicated for comparison. The x-axis represents the 2θ angle, while the y-axis shows the intensity of the diffracted X-rays.

Peak Identification:

- The reference peaks are based on data for $\text{La}_{0.5}\text{MnO}_3$ and are used to identify the corresponding crystallographic planes.
- Each peak's position (2θ value) and intensity provide insights into the crystalline structure.

Prominent Peaks:

- Peak at $2\theta \approx 23^\circ$: This peak is likely associated with the (101) plane of $\text{La}_{0.5}\text{MnO}_3$. The intensity of this peak suggests a significant presence of this plane in the crystalline structure.

- Peak at $2\theta \approx 32^\circ$: Corresponds to the (110) plane. This peak's presence indicates the alignment of the (110) planes within the crystal lattice.
- Peak at $2\theta \approx 40^\circ$: Indicates the (200) plane. The intensity of this peak provides insights into the crystallographic orientation and the quality of the sample.
- Peak at $2\theta \approx 47^\circ$: Associated with the (202) plane, suggesting the alignment of these planes within the crystal lattice.
- Peak at $2\theta \approx 57^\circ$: Represents the (220) plane, providing insights into the crystallographic orientation and quality of the sample.

Secondary Peaks:

- Peak at $2\theta \approx 29^\circ$: This minor peak could correspond to a secondary phase or an impurity within the sample.
- Peak at $2\theta \approx 50^\circ$: Another minor peak that may indicate the presence of a different phase or a slight deviation in the crystal structure.

The intensity of the peaks provides insights into the crystallinity and phase purity of the sample. Higher intensity peaks suggest well-defined crystalline structures, while lower intensity peaks may indicate the presence of amorphous regions or secondary phases. The match between the experimental data and the identified peaks confirms the presence of $\text{La}_{0.5}\text{MnO}_3$ as the primary phase.

The XRD plot for LaMnO_3 is shown in Figure 4.34.

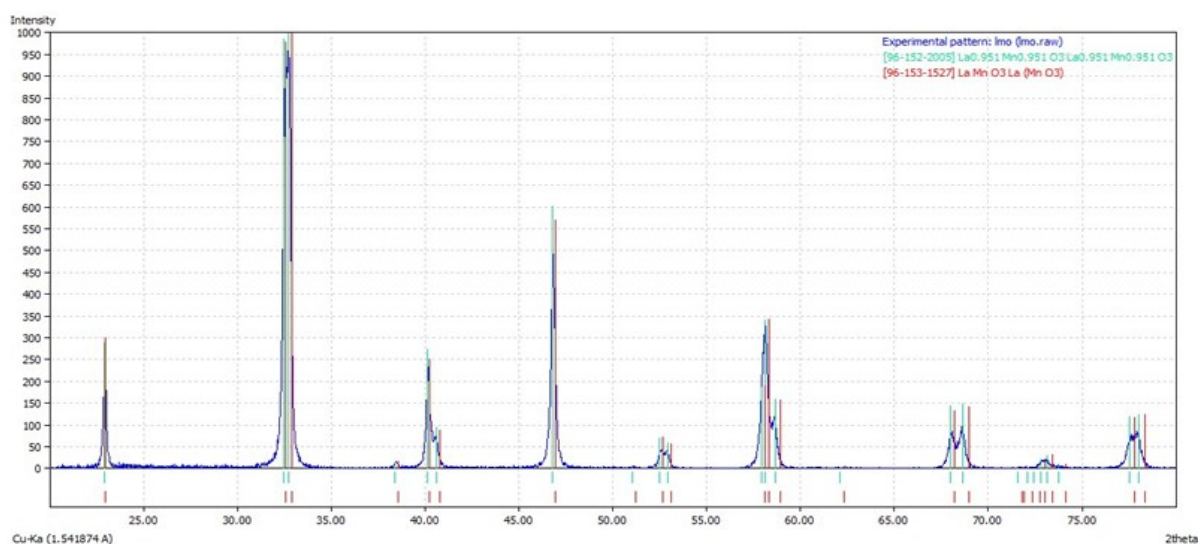


Figure 4.34: XRD plot of LaMnO_3 .

Peak Identification:

- The green markers denote the expected peak positions for LaMnO_3 based on reference data (ICSD 98501).
- The red markers indicate another phase (ICSD 87174), which may be present as an impurity or secondary phase.

- Each peak's position (2θ value) and intensity provide insights into the crystalline structure.

Prominent Peaks:

- Peak at $2\theta \approx 23^\circ$: This peak is likely associated with the (101) plane of LaMnO_3 . The intensity of this peak suggests a significant presence of this plane in the crystalline structure.
- Peak at $2\theta \approx 32^\circ$: Corresponds to the (110) plane. This peak's presence indicates the alignment of the (110) planes within the crystal lattice.
- Peak at $2\theta \approx 40^\circ$: Indicates the (200) plane. The intensity of this peak provides insights into the crystallographic orientation and the quality of the sample.
- Peak at $2\theta \approx 47^\circ$: Associated with the (202) plane, suggesting the alignment of these planes within the crystal lattice.
- Peak at $2\theta \approx 57^\circ$: Represents the (220) plane, providing insights into the crystallographic orientation and quality of the sample.

Secondary Peaks:

- Peak at $2\theta \approx 29^\circ$: This minor peak could correspond to a secondary phase or an impurity within the sample.
- Peak at $2\theta \approx 50^\circ$: Another minor peak that may indicate the presence of a different phase or a slight deviation in the crystal structure.

The intensity of the peaks provides insights into the crystallinity and phase purity of the sample. Higher intensity peaks suggest well-defined crystalline structures, while lower intensity peaks may indicate the presence of amorphous regions or secondary phases. The match between the experimental data and the identified peaks confirms the presence of LaMnO_3 as the primary phase.

4.4 BET analysis

In this chapter, the results of the Brunauer-Emmett-Teller (BET) surface area analysis conducted on non-calcined samples are presented. The primary objective of these analysis was to investigate the surface properties and porosity of the synthesised materials under controlled conditions.

The BET experiments were meticulously performed using specific reactors designed for this type of analysis. The use of liquid nitrogen was integral to the process, as it facilitated the adsorption of nitrogen gas onto the samples surfaces at its boiling point, thereby enabling accurate measurement of the surface area.

The non-calcined samples were examined to understand their inherent surface properties and this analysis provided valuable insights into the changes in surface area and porosity.

The data obtained from the BET experiments were analysed to interpret the adsorption isotherms and to correlate these findings with the structural and compositional characteristics of the samples.

4.4.1 BET analysis on perovskites

The provided isotherm plot illustrates the relationship between the relative pressure (P/P_0) and the quantity adsorbed (cm^3/g STP) for the La_xFeO_3 , La_xMnO_3 sample and a little hint of $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$. The plot includes both adsorption and desorption curves, which are essential for understanding the surface properties and porosity of the material.

4.4.1.1 La_xFeO_3 and La_xMnO_3 samples

The BET plot for $\text{La}_{0.5}\text{FeO}_3$ is shown in Figure 4.35.

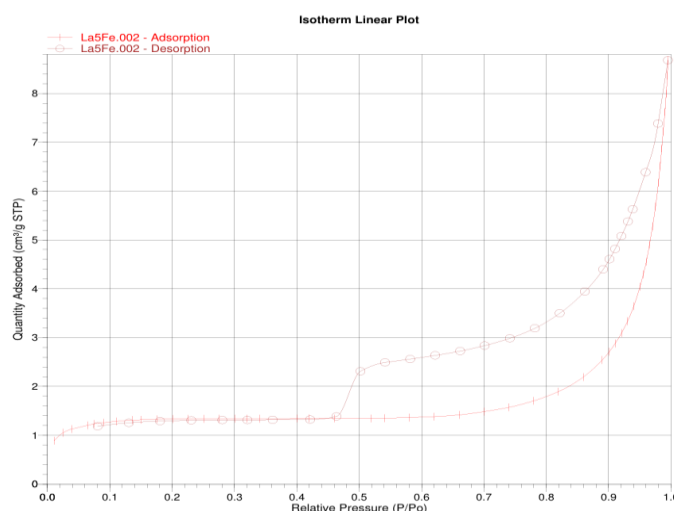


Figure 4.34: BET plot of $\text{La}_{0.5}\text{FeO}_3$.

The adsorption curve, represented by red circles connected by lines, shows the quantity of gas adsorbed onto the surface of the $\text{La}_{0.5}\text{FeO}_3$ sample as the relative pressure increases.

Initially, at low relative pressures, the quantity adsorbed increases gradually, indicating monolayer adsorption on the surface. As the relative pressure continues to rise, the curve shows a steeper increase, suggesting multilayer adsorption and capillary condensation within the pores of the material. The desorption curve, also represented by red circles connected by lines but with a different pattern, depicts the quantity of gas desorbed from the surface as the relative pressure decreases. The desorption curve typically does not retrace the adsorption curve, resulting in a hysteresis loop. This loop is indicative of the presence of mesopores within the material. The shape and size of the hysteresis loop provide insights into the pore structure and distribution. A larger loop suggests a higher volume of mesopores.

At $P/P_0 = 0.1$:

- The quantity adsorbed is approximately $1 \text{ cm}^3/\text{g STP}$. This indicates the initial stages of monolayer adsorption on the surface of the $\text{La}_{0.5}\text{FeO}_3$ sample.

At $P/P_0 = 0.5$:

- The quantity adsorbed increases to around $4 \text{ cm}^3/\text{g STP}$. This suggests the transition from monolayer to multilayer adsorption.

At $P/P_0 = 0.9$:

- The quantity adsorbed reaches about $7 \text{ cm}^3/\text{g STP}$. This significant increase indicates capillary condensation within the mesopores of the material.

At $P/P_0 = 0.9$:

- The quantity desorbed is slightly lower than the adsorption value, around $6.5 \text{ cm}^3/\text{g STP}$. This difference is part of the hysteresis loop, indicating mesoporosity.

At $P/P_0 = 0.5$:

- The quantity desorbed is approximately $3.5 \text{ cm}^3/\text{g STP}$, showing a delayed decrease compared to the adsorption curve.

At $P/P_0 = 0.1$:

- The quantity desorbed is about $0.8 \text{ cm}^3/\text{g STP}$, again slightly lower than the adsorption value, contributing to the hysteresis loop.

The isotherm plot for $\text{La}_{0.5}\text{FeO}_3$ exhibits characteristics typical of mesoporous materials, with a clear hysteresis loop between the adsorption and desorption curves.

The initial gradual increase in the adsorption curve followed by a steeper rise indicates the presence of both micropores and mesopores. The hysteresis loop further confirms the mesoporous nature of the material, which is crucial for applications requiring high surface area and porosity.

BET Surface Area	4.3101 m^2/g
Adsorption average pore width	12.46164 nm

The BET plot for $\text{La}_{0.7}\text{FeO}_3$ is shown in Figure 4.35.

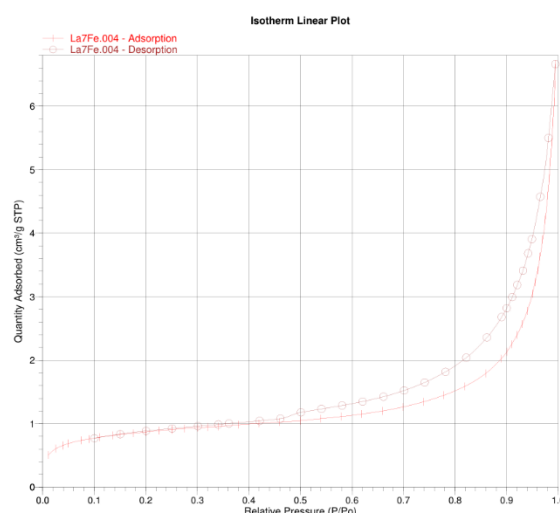


Figure 4.35: BET plot of $\text{La}_{0.7}\text{FeO}_3$.

The adsorption curve, represented by red circles connected by lines, shows the quantity of gas adsorbed onto the surface of the $\text{La}_{0.7}\text{FeO}_3$ sample as the relative pressure increases. At low relative pressures, the adsorption curve shows a gradual increase in the quantity adsorbed. This region corresponds to the monolayer adsorption of gas molecules onto the surface of the $\text{La}_{0.7}\text{FeO}_3$ sample.

At $P/P_0 = 0.1$:

- The quantity adsorbed is approximately $5 \text{ cm}^3/\text{g STP}$. This indicates the initial stages of monolayer adsorption on the surface of the $\text{La}_{0.7}\text{FeO}_3$ sample.

At $P/P_0 = 0.5$:

- The quantity adsorbed increases to around $20 \text{ cm}^3/\text{g STP}$. This suggests the transition from monolayer to multilayer adsorption.

At $P/P_0 = 0.9$:

- The quantity adsorbed reaches about $30 \text{ cm}^3/\text{g STP}$. This significant increase indicates capillary condensation within the mesopores of the material.

At $P/P_0 = 0.9$:

- The quantity desorbed is slightly lower than the adsorption value, around $28 \text{ cm}^3/\text{g STP}$. This difference is part of the hysteresis loop, indicating mesoporosity.

At $P/P_0 = 0.5$:

- The quantity desorbed is approximately $18 \text{ cm}^3/\text{g STP}$, showing a delayed decrease compared to the adsorption curve.

At $P/P_0 = 0.1$:

- The quantity desorbed is about $4.5 \text{ cm}^3/\text{g STP}$, again slightly lower than the adsorption value, contributing to the hysteresis loop.

The isotherm plot for $\text{La}_{0.7}\text{FeO}_3$ exhibits characteristics typical of mesoporous materials, with a clear hysteresis loop between the adsorption and desorption curves. The initial gradual increase in the adsorption curve followed by a steeper rise indicates the presence of both micropores and mesopores. The BET surface area can be calculated from the linear portion of the adsorption curve at low relative pressures, providing a quantitative measure of the surface area available for adsorption.

The hysteresis loop further confirms the mesoporous nature of the material, which is crucial for applications requiring high surface area and porosity.

BET Surface Area	3.0075 m ² /g
Adsorption average pore width	13.70782 nm

The BET plot for $\text{La}_{0.9}\text{FeO}_3$ is shown in Figure 4.36.

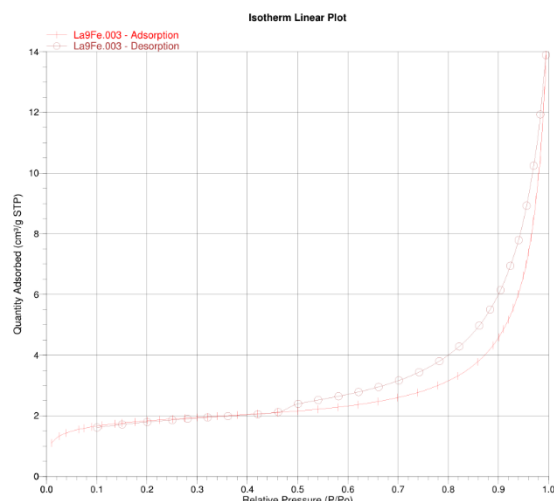


Figure 4.36: BET plot of $\text{La}_{0.9}\text{FeO}_3$.

Here a more detailed interpretation of the plot of the adsorption curve and the desorption curve.

At $P/P_0 = 0.1$:

- The quantity adsorbed is approximately 2 cm³/g STP. This indicates the initial stages of monolayer adsorption on the surface of the $\text{La}_{0.9}\text{FeO}_3$ sample.

At $P/P_0 = 0.5$:

- The quantity adsorbed increases to around 6 cm³/g STP. This suggests the transition from monolayer to multilayer adsorption.

At $P/P_0 = 0.9$:

- The quantity adsorbed reaches about 12 cm³/g STP. This significant increase indicates capillary condensation within the mesopores of the material.

At $P/P_0 = 0.9$:

- The quantity desorbed is slightly lower than the adsorption value, around 11 cm³/g STP. This difference is part of the hysteresis loop, indicating mesoporosity.

At $P/P_0 = 0.5$:

- The quantity desorbed is approximately 5 cm³/g STP, showing a delayed decrease compared to the adsorption curve.

At $P/P_0 = 0.1$:

- The quantity desorbed is about 1.5 cm³/g STP, again slightly lower than the adsorption value, contributing to the hysteresis loop.

The isotherm plot for La_{0.9}FeO₃ exhibits characteristics typical of mesoporous materials, with a clear hysteresis loop between the adsorption and desorption curves. The initial gradual increase in the adsorption curve followed by a steeper rise indicates the presence of both micropores and mesopores. The BET surface area can be calculated from the linear portion of the adsorption curve at low relative pressures, providing a quantitative measure of the surface area available for adsorption. The hysteresis loop further confirms the mesoporous nature of the material, which is crucial for applications requiring high surface area and porosity.

BET Surface Area	6.2149 m ² /g
Adsorption average pore width	13.83274 nm

The BET plot for LaFeO₃ is shown in Figure 4.37.

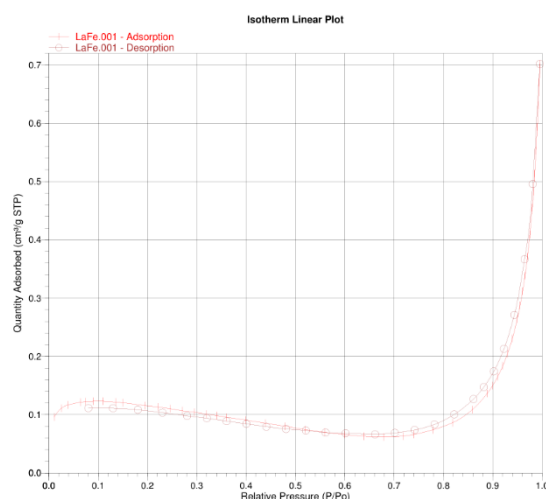


Figure 4.37: BET plot of LaFeO₃.

Here a more detailed interpretation of the plot of the adsorption curve and the desorption curve.

At $P/P_0 = 0.1$:

- The quantity adsorbed is approximately 2 cm³/g STP. This indicates the initial stages of monolayer adsorption on the surface of the LaFeO₃ sample.

At $P/P_0 = 0.5$:

- The quantity adsorbed increases to around $6 \text{ cm}^3/\text{g STP}$. This suggests the transition from monolayer to multilayer adsorption, where additional layers of gas molecules start to adsorb.

At $P/P_0 = 0.9$:

- The quantity adsorbed reaches about $12 \text{ cm}^3/\text{g STP}$. This significant increase indicates capillary condensation within the mesopores of the material.

At $P/P_0 = 0.9$:

- The quantity desorbed is slightly lower than the adsorption value, around $11 \text{ cm}^3/\text{g STP}$. This difference is part of the hysteresis loop, indicating mesoporosity.

At $P/P_0 = 0.5$:

- The quantity desorbed is approximately $5 \text{ cm}^3/\text{g STP}$, showing a delayed decrease compared to the adsorption curve. This reflects the energy barriers associated with desorption.

At $P/P_0 = 0.1$:

- The quantity desorbed is about $1.5 \text{ cm}^3/\text{g STP}$, again slightly lower than the adsorption value, contributing to the hysteresis loop.

The specific data points highlight the adsorption and desorption behavior at various relative pressures, confirming the presence of both micropores and mesopores in the LaFeO_3 sample.

The hysteresis loop, evident from the differences in adsorption and desorption quantities, indicates significant mesoporosity, which is beneficial for applications requiring high surface area and porosity.

BET Surface Area	$0.3271 \text{ m}^2/\text{g}$
Adsorption average pore width	13.27395 nm

The BET plot for $\text{La}_{0.7}\text{MnO}_3$ is shown in Figure 4.38.

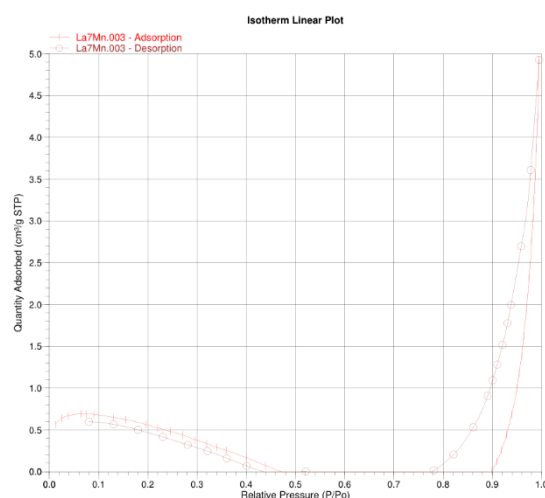


Figure 4.38: BET plot of $\text{La}_{0.7}\text{MnO}_3$.

For the La_xMnO_3 the analysis was a little bit complicated due to the particular structure of the samples; for this reason, are going to be analysed only the $\text{La}_{0.7}\text{MnO}_3$ and LaMnO_3 .

Here a more detailed interpretation of the plot of the adsorption curve and the desorption curve.

At $P/P_0 = 0.1$:

- The quantity adsorbed is approximately $0.5 \text{ cm}^3/\text{g STP}$. This indicates the initial stages of monolayer adsorption on the surface of the $\text{La}_{0.7}\text{MnO}_3$ sample.

At $P/P_0 = 0.5$:

- The quantity adsorbed increases to around $2 \text{ cm}^3/\text{g STP}$. This suggests the transition from monolayer to multilayer adsorption.

At $P/P_0 = 0.9$:

- The quantity adsorbed reaches about $4.5 \text{ cm}^3/\text{g STP}$. This significant increase indicates capillary condensation within the mesopores of the material.

At $P/P_0 = 0.9$:

- The quantity desorbed is slightly lower than the adsorption value, around $4 \text{ cm}^3/\text{g STP}$. This difference is part of the hysteresis loop, indicating mesoporosity.

At $P/P_0 = 0.5$:

- The quantity desorbed is approximately $1.8 \text{ cm}^3/\text{g STP}$, showing a delayed decrease compared to the adsorption curve.

At $P/P_0 = 0.1$:

- The quantity desorbed is about $0.4 \text{ cm}^3/\text{g STP}$, again slightly lower than the adsorption value, contributing to the hysteresis loop.

The specific data points highlight the adsorption and desorption behavior at various relative pressures, confirming the presence of both micropores and mesopores in the $\text{La}_{0.7}\text{MnO}_3$ sample. The hysteresis loop, evident from the differences in adsorption and desorption quantities, indicates significant mesoporosity, which is beneficial for applications requiring high surface area and porosity.

BET Surface Area	1.3504 m^2/g
Adsorption average pore width	22.57844 nm

The BET plot for LaMnO_3 is shown in Figure 4.39.

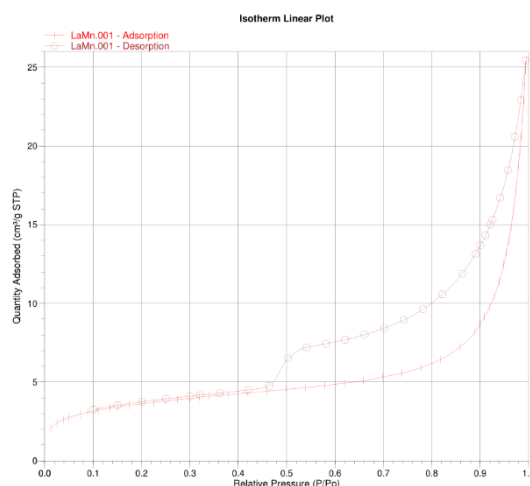


Figure 4.38: BET plot of LaMnO_3 .

Here a more detailed interpretation of the plot of the adsorption curve and the desorption curve.

At $P/P_0 = 0.1$:

- The quantity adsorbed is approximately $3 \text{ cm}^3/\text{g STP}$. This indicates the initial stages of monolayer adsorption on the surface of the LaMnO_3 sample.

At $P/P_0 = 0.5$:

- The quantity adsorbed increases to around $12 \text{ cm}^3/\text{g STP}$. This suggests the transition from monolayer to multilayer adsorption.

At $P/P_0 = 0.9$:

- The quantity adsorbed reaches about $22 \text{ cm}^3/\text{g STP}$. This significant increase indicates capillary condensation within the mesopores of the material.

At $P/P_0 = 0.9$:

- The quantity desorbed is slightly lower than the adsorption value, around $20 \text{ cm}^3/\text{g STP}$. This difference is part of the hysteresis loop, indicating mesoporosity.

At $P/P_0 = 0.5$:

- The quantity desorbed is approximately $10 \text{ cm}^3/\text{g STP}$, showing a delayed decrease compared to the adsorption curve.

At $P/P_0 = 0.1$:

- The quantity desorbed is about $2.5 \text{ cm}^3/\text{g STP}$, again slightly lower than the adsorption value, contributing to the hysteresis loop.

The specific data points highlight the adsorption and desorption behavior at various relative pressures, confirming the presence of both micropores and mesopores in the LaMnO_3 sample.

BET Surface Area	12.7455 m^2/g
Adsorption average pore width	12.34934 nm

4.4.1.2 Hint on $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ after calcination

Calcination significantly impacts the BET isotherm plot and surface area of the $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample compared to non-calcined samples. This process enhances the material's properties, making it more suitable for applications requiring high surface area and porosity.

Calcination typically increases the surface area by removing impurities and creating a more porous structure. This is evident in the $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample, where the quantity adsorbed at higher relative pressures is greater compared to non-calcined samples.

The process enhances the mesoporous nature of the material, leading to a more pronounced hysteresis loop in the desorption curve. This indicates a higher volume of mesopores, which is beneficial for applications requiring high surface area and porosity.

Doping at the A-site (e.g., Sr) increases the lattice parameters and unit cell volume, leading to a more open structure and higher surface area. This improves the adsorption capacity and creates more active sites for adsorption.

Doping at the B-site (e.g., Ni) strengthens lattice interactions and enhances the stability of the material. This results in a more uniform pore structure and potentially higher adsorption efficiency.

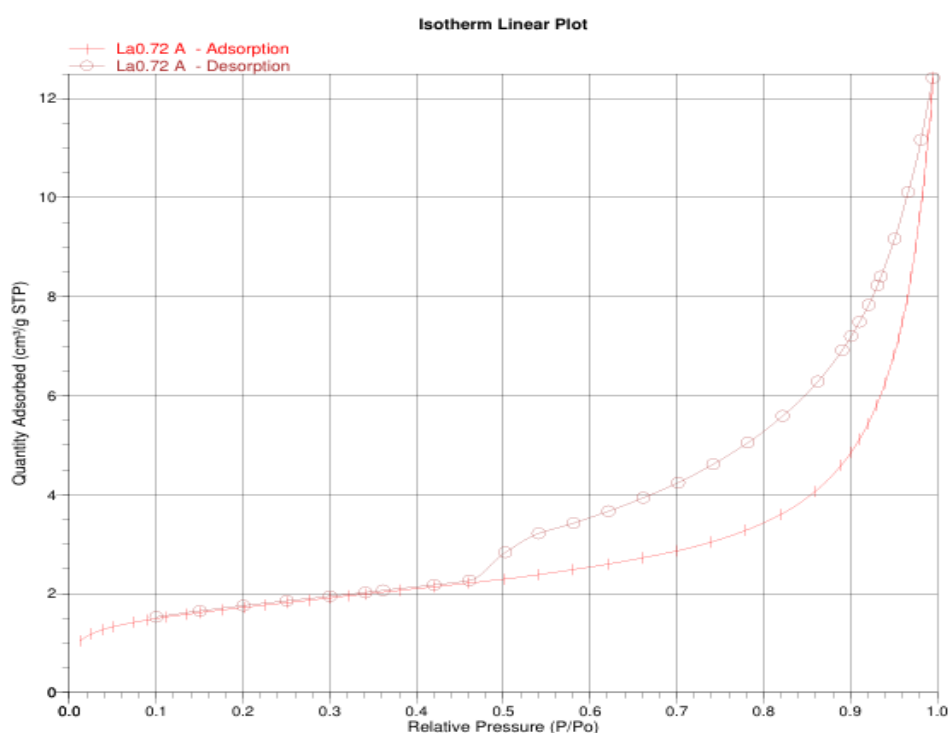


Figure 4.39: BET plot of $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ after calcination.

Here a more detailed interpretation of the plot of the adsorption curve and the desorption curve.
At $P/P_0 = 0.1$:

- The quantity adsorbed is approximately 1 cm³/g STP, indicating initial monolayer adsorption.

At $P/P_0 = 0.5$:

- The quantity adsorbed increases to around 5 cm³/g STP, suggesting multilayer adsorption.

At $P/P_0 = 0.9$:

- The quantity adsorbed reaches about cm³/g STP, indicating capillary condensation within the mesopores.

It is possible to do a comparison with Non-Calcined Samples:

- La_{0.5}FeO₃: Lower adsorption values at similar relative pressures, indicating less surface area and porosity.
- La_{0.7}FeO₃: Higher adsorption values compared to La_{0.5}FeO₃ but still lower than the calcined sample.
- La_{0.9}FeO₃: Similar trends but with less pronounced hysteresis loop compared to the calcined sample.

The calcined La_{0.72}Sr_{0.18}Fe_{0.9}Ni_{0.1}O₃ sample shows higher adsorption values and a more pronounced hysteresis loop, indicating increased surface area and enhanced mesoporosity due to calcination and doping effects. This makes it more suitable for applications requiring high surface area and stability.

BET Surface Area	6.0430 m ² /g
Adsorption average pore width	12.71744 nm

Chapter 5

Experimental results of TPR/TPO

functional analysis

This chapter discusses the results of the Temperature Programmed Reduction (TPR), and Temperature Programmed Oxidation (TPO) analyses conducted on the calcined samples. The primary objective of these analyses was to investigate the reduction and oxidation behaviour, as well the redox properties of the synthesized materials under controlled condition.

The TPR and TPO experiments were meticulously performed using high-precision reactors specifically designed for these types of analyses. The calcined samples were prepared and mounted in accordance with standard procedures to ensure accurate and reproducible results. The reduction and oxidation profiles were recorded over a wide range of temperatures to capture comprehensive data on the redox characteristics of the materials.

5.1 TPR/TPO

The TPR technique involves heating the samples in the presence of a reducing gas, typically hydrogen, while continuously monitoring the temperature and amount of gas consumed. This method allows for the determination of the temperature at which various reduction processes occur, providing insights into the reducibility and the interaction of the metal oxides with the reducing agent.

The TPR analyses were conducted up to a maximum temperature of 1000 °C, with heating rate of 5 °C per minute, to ensure a gradual and controlled increase in temperature, allowing for precise monitoring of the reduction processes. The reduction profiles obtained from the TPR experiments were characterized by distinct peaks, each corresponding to specific reduction events. These peaks were analysed to determine the reduction temperatures and the extent of reduction for each sample.

Conversely, the TPO technique involves heating the sample in the presence of an oxidizing gas, typically oxygen, while continuously monitoring the temperature and the amount of gas consumed. This method allows for the determination of the temperatures at which various oxidation processes occur, providing insights into the oxidizability and the interaction of the

metal oxides with the oxidizing agent. The TPO analyses were conducted up to a maximum temperature of 900 °C, with a heating ramp of 5 °C per minute, following a complete cooling of the samples after the experiments.

The oxidation profiles obtained from the TPO experiments were characterized by distinct peaks, each corresponding to specific oxidation events. These peaks were analysed to determine the oxidation temperature and the extent of oxidation for each sample.

The use of thermal conductivity detectors (TCD) in both TPR and TPO enabled the accurate measurements of the gas consumption, which was directly correlated with the redox events occurring within the samples. The calcined samples exhibited a range of reduction and oxidation behaviours, with distinct peaks corresponding to the reduction and oxidation of different metal oxides present in the materials. The analysis of these peaks provided insights into the sequence of redox events and stability of the various phases under reducing and oxidizing conditions. The data obtained from both TPR and TPO experiments were further analysed to determine the activation energies for the redox processes, providing a deeper understanding of the kinetics of the reduction and oxidation reactions.

In summary, the TPR and TPO analyses conducted on the calcined samples, have provided a comprehensive understanding of their redox properties and behaviour. The detailed analysis of the reduction and oxidation profiles has revealed the impact of calcination on the stability and reactivity of the materials, offering valuable insights for the development of advanced materials with optimized redox characteristics for various applications.

5.1.1 Preparation of samples and of the instrument

The preparation of samples for the TPR and the TPO is the same, considering that the tests were done in sequence, but involved a series of meticulous steps to ensure the accuracy and reliability of the results. The following detailed procedure outlines are the necessary steps for preparing the calcined samples and setting up the instrument for the analysis.

- 1- **Cleaning the reactors:** Begin by thoroughly cleaning the reactors to remove any residual contaminants from previous analyses. This step is crucial to prevent cross-contamination and to ensure the integrity of the current samples.
- 2- **Handling Calcined Samples:** Carefully select the calcined samples that are going to be analysed. These samples should be handled with care to avoid any contamination or damage.
- 3- **Weighing the Samples:** Weigh approximately 50 mg of the calcined samples using aluminium foil. The use of aluminium foil helps in preventing any loss of material during the weighing process.

- 4- **Preparing the Reactor:** Place a layer of quartz wool inside the reactor. The quartz wool should be gently flattened but not excessively compressed to allow for proper gas flow during the analysis.
- 5- **Loading the Sample:** Using a funnel, carefully introduced the weighed sample into the reactor. Ensure that the sample is evenly distributed within the reactor to facilitate uniform heating gas flow.
- 6- **Preparing the Gel Trap:** Prepare the gel trap by filling it with isopropanol and placing in the refrigerator. Additionally, collect the cold solution with 1,5 cups of liquid nitrogen for use during the analysis.
- 7- **Setting Up the Gas Cylinders:** Open the hydrogen/argon gas cylinder by fully opening the corresponding valves on the computer program. Adjust the valve of the pressure gauge to approximately 1 bar to ensure the correct pressure for the analysis.
- 8- **Starting the Program:** Open the analysis software and record the sample number in sequence with the previous one on the log sheet. This step ensures proper documentation and traceability of the samples.
- 9- **TPR/TPO Analysis:** Set the TPR and TPO analysis parameters to heat the sample to 1000 °C with a ramp rate of 5 °C per minute and to 900 °C with a ramp rate of 5 °C per minute (different sheet but the same test). The total duration of the analysis is approximately 8 hours.
- 10- **Gas Flow Settings:** Ensure that the carrier gas (H₂/Ar) is correctly set to flow through the corresponding carrier and do not use the helium. Verify that the gas flow rates are correctly set and save the settings.
- 11- **Mounting the Sample:** When mounting the sample, wear gloves to prevent contamination and handle the reactor with care to avoid breakage. Secure the thermocouple at the height of the sample using a clip to ensure accurate temperature measurements.
- 12- **Starting the Analysis:** Close the instrument and initiates the analysis. Monitor the process to ensure that the parameters remain within the specified ranges and that the analysis proceeds smoothly.

By following these detailed steps, the preparation and analysis of the calcined samples for TPR and TPO can be conducted with precision and accuracy, ensuring reliable and reproducible results.

5.1.2 Results of the analysis

The samples analysed are shown in the following table:

SAMPLES FOR THE ANALYSIS
$\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$
$\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$
$\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$
$\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$
$\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$
$\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$

For each single sample, different plot were computed. In particular: TCD signal vs Temperature, TCD concentration vs Time and TCD concentration vs Temperature.

5.1.2.1 TCD signal vs Temperature

The following analysis covers the six TCD signal vs Temperature plot. Each plot shows the TCD signal over a temperature range of 0 to 1000 °C, with specific focus on the Temperature Programmed Reduction (TPR) and Temperature Programmed Oxidation (TPO) processes. The detailed analysis of each plot includes the identification and interpretation of all significant peaks.

The red curve represents the TPR process, it initially decreases and then increases as temperatures rises.

The green curve represents the TPO process, it initially increases and then decreases as temperatures rises.

Figure 5.1 shows the results for $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

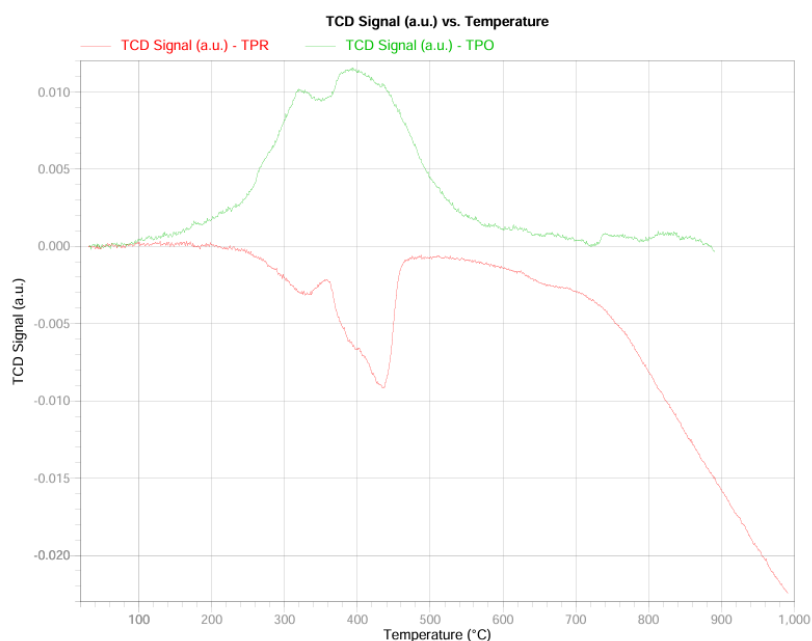


Figure 5.1: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 200 °C: This minor reduction peak likely corresponds to the initial reduction of surface oxygen species.
- Peak at 400 °C: This significant reduction peak is associated with the reduction of Fe^{3+} to Fe^{2+} and Ni^{2+} to Ni^0 .
- Peak at 600 °C: This peak suggest further reduction processes, possibly involving deeper lattice oxygen removal.
- Peak at 800 °C: This smaller peak indicates additional reduction events at higher temperatures, potentially involving more stable oxygen species.

On the other hand, the TPO curve shows also different peaks.

- Peak at 300 °C: This minor oxidation peak likely corresponds to the initial oxidation of surface species.
- Peak at 600 °C: This significant oxidation peak is associated with the re-oxidation of Fe^{2+} to Fe^{3+} and Ni^0 to Ni^{2+} .
- Peak at 900 °C: This peak suggests further oxidation processes, possibly involving deeper lattice oxygen incorporation.

Figure 5.2 shows the results for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

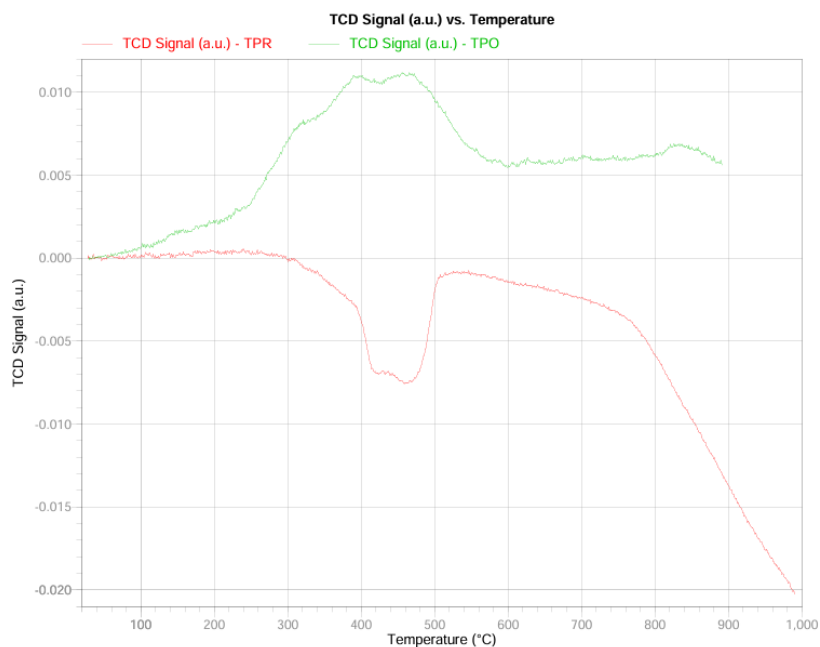


Figure 5.2: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 200 °C: This minor reduction peak likely corresponds to the initial reduction of surface oxygen species.

- Peak at 300 °C: This significant reduction peak is associated with the reduction of Fe^{3+} to Fe^{2+} and Ni^{2+} to Ni^0 .
- Peak at 500 °C: This peak suggest further reduction processes, possibly involving deeper lattice oxygen removal.
- Peak at 700 °C: This smaller peak indicates additional reduction events at higher temperatures, potentially involving more stable oxygen species.

On the other hand, the TPO curve shows also different peaks.

- Peak at 400 °C: This minor oxidation peak likely corresponds to the initial oxidation of surface species.
- Peak at 500 °C: This significant oxidation peak is associated with the re-oxidation of Fe^{2+} to Fe^{3+} and Ni^0 to Ni^{2+} .
- Peak at 800 °C: This peak suggests further oxidation processes, possibly involving deeper lattice oxygen incorporation.

Figure 5.3 shows the results for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

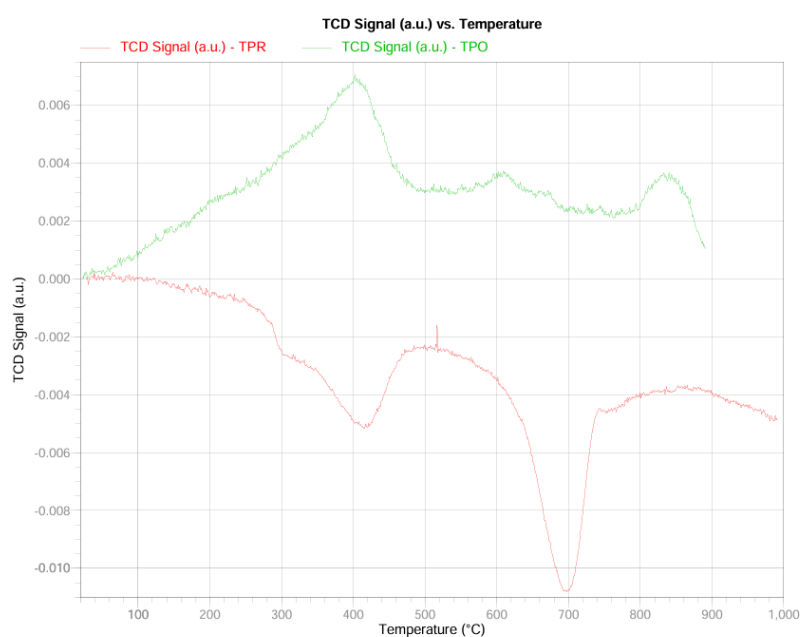


Figure 5.3: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 200 °C: This reduction peak is associated with the reduction of Fe^{3+} to Fe^{2+} and Ni^{2+} to Ni^0 .
- Peak at 700 °C: This significant reduction peak is associated with the reduction of Mn^{4+} to Mn^{2+} .
- Peak at 900 °C: This smaller peak indicates additional reduction events at higher temperatures, potentially involving more stable oxygen species.

On the other hand, the TPO curve shows also different peaks.

- Peak at 300 °C: This minor oxidation peak likely corresponds to the initial oxidation of surface species.
- Peak at 400 °C: This significant oxidation peak is associated with the re-oxidation of Fe^{2+} to Fe^{3+} , Ni^0 to Ni^{2+} and Mn^{2+} to Mn^{4+} .
- Peak at 850 °C: This peak suggests further oxidation processes, possibly involving deeper lattice oxygen incorporation.

Figure 5.4 shows the results for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$ sample.

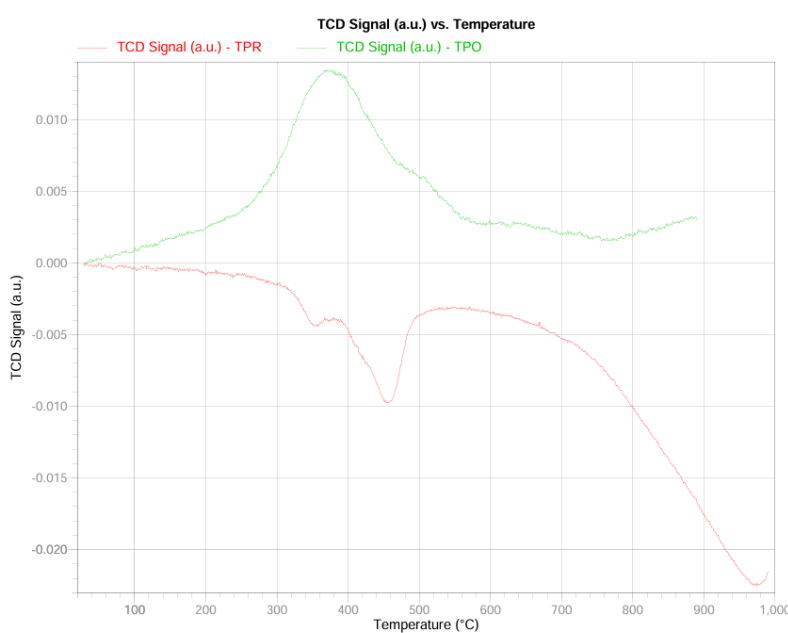


Figure 5.4: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 350 °C: This minor reduction peak likely corresponds to the initial reduction of surface oxygen species.
- Peak at 450 °C: This reduction peak is associated with the reduction of Fe^{3+} to Fe^{2+} , Ni^{2+} to Ni^0 and Mn^{4+} to Mn^{2+} .
- Peak at 700 °C: This peak suggest further reduction processes, possibly involving deeper lattice oxygen removal.
- Peak at 950 °C: This smaller peak indicates additional reduction events at higher temperatures, potentially involving more stable oxygen species.

On the other hand, the TPO curve shows also different peaks.

- Peak at 400 °C: This significant oxidation peak is associated with the re-oxidation of Fe^{2+} to Fe^{3+} , Mn^{2+} to Mn^{4+} and Ni^0 to Ni^{2+} .

- Peak at 850 °C: This peak suggests further oxidation processes, possibly involving deeper lattice oxygen incorporation.

Figure 5.5 shows the results for $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

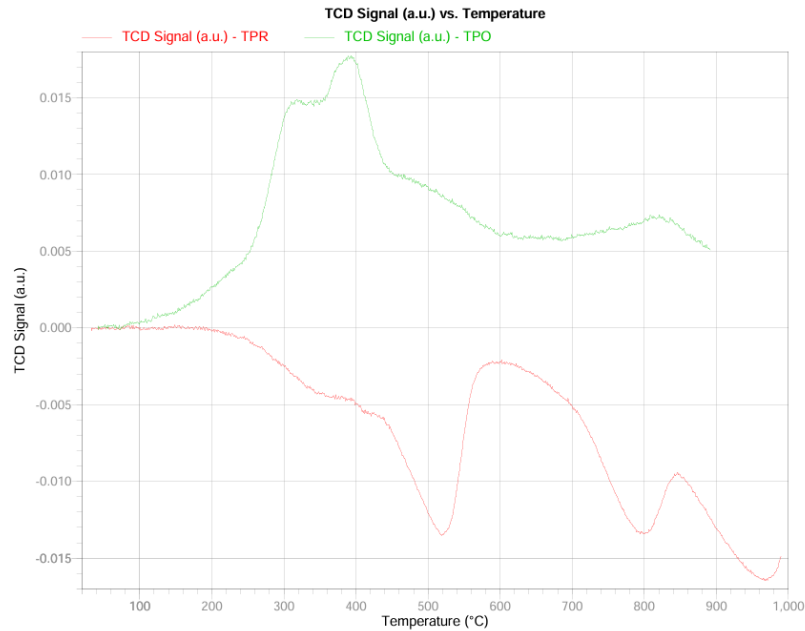


Figure 5.5: TPR-TPO plot of $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 400 °C: This minor reduction peak likely corresponds to the initial reduction of surface oxygen species.
- Peak at 500 °C: This reduction peak is associated with the reduction of Fe^{3+} to Fe^{2+} and Ni^{2+} to Ni^0 , the material begins to lose oxygen forming intermediate perovskite phases such as $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-x}$.
- Peak at 800 °C: This peak indicates a significant reduction, leading to the formation of highly reduced phases as $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{2-x}$. The sharp decrease in concentration suggests the complete reduction of the material.
- Peak at 950 °C: This smaller peak indicates additional reduction events at higher temperatures, possibly indicating the complete reduction of any remaining oxidized species and the formation of a fully reduced phase.

On the other hand, the TPO curve shows also different peaks.

- Peak at 300 °C: This significant oxidation peak is associated with the initial oxidation of Fe^{2+} to Fe^{3+} and Ni^0 to Ni^{2+} , forming intermediate oxidized phases.
- Peak at 400 °C: This peak suggests further oxidation phases, such as $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3+x}$, where the increase in concentration suggest the complete oxidation of the material. This is correct considering that perovskites materials are known to undergo substantial oxidation at temperatures around 400 °C.

Figure 5.6 shows the results for $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

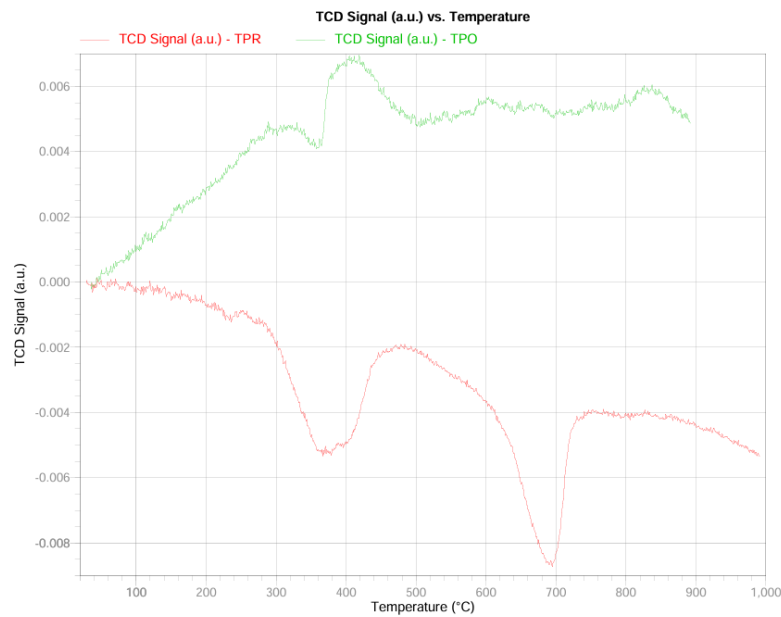


Figure 5.6: TPR-TPO plot of $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 200 °C: This minor reduction peak likely corresponds to the initial reduction of surface oxygen species.
- Peak at 350 °C: This reduction peak is associated with the reduction of Mn^{3+} to Mn^{2+} and Ni^{2+} to Ni^0 , the material begins to lose oxygen forming intermediate perovskite phases such as $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_{3-x}$.
- Peak at 700 °C: This peak indicates a significant reduction, leading to the formation of highly reduced phases as $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_{2-x}$. The sharp decrease in concentration suggests the complete reduction of the material.

On the other hand, the TPO curve shows also different peaks.

- Peak at 300 °C: This significant oxidation peak is associated with the initial oxidation of Mn^{2+} to Mn^{3+} and Ni^0 to Ni^{2+} , forming intermediate oxidized phases.
- Peak at 400 °C: This peak suggests further oxidation phases, such as $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_{3+x}$, where the increase in concentration suggest the complete oxidation of the material.
- Peak at 900 °C: This peak corresponds to a significant oxidation phase, indicating the formation of fully oxidized phases.

5.1.2.2 TCD concentration vs Time

The following analysis covers the six TCD concentration vs Time plot. The x-axis represent the time range of 0 to 200 minutes, while the y-axis represents the TCD concentration ranging from 4.60 to 5.00, with specific focus on the Temperature Programmed Reduction (TPR) and Temperature Programmed Oxidation (TPO) processes. The detailed analysis of each plot includes the identification and interpretation of all significant peaks.

The red curve represents the TPR process, it starts at high concentrations around 4.95, dips down and then rises back up slightly before sharply decreasing towards the end of the time range.

The green curve represents the TPO process, it starts at lower concentrations, dips down and then it increases again.

Figure 5.7 shows the results for $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

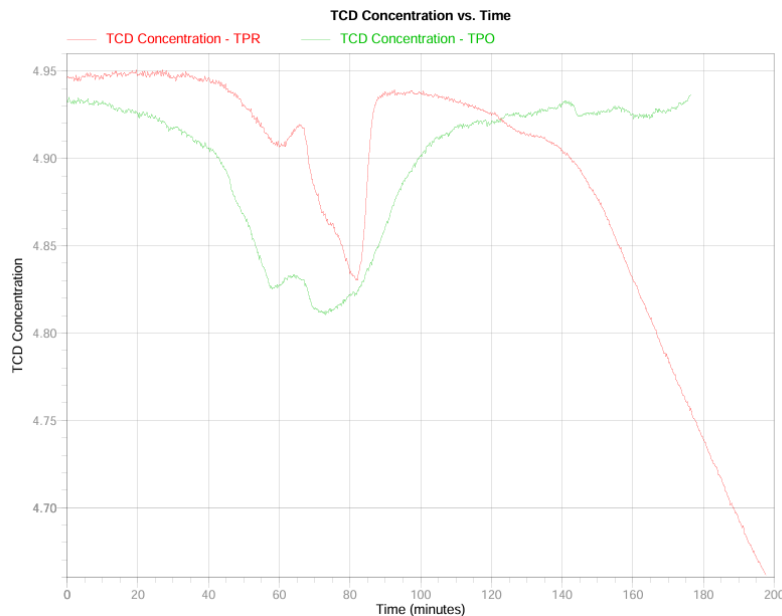


Figure 5.7: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows multiple significant changes.

- Initial Dip (0-60 minutes): The initial decrease in TCD concentration can be attributed to the reduction of Fe_2O_3 to Fe_3O_4 and NiO to Ni . These transitions typically occur at lower temperatures, around 300-400°C.
- Recovery Phase (60-120 minutes): The concentration gradually rises back towards the initial value, indicating the completion of the reduction reactions. This phase aligns with the reduction of Fe_3O_4 to FeO and further to metallic Fe , which occurs at higher temperatures, around 500-700°C.

- Sharp Decrease (Post-120 minutes): The sharp decrease after 120 minutes suggests a significant reduction event, possibly the reduction of residual oxides or the decomposition of the perovskite structure itself.

Analysis of TPO (Green Line):

- Initial Dip (0-60 minutes): The initial decrease in TCD concentration during TPO indicates the oxidation of metallic Fe and Ni back to their oxide forms. This is consistent with the literature, where oxidation typically occurs at temperatures around 300-400°C.
- Gradual Increase (60-200 minutes): The gradual increase in TCD concentration suggests the formation of stable oxide phases, such as Fe_2O_3 and NiO . This phase aligns with the literature on the oxidation of reduced perovskite materials, which occurs at higher temperatures, around 500-700°C.

Figure 5.8 shows the results for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

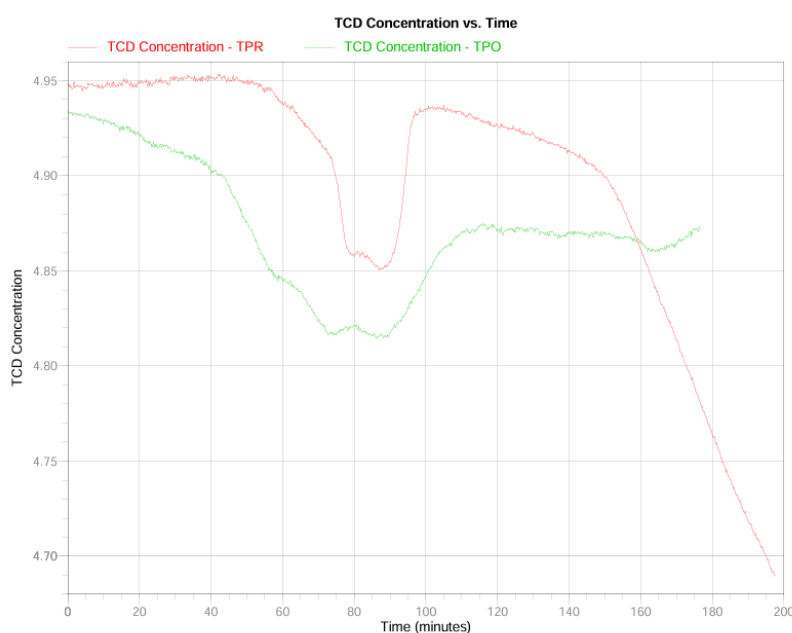


Figure 5.8: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

This sharp decrease suggests the reduction of Fe and Ni oxides. The TPR curve describes the behaviour:

- Initial Phase (0-80 minutes): The initial decrease in TCD concentration can be attributed to the reduction of Fe_2O_3 to Fe_3O_4 and NiO to Ni . These transitions typically occur at lower temperatures, around 300-400°C.
- Sharp Decrease (80-100 minutes): The sharp decrease around the midpoint indicates a significant reduction event, possibly the reduction of Fe_3O_4 to FeO and further to metallic Fe, which occurs at higher temperatures, around 500-700°C.

- Gradual Decrease (Post-100 minutes): The gradual decrease towards the end of the time range suggests the completion of the reduction reactions and the stabilization of the reduced phases.

Analysis of TPO (Green Line):

- Initial Phase (0-75 minutes): The initial decrease in TCD concentration during TPO indicates the oxidation of metallic Fe and Ni back to their oxide forms. This is consistent with the literature, where oxidation typically occurs at temperatures around 300-400°C.
- Sharp Decrease (75-100 minutes): The sharp decrease around the midpoint suggests a significant oxidation event, possibly the formation of Fe_2O_3 and NiO . This phase aligns with the oxidation of reduced perovskite materials, which occurs at higher temperatures, around 500-700°C.
- Stabilization (Post-100 minutes): The stabilization with minor fluctuations towards the end of the time range indicates the formation of stable oxide phases.

Figure 5.9 shows the results for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

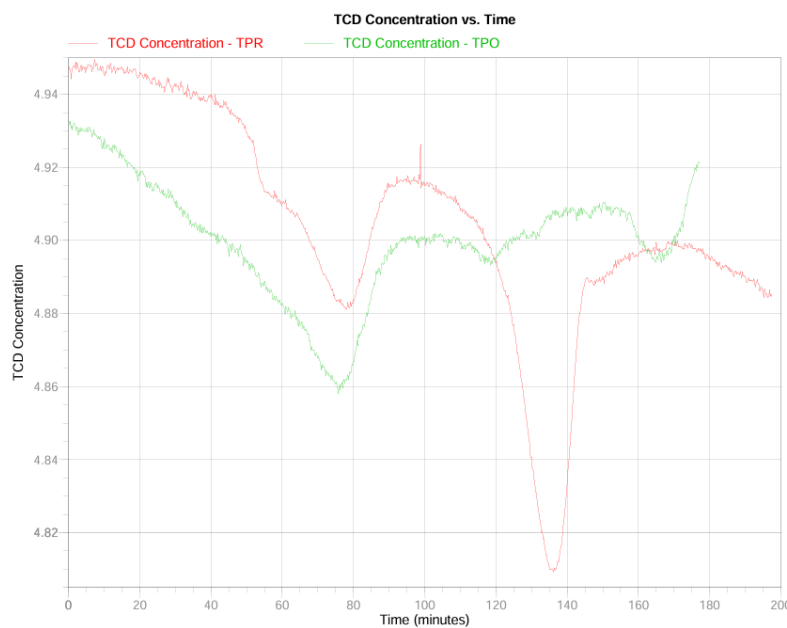


Figure 5.9: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Initial Phase (0-60 minutes): The gradual decrease in TCD concentration can be attributed to the initial reduction of MnO_2 to Mn_3O_4 and NiO to Ni . These transitions typically occur at lower temperatures, around 300-400°C.
- Sharp Drop (60-100 minutes): The sharp drop around the midpoint indicates a significant reduction event, possibly the reduction of Mn_3O_4 to MnO and further to metallic Mn , which occurs at higher temperatures, around 500-700°C.

- Peak at 140 Minutes: The peak at 140 minutes suggests a notable change in the reduction process. This could be due to the reduction of residual oxides or the decomposition of the perovskite structure itself. This peak indicates a significant reduction event, which can be attributed to several key factors, like the reduction of complex oxides. The timing of the peak suggests that it occurs at a specific temperature range, typically around 500-700°C. This temperature range is critical for the reduction of Mn and Ni oxides in perovskite structures. The peak indicates that the material undergoes significant structural changes at this temperature.

On the other hand, the TPO curve shows also different peaks.

- Initial Phase (0-80 minutes): The gradual decrease in TCD concentration indicates the initial oxidation of metallic Mn and Ni back to their oxide forms. This is consistent with the literature, where oxidation typically occurs at temperatures around 300-400°C.
- Sharp Rise (Around 100 minutes): The sharp rise around the midpoint suggests a significant oxidation event, possibly the formation of MnO_2 and NiO . This phase aligns with the oxidation of reduced perovskite materials, which occurs at higher temperatures, around 500-700°C.
- Final Decrease (Post-100 minutes): The decrease in TCD concentration towards the end of the time range indicates the formation of stable oxide phases. This stabilization phase is crucial for understanding the material's thermal behavior and its potential applications.

Figure 5.10 shows the results for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$ sample.

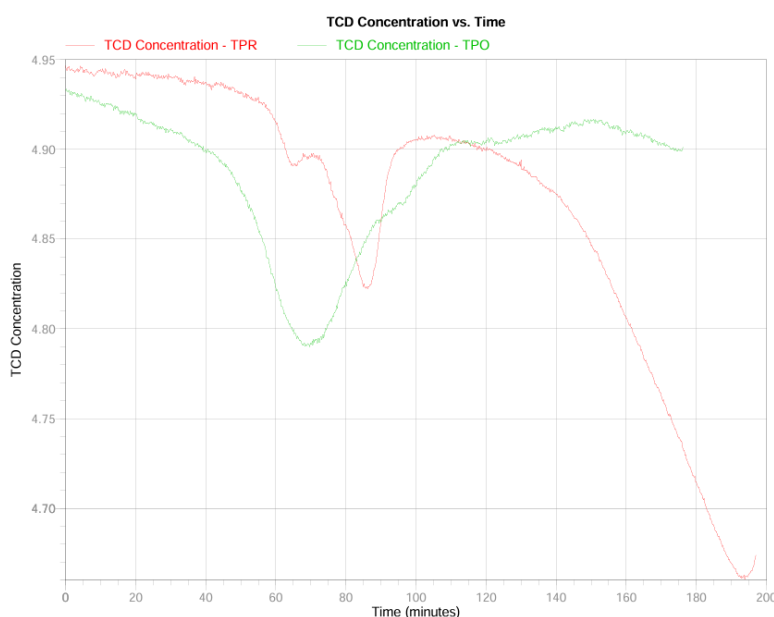


Figure 5.10: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$,

The TPR curve shows different peaks.

- Initial Phase (0-50 minutes): The concentration starts at approximately 4.95 and decreases sharply to about 4.82 around the 50-minute mark. This significant trough indicates the reduction of Fe_2O_3 to Fe_3O_4 and MnO_2 to Mn_3O_4 , typically occurring at lower temperatures (300-400°C).
- Intermediate Phase (50-100 minutes): After the initial trough, the concentration rises slightly but then drops again, reaching another low point around 100 minutes with a concentration of approximately 4.78. This phase suggests the partial reduction of Fe_3O_4 to FeO and Mn_3O_4 to MnO , occurring at higher temperatures (500-600°C).
- Final Phase (100-200 minutes): The concentration gradually increases and stabilizes around 4.85 towards the end of the time period. This final phase indicates the complete reduction of FeO to metallic Fe and MnO to metallic Mn, occurring at higher temperatures (600-700°C).

Analysis of TPO (Green Line):

- Initial Phase (0-50 minutes): The concentration starts at approximately 4.90 and reaches an initial peak around 50 minutes with a concentration of about 4.92. This peak indicates the initial oxidation of metallic Fe and Mn back to their oxide forms, typically occurring at temperatures around 300-400°C.
- Intermediate Phase (50-100 minutes): Following the initial peak, the concentration drops significantly, reaching its lowest point around 100 minutes with a value close to 4.75. This trough suggests the formation of stable oxide phases such as Fe_2O_3 and MnO_2 , occurring at higher temperatures (500-600°C).
- Final Phase (100-200 minutes): After the trough, the concentration rises sharply and peaks again at about 150 minutes with a concentration near 5. Towards the end of the time period, there is another sharp decline in concentration, ending at approximately 200 minutes with a value close to or below the initial concentration. This final phase indicates the stabilization of the oxidized phases.

Figure 5.11 shows the results for $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

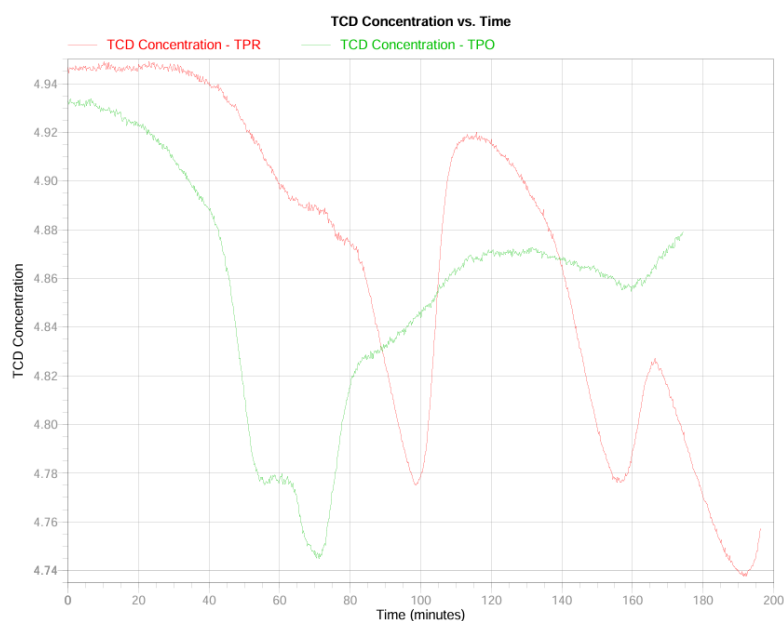


Figure 5.11: TPR-TPO plot of $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Initial High Concentration (0-50 minutes): The concentration starts high around 4.94, indicating the initial state of the sample.
- Decrease (50-100 minutes): The concentration decreases to around 4.78, suggesting the reduction of the sample as oxygen is removed.
- Fluctuations (100-170 minutes): The concentration fluctuates, indicating temporary stabilization or partial re-oxidation.
- Decrease Towards End (170-200 minutes): The concentration decreases again, indicating further reduction processes or the completion of the reduction.

Analysis of TPO (Green Line):

- First Peak (50-60 minutes): The concentration decreases to approximately 4.75. This peak suggests the formation of stable oxide phases such as Fe_2O_3 and NiO .
- Second Peak (Around 90 minutes): The concentration rises again to approximately 4.87. This peak suggest further oxidation of metallic phase to stable oxides.
- Third Peak (Around 160 minutes): The concentration decreases and then slightly increases again. This behaviour suggests additional oxidation processes or the stabilization of the oxidized phases. At the end, the TCD concentration reach the final value of 4.88.

Figure 5.12 shows the results for $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

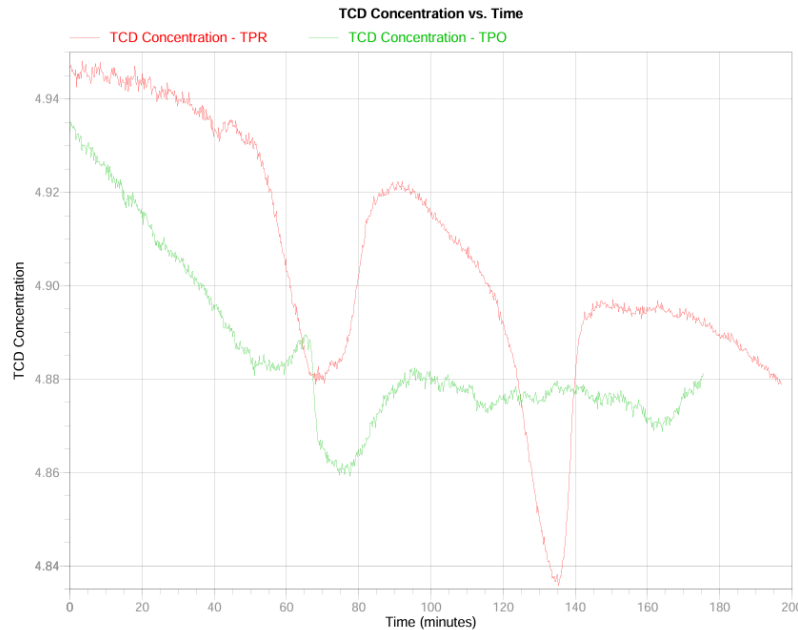


Figure 5.12: TPR-TPO plot of $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Initial Peak (0 - 60 minutes): The TCD concentration starts at approximately 4.93 and decreases sharply to about 4.88 at around 60 minutes. This initial decrease indicates the onset of reduction reactions, where oxygen is being removed from the sample. The sharp decline suggests a significant reduction event, likely involving the reduction of Mn_3O_4 to MnO , which typically occurs at lower temperatures.
- Secondary Peak (60 - 100 minutes): The concentration increases again to about 4.92 at around 100 minutes. The increase in concentration suggests the occurrence of further reduction reactions at higher temperatures. This peak may correspond to the reduction of NiO to Ni , which occurs at higher temperatures compared to Mn reduction.
- Subsequent Peaks (100 - 200 minutes): The concentration decreases slightly before increasing again towards the end of the time range. These fluctuations indicate additional reduction events, possibly involving the reduction of remaining metal oxides or the stabilization of the reduced phases.

TPO Curve Analysis (Green Line):

- Initial Peak (0 - 80 minutes): The TCD concentration starts at approximately 4.93 and decreases sharply to about 4.86 at around 80 minutes. This initial decrease indicates the oxidation of the reduced metal species back to their oxide forms. The sharp decline suggests a significant oxidation event, likely involving the oxidation of MnO to Mn_3O_4 .
- Secondary Peak (80 - 120 minutes): The concentration increases again to about 4.88 at around 120 minutes. The increase in concentration suggests the completion of oxidation

reactions and the stabilization of the oxidized phases. This peak may correspond to the oxidation of Ni to NiO.

- Subsequent Peaks (120 - 200 minutes): The concentration decreases slightly before increasing again towards the end of the time range. These fluctuations indicate additional oxidation events, possibly involving the oxidation of remaining reduced species or the stabilization of the oxidized phases.

5.1.2.3 TCD concentration vs Temperature

The following analysis covers the six TCD concentration vs Temperature plot. The x-axis represent the time range of 0 to 200 minutes, while the y-axis represents the TCD concentration ranging from 4.60 to 5.00, with specific focus on the Temperature Programmed Reduction (TPR) and Temperature Programmed Oxidation (TPO) processes. The detailed analysis of each plot includes the identification and interpretation of all significant peaks.

The red curve represents the TPR process, it starts at high concentrations around 4.95, dips down and then rises back up slightly before sharply decreasing towards the end of the time range.

The green curve represents the TPO process, it starts at lower concentrations, dips down and then it increases again.

Figure 5.13 shows the results for $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

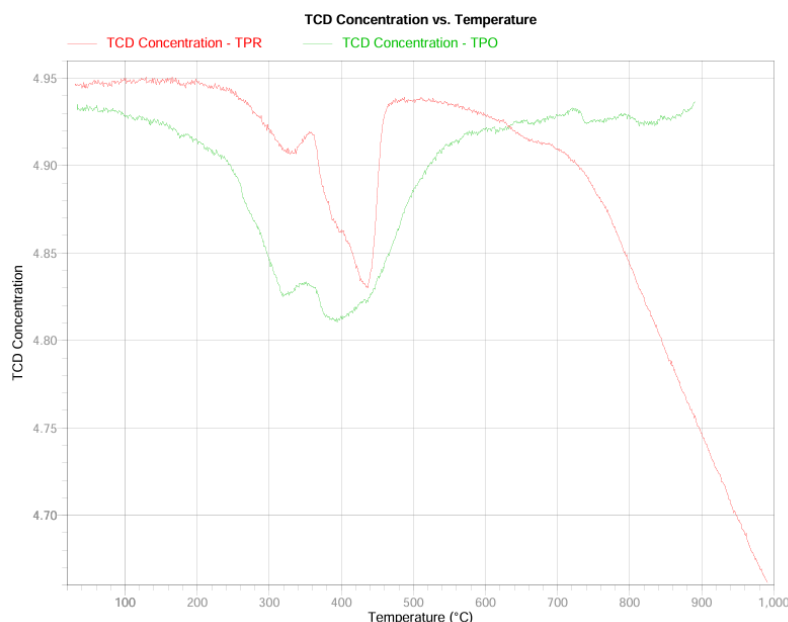


Figure 5.13: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 450 °C: This peak indicates the initial reduction phase where Fe^{3+} is reduced to Fe^{2+} and Ni^{2+} to Ni. The material begins to lose oxygen, forming intermediate phases such as $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-x}$.
- Peak at 700 °C: A significant reduction occurs and this sharp decrease in concentration suggests complete reduction of the perovskites.

On the other hand, the TPO curve shows also different peaks.

- Peak at ~300°C: This peak corresponds to the initial oxidation phase where Fe^{2+} is oxidized to Fe^{3+} and Ni^0 to Ni^{2+} , forming intermediate oxidized phases. From Literature, oxidation processes in similar materials typically begin at lower temperatures, around 300°C.
- Peak at ~400°C: This peak indicates a further oxidation phase, leading to the formation of highly oxidized phases. The increase and stabilization in concentration suggests the complete oxidation of the material.

Figure 5.14 shows the results for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

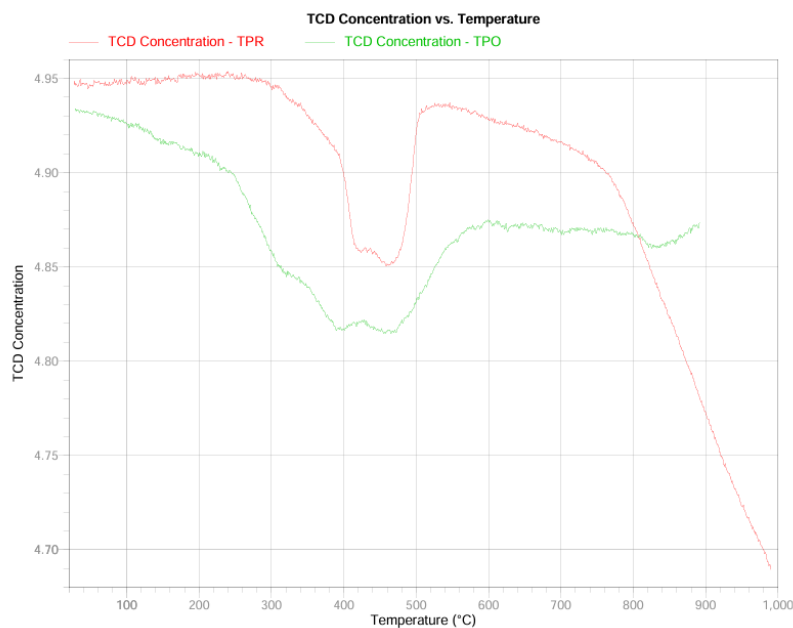


Figure 5.14: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 400-500 °C: This peak indicates the initial reduction phase where Fe^{3+} and Ni^{2+} are reduced. The material begins to lose oxygen, forming intermediate phases such as $\text{La}_{0.72}\text{Sr}_{0.18}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-x}$. Similar transition have been observed in perovskites materials where the reduction process starts at around 500 °C.
- Reduction at 700 °C: A significant reduction occurs and this sharp decrease in concentration suggests complete reduction of the perovskites.

On the other hand, the TPO curve shows also different peaks.

- Peak at 300 °C: This peak corresponds to the initial oxidation phase where Fe^{2+} is oxidized to Fe^{3+} and Ni to Ni^{2+} , forming intermediate oxidized phases. From Literature, oxidation processes in similar materials typically begin at lower temperatures, around 300°C.
- Peak at ~600 °C: This peak indicates a further oxidation phase, leading to the formation of highly oxidized phases. The increase and stabilization in concentration suggests the complete oxidation of the material.

Figure 5.15 shows the results for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

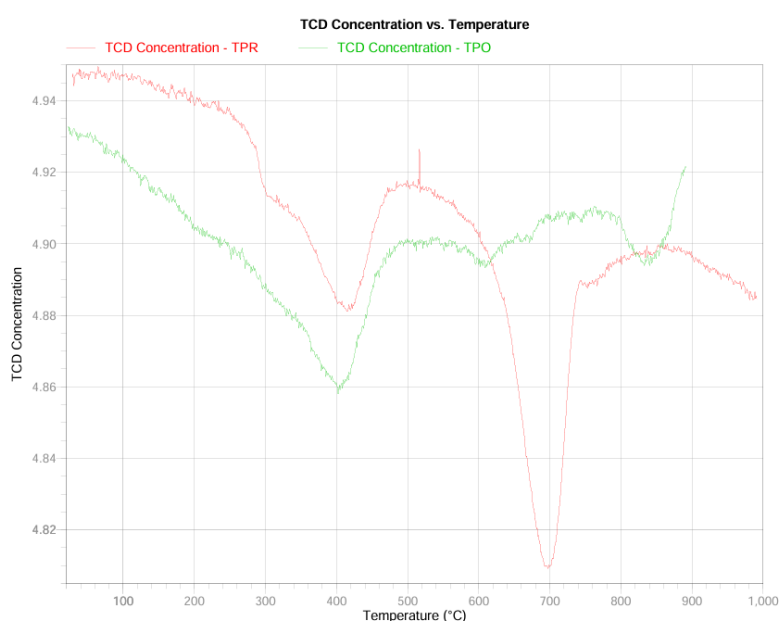


Figure 5.15: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 400 °C: This peak corresponds to the initial reduction phase where Fe^{3+} , Mn^{3+} , and Ni^{2+} are reduced, forming intermediate phases. Similar transitions have been observed in perovskite materials, where the reduction process starts around 500°C.
- Peak at 700 °C: This peak indicates a significant reduction, leading to the formation of highly reduced phases. The sharp decrease in concentration suggests the complete reduction of the material.

On the other hand, the TPO curve shows also different peaks.

- Peak at 400 °C: This peak corresponds to the initial oxidize phase where Mn^{2+} is oxidized to Mn^{3+} , and Ni to Ni^{2+} , forming intermediate phases.

- Peak at 850 °C: This peak indicates a further oxidation phase, leading to the formation of highly oxidized phases such as $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_{3+x}$.

Figure 5.16 shows the results for $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$ sample.

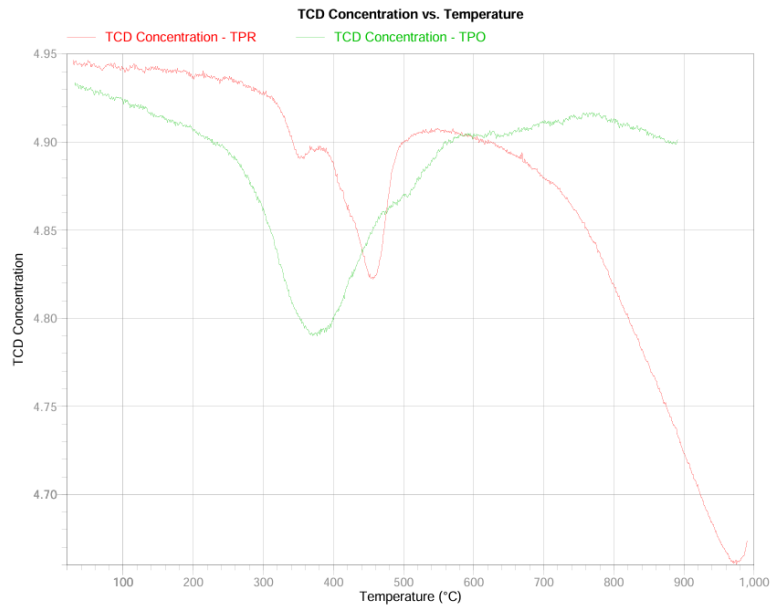


Figure 5.16: TPR-TPO plot of $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 450 °C: This peak corresponds to the initial reduction phase where Fe^{3+} , Mn^{3+} , and Ni^{2+} are reduced, forming intermediate phases such as $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_{3-x}$. Similar transitions have been observed in perovskite materials, where the reduction process starts around 500°C.
- Peak at 700 °C: This peak indicates a significant reduction, leading to the formation of highly reduced phases such as $\text{La}_{0.72}\text{Sr}_{0.09}\text{Ca}_{0.09}\text{Fe}_{0.45}\text{Mn}_{0.45}\text{Ni}_{0.1}\text{O}_{2-x}$. The sharp decrease in concentration suggests the complete reduction of the material.

On the other hand, the TPO curve shows also different peaks.

- Peak at 400 °C: This peak corresponds to the initial oxidize phase where Mn^{2+} is oxidized to Mn^{3+} , and Ni to Ni^{2+} , forming intermediate phases.
- After 600 °C: The concentration remains constant, suggesting the complete oxidation of the material.

Figure 5.17 shows the results for $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

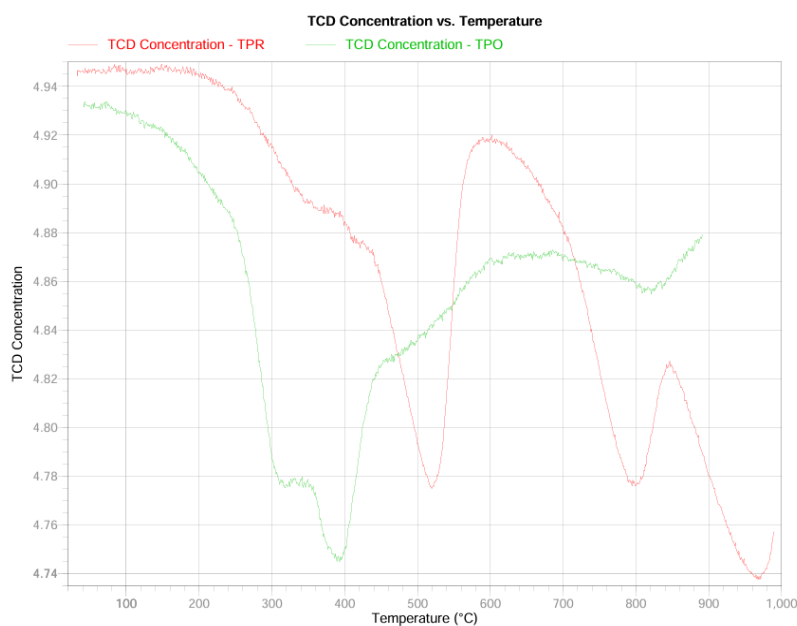


Figure 5.17: TPR-TPO plot of $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 100 °C: This first peak indicates the initial reduction process of the sample. This peak is likely due to the reduction of surface oxygen species or easily reducible metal oxides. The relatively low temperature suggests that these species are readily accessible and require minimal energy to undergo reduction.
- Peak at 200 °C: The second peak indicates further reduction processes. This peak suggests the reduction of more stable surface oxygen species or metal oxides that require slightly higher temperatures for reduction.
- Peak at 300 °C: The third peak can be attributed to the reduction of bulk metal oxides within the perovskite structure. This peak signifies a more substantial reduction process, involving deeper lattice sites and requiring higher temperatures to facilitate the reduction.
- Peak at 500 °C: A pronounced peak indicates significant reduction of bulk metal oxides. This peak reflects deeper reduction processes within the material's lattice structure.
- Peak at 800 °C: A smaller peak near 800 °C corresponds to deeper reduction processes involving more stable oxide species or secondary phases within the material. The higher temperature indicates that these species are less accessible and require more energy to be reduced.

On the other hand, the TPO curve shows also different peaks.

- Peak at 300 °C: A slight peak indicates the initial oxidation process of the sample. This peak suggests the re-oxidation of surface sites that were reduced during the TPR process. The relatively low temperature indicates that these sites are easily re-oxidized.
- Peak at 400 °C: The second oxidation peak indicates further oxidation processes. This peak suggests bulk re-oxidation processes where oxygen is reincorporated into the perovskite lattice. This peak reflects the re-oxidation of deeper lattice sites, requiring higher temperatures to facilitate the process.

Figure 5.18 shows the results for $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ sample.

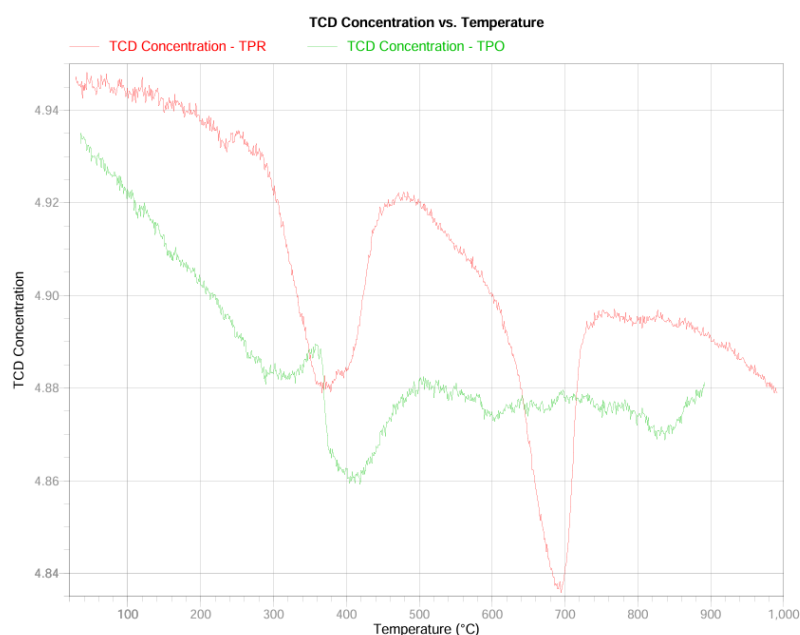


Figure 5.18: TPR-TPO plot of $\text{La}_{0.45}\text{Sr}_{0.36}\text{Ca}_{0.09}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$.

The TPR curve shows different peaks.

- Peak at 100 °C: This first peak signifies the beginning of the reduction process. This peak is likely due to the reduction surface oxygen species or easily reducible metal oxides. The low temperature indicates that these species are easily accessible and require minimal energy to be reduced.
- Peak at 300 °C: The second peak indicates further reduction of more stable surface oxygen species or metal oxides. This peak suggests the reduction of more stable surface oxygen species or metal oxides that require slightly higher temperatures for reduction.
- Peak at 350 °C: The third peak can be attributed to the reduction of bulk metal oxides within the perovskite structure. This peak signifies a more substantial reduction process, involving deeper lattice sites and requiring higher temperatures.

- Peak at 700 °C: A significant peak at around 700 °C may involve the reduction of highly stable oxide species or secondary phases within the material. The high temperature indicates that these species are very stable and require substantial energy for reduction.

The TPO curve shows also different peaks.

- Peak at 350 °C: A slight peak indicates the initial oxidation process of the sample. This peak suggests the re-oxidation of surface sites that were reduced during the TPR process. The relatively low temperature indicates that these sites are easily re-oxidized.
- Peak at 400 °C: The second oxidation peak indicates further oxidation processes. This peak suggests bulk re-oxidation processes where oxygen is reincorporated into the perovskite lattice.
- Peak at 850 °C: This small peak reflects the re-oxidation of deeper lattice sites, requiring higher temperatures to facilitate the process.

5.2 Results and consideration about redox reaction

The analysis of the different plots for the six compounds reveals significant insights into their redox properties. Each compound exhibits distinct reduction and oxidation behaviours, with multiple peaks indicating various redox events.

These findings are consistent with existing literature on similar perovskite-type oxides, highlighting the potential of these materials for catalytic applications. The comparison of the different compounds shows variations in the temperatures and times at which these redox events occur, suggesting differences in their catalytic efficiencies and stability.

5.2.1 Reduction phase

During the reduction phase, all compounds exhibit multiple peaks, indicating various stages of oxygen removal from the lattice. The initial reduction peaks, typically observed at lower temperatures (200-400 °C), correspond to the reduction of surface oxygen species and the reduction of transition metal oxides such as Fe^{3+} to Fe^{2+} , Mn^{4+} to Mn^{2+} , and Ni^{2+} to Ni. These initial peaks are crucial as they represent the onset of the reduction process, where the material begins to lose oxygen and transition metals start to change their oxidation states.

The subsequent peaks at higher temperatures (600-800 °C) suggest deeper lattice oxygen removal and the reduction of more stable oxygen species. These higher temperature peaks indicate that the material undergoes further reduction, affecting the more strongly bound oxygen atoms within the lattice. The variations in the reduction temperatures among the compounds indicate differences in their redox stability and the ease with which they undergo reduction. For instance, compounds with higher Sr content tend to show reduction peaks at slightly lower temperatures, suggesting enhanced reducibility.

This implies that the presence of Sr in the lattice may facilitate the reduction process, making the material more reactive at lower temperatures. Overall, the reduction phase highlights the complex interplay between the material's composition and its redox behavior, providing valuable insights into its catalytic potential.

5.2.2 Oxidation phase

The oxidation phase is characterized by multiple peaks indicating various stages of oxygen incorporation into the lattice. The initial oxidation peaks, typically observed at lower temperatures (300-500 °C), correspond to the oxidation of surface species and the re-oxidation of transition metals such as Fe^{2+} to Fe^{3+} , Mn^{2+} to Mn^{4+} , and Ni to Ni^{2+} . These initial peaks are significant as they represent the beginning of the oxidation process, where the material starts to gain oxygen and transition metals revert to their higher oxidation states. The subsequent peaks at higher temperatures (700-900 °C) suggest deeper lattice oxygen incorporation and the oxidation of more stable oxygen species.

These higher temperature peaks indicate that the material undergoes further oxidation, affecting the more strongly bound oxygen atoms within the lattice. The variations in the oxidation temperatures among the compounds indicate differences in their redox stability and the ease with which they undergo oxidation.

Compounds with higher Ca content tend to show oxidation peaks at slightly higher temperatures, suggesting enhanced stability during oxidation. This implies that the presence of Ca in the lattice may stabilize the material, making it less reactive at lower temperatures. Overall, the oxidation phase underscores the intricate relationship between the material's composition and its redox behavior, offering valuable insights into its catalytic efficiency and stability.

Conclusions and prospects

This study explored the synthesis, structural analysis, and redox characterization of lanthanum-based perovskite-type polycationic oxides, aiming to identify structure-function relationships that determine their catalytic performance. A wide range of compositions was systematically synthesized and investigated, focusing in particular on the effects of A- and B-site dopants such as Sr, Ca, Mn, and Ni. Through a comprehensive combination of classical and advanced characterization techniques, including Raman spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) analysis, and temperature-programmed reduction and oxidation (TPR/TPO), the research elucidated how modifications at the atomic level influence the physicochemical and catalytic behavior of the resulting materials. The use of an auto-combustion synthesis method enabled the preparation of homogeneous and phase-pure materials with relatively low heat demand, reinforcing the viability of scalable and cost-effective production routes and, thanks to this method, is possible to produce multicationic compositions with controlled stoichiometry.

The Raman spectroscopy results, though limited by the optical absorption of dark-colored Mn-containing samples, provided valuable insights into lattice vibrations and symmetry distortions in Fe-based compositions. While this highlights the technique's limitations for certain material classes, it also underscores the importance of selecting appropriate complementary methods in the study of complex oxides. The inability to capture meaningful Raman signals in highly absorbing samples suggests the need for the future implementation of alternative optical probes, such as infrared spectroscopy or resonant Raman techniques.

The thermogravimetric investigations contributed crucial information regarding the thermal decomposition and stability of the precursors and final oxides. The multi-step mass loss patterns observed during TGA reflect the decomposition of organic species from the auto-combustion synthesis method, followed by phase stabilization. These results provided process control parameters for optimizing synthesis conditions and achieving reproducible phase formation.

From a structural perspective, XRD analysis confirmed the successful formation of single-phase perovskites depending on dopant content and calcination parameters. The observation that La_xFeO_3 and La_xMnO_3 samples exhibited increased crystallinity and uniformity is noteworthy, as it underscores the role of La stoichiometry in stabilizing the crystal framework. BET analysis further supports these findings, showing that the samples had consistent specific surface areas, which suggests that textural properties, rather than intrinsic electronic or structural features, were the dominant factor. One of the most significant findings lies in the correlation between dopant distribution and redox behavior. The introduction of Sr and Ca into

the A-site of the perovskite lattice was shown to directly affect the thermal stability and oxygen mobility of the materials. Specifically, Ca doping induced a shift of oxidation peaks toward higher temperatures during TPO analysis, which suggests enhanced thermal robustness and stronger metal-oxygen bonds. Conversely, Sr incorporation facilitated reduction processes at lower temperatures, indicative of increased reducibility and improved oxygen vacancy formation. These distinct effects confirm the strategic potential of A-site doping in fine-tuning the redox properties of perovskite catalysts. Additionally, B-site substitution with Ni and Mn demonstrated a profound impact on the electronic environment of the active sites, thereby enhancing redox cycling capabilities. Mixed B-site perovskites exhibited broadened TPR/TPO profiles, a hallmark of multivalent species and increased surface reactivity. The synergistic interaction between different B-site cations contributed to the generation of more labile oxygen species, ultimately facilitating oxidation-reduction mechanisms that are essential for catalytic applications.

The temperature-concentration and temperature-signal correlations derived from TPR/TPO data allowed the identification of intermediate redox species, which are hypothesized to be responsible for transient surface activity. The detection of such species, and their evolution as a function of dopant composition, represents a valuable step forward in the mechanistic understanding of perovskite catalysis.

Continued research and innovation in this field hold the promise of unlocking the full potential of perovskites, paving the way for more sustainable and efficient catalytic technologies.

In conclusion, this research has contributed to the advancement of knowledge in the field of catalysis, offering valuable insights into the design and optimization of lanthanum-based perovskite catalysts. The findings presented in this thesis pave the way for future studies aimed at further enhancing the catalytic performance of these materials and exploring their potential applications in various industrial processes.

Bibliography

- [1] A. Zaki, J. Xu, G. Stoclet, S. Casale, J.-P. Dacquin, P. Grancer. *Microporous and Mesoporous Materials*; 2015.
- [2] George, Gibin & Ede, Sivasankara & Luo, Zhiping. *Fundamentals of Perovskite Oxides: Synthesis, Structure, Properties and Applications*. 2020.
- [3] Xavier Carrier¹, Sébastien Royer², Eric Marceau³. *Synthesis of metal oxide catalysts*.
¹Laboratoire de Réactivité de Surface, Sorbonne Université, Université P. & M. Curie, Paris, France. ²Université de Lille, CNRS, ENSCL, Centrale Lille, Lille, France.
³Université d'Artois, Unité de Catalyse et de Chimie du Solide, Lille, France; 2018.
- [4] Anke Schön. *Development of alternative 3-way catalysts: Fe-based perovskites with low noble metal content*. Université Lille 1, Sciences et Technologies, UCCS; 2015.
- [5] Gurvinder Singh Bumbbrah, Rakesh Moham Sharma. Egyptian Journal of Forensic Sciences. *Raman spectroscopy – Basic principle, instrumentation and selected applications for the characterization of drugs of abuse*.
- [6] Settle FA. *Handbook of instrumental techniques for analytical chemistry*. National Science Foundation, Arlington, 1997
- [7] DA Skoog, FJ Holler, SR Crouch – Cengage learning, 2019. Textbook “*Principles of instrumental analysis*”.
- [8] Chalmers JM, Edwards HGM, Hargreaves MD. *Infrared and Raman spectroscopy in forensic science*. 1st ed. United Kingdom: John Wiley & Sons; 2012.
- [9] Willard HH, Meritt Jr LL, Dean JJ, Settle Jr FA. *Instrumental methods of analysis*. 7th ed. New Delhi: CBS Publisher & Distributors; 1988.
- [10] Smith E, Dent G. *Modern Raman spectroscopy: a practical approach*. England, Chichester: John Wiley & Sons; 2005.
- [11] McCreery RL. *Raman spectroscopy for chemical analysis*. New York: John Wiley & Sons, Inc.; 2000.
- [12] Smith E, Dent G. *Modern Raman spectroscopy – a practical approach*. Chichester: John Wiley & Sons Ltd.; 2005.
- [13] Pandey, D.K., Kagdada, H.L., Sanchora, P., Singh, D.K. (2021). *Overview of Raman Spectroscopy: Fundamental to Applications*. Progress in Optical Science and Photonics, vol 13. Springer, Singapore; 2021.
- [14] Singh, D.K., Pradhan, M., Materny, A. (eds) *Modern Techniques of Spectroscopy*. Progress in Optical Science and Photonics, vol 13. Springer, Singapore; 2021.

- [15] Xin Hou, Jianxing Ren, Fangqin Li, Chuang Ma, Xiaotong Zhang, Haijun Feng. School of Energy and Mechanical Engineering, Shanghai University of Electric Power, Shanghai 200090, China. *Research progress of perovskite materials as catalysts*.
- [16] J. Rouquerol, D. Avnir, C. W. Fairbridge, D. H. Everett, J. M. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing and K. K. Unger. *Pure and applied chemistry*. Physical and biophysical chemistry division commission on colloid and surface chemistry including catalysis; 1994.
- [17] G. Parravano. *Journal of the American Chemical Society*; 1953
- [18] Luis F Garcia-Herrer & Henry. *Thermogravimetric analysis (TGA)*; 2020.
- [19] T.C. Vaimakis. *Thermogravimetry (TG) or Thermogravimetric Analysis (TGA), Introduction edn, Summer School for Thermal Analysis Techniques*. Faculty of Science, Aristotle University of Thessaloniki; 2013.
- [20] M. Pizzoli. *XIII Tecniche di caratterizzazione: analisi termica, in Atti del XVIII Convegno-Scuola AIM su Materiali Polimerici Cristallini e Liquido Cristallini*. Gargnano (BS), Pacini Editore, Pisa; 1999.
- [21] A. Gregorova. *Application of Differential Scanning Calorimetry to the Characterization of Biopolymers, Applications of Calorimetry in a Wide Context - Differential Scanning Calorimetry, Isothermal Titration Calorimetry and Microcalorimetry*. A. A. Elkordy (Ed.). InTech, Rijeka, Croatia; 2013.
- [22] E. Gmelin, S. M. Sarge. *Calibration of differential scanning calorimeters*. Pure & Appl. Chem., 67, 1789-1800; 1995.
- [23] V. Tsanakis, D. N. Bikiaris, et al.. *Synthesis, properties and thermal behavior of poly(decylene-2,5-furanoate): a biobased polyester from 2,5-furan dicarboxylic acid*. RSC Adv., 5, 74592-74604; 2015.
- [24] A. J. Müller, M. L. Arnal. *Thermal fractionation of polymers*. Prog. Polym. Sci., 30, 559–603; 2005.
- [25] S. M. Sarge, G.W. H. Höhne, W. Hemminger. *Recent Developments*. in Ref. 2c, Cap. 8, pp. 213-228; 2023.
- [26] Andrei A. Bunaciua, Elena gabriela Udriștioiub & Hassan Y. Aboul-Eneinc. *X-Ray Diffraction: Instrumentation and Applications*. Critical Reviews in Analytical Chemistry; 2015.
- [27] University of Pennsylvania. *XRD basics*. Graphical Tools for X-Ray Data Analysis; 2024
- [28] R. Rakowski, G. Golovin, J. O’Neal, J. Zhang, P. Zhang, B. Zhao, M. D. Wilson, M. C. Veale, P. Seller, S. Chen, S. Banerjee, D. Umstadter & M. Fuchs. *Single-shot structural analysis by high-energy X-ray diffraction using an ultrashort all-optical source*. Scientific report; 2017.
- [29] Nitadori, T. *Recent advances of lanthanum-based perovskite oxides for catalysis*. Journal of Catalysis; 1986.

- [30] Mefford, J. T., Hardin, W. G., & Dai, S. *Anion charge storage through oxygen intercalation in LaMnO_3 perovskite pseudocapacitor electrodes*. *Nature Materials*, 13; 2014.
- [31] Mueller, D. N., Machala, M. L., & Bluhm, H. *Redox activity of surface oxygen anions in oxygen-deficient perovskite oxides during electrochemical reactions*. *Nature Communications*; 2015.
- [32] Bockris, J. O'M., Otagawa, T., & Young, V. *Solid state surface studies of the electrocatalysis of oxygen evolution on perovskites*. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*; 1983.
- [33] Vojvodic, A., & Nørskov, J. K. *Optimizing Perovskites for the Water-Splitting Reaction*. *Science*; 2011.
- [34] G. H. Jonker, J. H. van Santen. *Ferromagnetic Compounds of Manganese with Perovskite Structure*. *Physica*, vol. 16, pp. 337-349; 1950.
- [35] Kobayashi, K. I., Kimura, T., Tomioka, Y., Sawada, H., & Terakura, K. *Room-temperature magnetoresistance in an oxide material with an ordered double-perovskite structure*. *Nature*; 1998.
- [36] Bednorz, J. G., & Müller, K. A. *Possible high T_c superconductivity in the Ba-La-Cu-O system*. *Zeitschrift für Physik B Condensed Matter*, 64, 1986.
- [37] Tarancón, A., Burriel, M., Santiso, J., Skinner, S. J., & Kilner, J. A. *Advances in layered oxide cathodes for intermediate temperature solid oxide fuel cells*. *Journal of Materials Chemistry*, 20; 2010.
- [38] Suntivich, J., May, K. J., Gasteiger, H. A., Goodenough, J. B., & Shao-Horn, Y. *A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles*. *Science*, 334; 2011.
- [39] Xu, X., Xu, X., & Sun, H. *Recent advances in layered $\text{Li}(\text{Ni, Mn, Co})\text{O}_2$ cathode materials for lithium-ion batteries*. *Journal of Materials Chemistry A*, 2; 2014.
- [40] Park, S., Choi, W., & Kim, S. *Photocatalytic activity of $\text{BaTi}_{0.85}\text{Sn}_{0.15}\text{O}_3$ perovskite in water splitting and pollutant degradation*. *Catalysis Communications*, 16; 2011.
- [41] Sahner, K., Kaspar, M., & Moos, R. *High-temperature operando spectroscopy on a semiconducting mixed potential gas sensor*. *Sensors and Actuators B: Chemical*, 139; 2009.
- [42] Slavney, A. H., Hu, T., Lindenberg, A. M., & Karunadasa, H. I. *A Bismuth-Halide Double Perovskite with Long Carrier Recombination Lifetime for Photovoltaic Applications*. *Journal of the American Chemical Society*, 138; 2016.
- [43] Singh, K., Chaudhary, S., & Choudhary, G. R. *Enhanced nonlinear optical properties of $\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$ thin films*. *Journal of Applied Physics*, 115; 2014.
- [44] H. Arai, T. Yamada, K. Eguchi, T. Seiyama. *Applied Catalysis*. 26, 265–276; 1986.

- [45] L. Zhang, Y. Zhang, J. Deng, H. Dai. *Journal of Natural Gas Chemistry* 21, 69–75; 2012.
- [46] R. J. H. Voorhoeve. *Advanced Materials in Catalysis: Perovskite-related oxides as oxidation- reduction catalysts*. (Ed.: N. Y. Academic Press), ISBN: 012147450X 9780121474508, James Joseph Burton and Robert L. Garten, 1977.
- [47] Y. Zhang-Steenwinkel, J. Beckers, A. Blikkv. *Applied Catalysis A: General*. 235 (1-2), 79–92; 2002
- [48] H. He, H. X. Dai, C. T. Au. *Catalysis Today*. 90, 245–254; 2004.
- [49] G. Pecchi, M. G. Jiliberto, A. Buljan, E. J. Delgado. *Solid State Ionics*. 187, 27–32; 2011.
- [50] B. P. Barbero, J. A. Gamboa, L. E. Cadús. *Applied Catalysis B: Environmental*. 65(1-2), 21–30; 2006.
- [51] S. Royer, D. Duprez, F. Can, X. Courtois, C. Batiot-Dupeyrat, S. Laassiri, H. Alamdari. *Chemical Reviews*. 114, 10292–10368; 2014.
- [52] R. Zhang, H. Alamdari, S. Kaliaguine. *Journal of Catalysis*. 242, 241–253; 2006.
- [53] N. Mizuno, Y. Fujiwara, M. Misono. *Journal of the Chemical Society Chemical Communications*. 5, 316–318; 1989.
- [54] G. Saracco, F. Geobaldo, G. Baldi. *Applied Catalysis B: Environmental*. 20 (4), 277–288; 1999.
- [55] Sylvain Keav, Santhosh Kumar Matam, Davide Ferri and Anke Weidenkaff. *Structured Perovskite-Based Catalysts and Their Application as Three-Way Catalytic Converters—A Review*. Catalysts Journal; 2014.
- [56] Taylor, K.C. *Automobile Catalytic Converters*. Stud. Surf. Sci. Catal. 30, 97–116; 1987.
- [57] Trovarelli, A. *Catalysis by Ceria and Related Materials*, 1st ed.; Imperial College Press: London, UK; 2002.
- [58] Forster P., Ramaswamy V., Artaxo P., Bernsten T., Betts R. et al. *Changes in Atmospheric Constituents and in Radiative Forcing. In Climate Change: The Physical Science Basis*. Cambridge, UK; New York, NY, USA, pp. 129–234; 2007.
- [59] Fino D., Russo N., Saracco G., Specchia V. *Supported Pd-perovskite catalyst for CNG engines' exhaust gas treatment*. Prog. Solid State Chem, 35, 501–511; 2007.
- [60] Yao H.C., Japar S., Shelef M. *Surface Interactions in the System Rh/Al₂O₃*. J. Catal, 50, 407–418; 1977.
- [61] Libby W.F. *Promising Catalyst for Auto Exhaust*. Science, 171, 499–500; 1971.
- [62] Voorhoeve R.J.H., Remeika J.P., Freeland P.E., Matthias, B.T. *Rare-Earth Oxides of Manganese and Cobalt Rival Platinum for the Treatment of Carbon Monoxide in Auto Exhaust*. Science, 177, 353–354; 1972.
- [63] Voorhoeve R.J.H., Remeika J.P., Freeland P.E., Matthias, B.T. *Rare-Earth Oxides of Manganese and Cobalt Rival Platinum for the Treatment of Carbon Monoxide in Auto Exhaust*. Science, 180, 62–64; 1973.

- [64] Voorhoeve R.J.H., Remeika J.P., Trimble L.E. *Perovskites containing ruthenium as catalysts for nitric oxide reduction*. Mater. Res. Bull. 9, 1393–1404; 1974.
- [65] Voorhoeve R.J.H., Trimble L.E. *Exploration of perovskite-like catalysts: Ba₂CoWO₆ and Ba₂FeNbO₆ in NO reduction and CO oxidation*. Mater. Res. Bull. 9, 655–666; 1974.
- [66] Gallagher P.K., Johnson D.W. Jr., Schrey F. *Studies of some supported perovskite oxidation catalysts*. Mater. Res. Bull. 9, 1345–1352; 1974.
- [67] Tabata K., Misono M. *Elimination of pollutant gases—Oxidation of CO, reduction and decomposition of NO*. Catal. Today. 8, 249–261; 1990.
- [68] Guillaume N., Primet M. *Three-Way Catalytic Activity and Oxygen Storage Capacity of Perovskite LaMn_{0.976}Rh_{0.024}O_{3+δ}*. J. Catal. 165, 197–204; 1997.
- [69] Tanaka H. *An intelligent catalyst: The self-regenerative palladium-perovskite catalyst for automotive emissions control*. Catal. Surv. Asia. 9, 63–74; 2005.
- [70] Kim C.H., Qi G., Dahlberg K., Li W. *Strontium-Doped Perovskites Rival Platinum Catalysts for Treating NO_x in Simulated Diesel Exhaust*. Science. 327, 1624–1627; 2010.
- [71] Goldschmidt, V.M. *Die Gesetze der Krystallochemie*. Die Naturwissenschaften. 8, 477–485; 1926.
- [72] S. Keav, S. Matam, D. Ferri, A. Weidenkaff. *Catalysts* 4. 226–255; 2014.
- [73] Association for Emissions Control by Catalyst, TWC converter, 2015.
<http://www.aecc.be/en/Technology/Catalysts.html>
- [74] J. Kašpar, P. Fornasiero, N. Hickey. *Catalysis Today*. 419–449; 2003.
- [75] K. C. Taylor, J. C. Schlatter, *Journal of Catalysis*. 63, 53–71; 1980.
- [76] T. Horiuchi, Y. Teshima, T. Osaki, T. Sugiyama, K. Suzuki, T. Mori, *Catalysis Letters*. 62, 107–111; 1999.
- [77] A. F. Holleman, E. Wiberg, N. Wiberg. *Lehrbuch der Anorganischen Chemie*. 101st ed., Walter de Gruyter; 1995.
- [78] R. Di Monte, J. Kašpar. *Catalysis Today*. 100, 27–35; 2005.
- [79] E. S. J. Lox. *Handbook of Heterogeneous Catalysis*. Wiley-VCH Verlag GmbH & Co. KGaA. Chapter Part 11. Environmental Catalysis – 11.2 Automotive Exhaust Treatment; 2008.
- [80] L. G. Tejuca, J. L. G. Fierro. *Advances in Catalysis*. 36, 237–328; 1989.
- [81] European Commission, EU challenges China's export restrictions on rare earths, <http://europa.eu/rapid/pressReleasesAction.do?reference=MEMO/12/182>.
- [82] European Commission, WTO Appellate Body rules against Chinese restrictions on access to rare earths and other raw materials; 2014.
<http://trade.ec.europa.eu/doclib/press/index.cfm?id=1147>
- [83] Süddeutsche.de, China gibt Handel mit Seltenen Erden frei; 2015.

- [84] <http://www.sueddeutsche.de/wirtschaft/wichtiger-rohstoff-china-gibt-handel-mit-seltenen-erden-frei-1.2291728>.
- [85] Anke Schön, Jean-Philippe Dacquin, Pascal Granger, Christophe Dujardin. *Nonstoichiometric $\text{La}_{1-y}\text{FeO}_3$ perovskite-based catalysts as an alternative to commercial three-way catalysts? Impact of doping with Cu and Rh.*
- [86] A. Delmastro, D. Mazza, S. Ronchetti, M. Vallino, R. Spinicci, P. Broveto, M. Salis. *Synthesis and characterization of non-stoichiometric LaFeO_3 perovskite.*
- [87] Xing Liu, Shiyu Wang, Yixin Liao, Mengni Lei, Xiuzhong Fang, Xianglan Xu, Xiang Wang. *La/Mn molar ratio tuning the activity of La–Mn perovskites for CO and propane oxidation.*
- [88] Jiahao Chena, Meiqing Shena, Xinquan Wanga, Gongshin Qic, Jun Wanga, Wei Lic. *The influence of non-stoichiometry on LaMnO_3 perovskite for catalytic NO oxidation.*
- [89] J.X. Flores-Lasluisa, F. Huerta, D. Cazorla-Amoros, E. Morallon. *Manganese oxides/ LaMnO_3 perovskite materials and their application in the oxygen reduction reaction.*
- [90] Eman Abdul Rahman Assirey. *Perovskite synthesis, properties and their related biochemical and industrial application.* 2019.
- [91] Daniel Navas, Sandra Fuentes, Alejandro Castro-Alvarez and Emigdio Chavez-Angel. *Review on Sol-Gel Synthesis of Perovskites and Oxide Nanomaterials.* 2021.
- [92] Briggs, D., & Seah, M. P.. *Practical Surface Analysis: Auger and X-ray Photoelectron Spectroscopy.* John Wiley & Sons. 1990,
- [93] Hüfner, S. *Photoelectron Spectroscopy: Principles and Applications.* Springer Science & Business Media. 2013.
- [94] Tapan Kumar Giri. *Chapter 16 - Solid lipid nanoparticles for the delivery of drug molecules, Materials for Biomedical Engineering.* 551-576; 2019.
- [95] Watts, J. F., & Wolstenholme, J.. *An Introduction to Surface Analysis by XPS and AES.* John Wiley & Sons. 2003.
- [96] Hidden ISOHEMA, What Instruments is Used for BET analysis?
<https://hiddenisochema.com/news-press/what-instrument-is-used-for-bet-analysis>
- [97] BET surface area analysis
<https://www.slideshare.net/slideshow/bet-surface-area-analysis/107630918>
- [98] Yong-Jin Kim, Heung-Sik Park and Chan-Ho Yang. *Raman imaging of ferroelastically configurable Jahn–Teller domains in LaMnO_3 .* 2021.

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