

Synthesis, physic and structural characterization of rare-earth oxynitrides REFeO_{3-x}N_x (RE=La, Pr, Nd, Sm)

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Universidad Nacional de Colombia Facultad de Minas, Departamento de Materiales Medellín, Colombia 2015

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No Retreat, No Surrender.

New world Pictures

This is to my three ladies:

To my Mom, thanks for giving me your wings to fly, To Daniela, my angel who guides me and protects me from up in the sky. And to Angela, the light that makes my days shine.

"It is the time you have wasted for your rose that makes your rose so important."

- Antoine de Saint-Exupéry, The Little Prince

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Abstract

This work studies the synthesis of the perovskite oxynitrides REFeO_{3-x}N_x (RE=La, Pr, Nd, Sm). For comparison purposes and as precursors in some of the synthesis reactions studied; their respective oxides, the orthoferrites REFeO₃ (RE=La, Pr, Nd, Sm), have been synthetized by the self-combustion glycine-nitrate process. The oxides synthetized were characterized by XRD, Rietveld refinement, SEM and EDS in order to determine their purity and correct stoichiometry. These measurements establish that all the oxides synthetized crystallize as distorted perovskites with the orthorhombic space group *pbnm* and due to the synthesis method are highly porous materials with an open flakes morphology. Meanwhile the FT-IR measurements determined the presence of the bond Fe-O and the Mössbauer spectra of these oxides confirmed the location of iron in the structure in equivalent octahedral sites with oxidation state Fe⁺³. The thermal analysis results of the DSC and TGA curves showed a high content of mobile oxygen in the structure of the oxides. Moreover the magnetics curves of M vs H at 300K revealed antiferromagnetic behavior of the compounds, confirmed by the ZFC and FC curves, where also a weak ferromagnetism was observed at low temperatures. The electrical resistivities of the oxides were calculated by V vs I curves to be among the 0.2 and 4.9 M Ω cm. Finally the polarization loops determined ferroelectric behavior for the four oxides with the greatest intensity found for the LaFeO₃ composition.

For the synthesis of the perovskite oxynitrides $REFeO_{3-x}N_x$ (RE=La, Pr, Nd, Sm) different synthesis methods were evaluated. The thermal ammonolysis of the orthoferrites $REFeO_3$ (RE=La, Pr, Nd, Sm) showed the reduction of iron in the structure to lower oxidation states promoting the formation of secondary oxides phases even at low temperatures and short reaction times. Moreover the nitriding tests by ammonia microwave-induced plasma (MIP) of the orthoferrites despite of the lower temperatures showed the reduction of iron in the structure too, indicating that in the same way that the ammonia reactivity increases due to the plasma state, the reactivity of the reduction potential of hydrogen also increases.

Meanwhile solid state reactions under nitrogen atmosphere using oxide or nitrides precursors and urea as nitriding agent, result in the formation of the orthoferrites but any nitridation, which means the ammonia produced during the decomposition of urea is not efficient enough to promote the change in oxidation state of the iron for the formation of the oxynitride. Tests using urea and the orthoferrites as precursors in a high energy ball milling showed the formation of undesired carbonate phases due to the high energy collisions, indicating that the urea is not an adequate nitriding agent for this synthesis technique. Additionally a sol gel approximation to the synthesis of oxynitrides yielded mixtures of secondary oxides with high content of organic residues; where in order to obtain the perovskite structure calcinations under oxygen or air atmosphere around the 700 °C had to be performed. In this way the orthoferrites were obtained but without nitridation. Finally as a complementary work presented as an annex in this book, from the transmission Mössbauer spectra recorded at room-temperature, the relative recoilless F-factor of the REFeO₃ (RE =La, Pr, Nd, Sm) compounds were estimated. Applying a method based on the correct determination of the two subspectral areas present in a mixture of known amounts of the

compound under study and a standard sample (α -Fe).

Keywords: Oxynitride, Perovskite, Orthoferrite, Rare-earth, Self-Combustion

Resumen

En este trabajo se estudia la síntesis de los oxínitruros con estructura perovskita $REFeO_{3-x}N_x$ (RE=La, Pr, Nd, Sm). Para fines de comparación y como precursores de algunas de las reacciones estudiadas; sus óxidos respectivos, las ortoferritas REFeO₃ (Re=La, Pr, Nd, Sm), fueron sintetizadas por el proceso de auto-combustión de nitratos y glicina. Los óxidos sintetizados fueron caracterizados mediante XRD, refinamiento Rietveld, SEM y EDS para determinar su pureza y adecuada estequiometria. Estas medidas establecieron que todos los óxidos sintetizados cristalizan como perovskitas distorsionadas con el grupo espacial ortorrómbico *pbnm* y que debido al método de síntesis son materiales altamente porosos que presentan una morfología de hojuelas abiertas. Por su parte las medidas FT-IR determinaron la presencia del enlace Fe-O y los espectros Mössbauer de estos óxidos confirmaron la ubicación del hierro en la estructura en sitios octaedrales en el estado de oxidación Fe⁺³. A su vez las curvas de análisis térmico de DSC y TGA mostraron que estos óxidos presenta un alto contenido de oxigeno móvil en su estructura. Las curvas magnéticas M vs H a 300K determinaron un comportamiento antiferromagnético de los compuestos, el cual fue confirmado en las curvas de ZFC y FC donde además se observó un débil ferromagnetismo a bajas temperaturas. Las resistividades eléctricas de los óxidos fueron calculadas mediante curvas V vs I donde se obtuvieron valores entre los 0.2 y 4.9 M Ω ·cm. Finalmente las curvas de polarización permitieron determinar un comportamiento ferroeléctrico en los cuatro compuestos con una mayor intensidad para la composición LaFeO₃.

Para la síntesis de los oxínitruros tipo perovskita REFeO_{3-x}N_x (RE=La, Pr, Nd, Sm) diferentes métodos de síntesis fueron evaluados. La amonólisis térmica de las ortoferritas REFeO₃ (RE=La, Pr, Nd, Sm) mostró la reducción del hierro en la estructura a estados de oxidación más bajos promoviendo la formación de fases de óxidos secundarios incluso a bajas temperaturas y cortos tiempos de reacción. Por otro lado las pruebas de nitruración de las ortoferritas por plasma de amoniaco asistido por microondas (MIP) a pesar de tener temperaturas más bajas de reacción, también mostraron la reducción del hierro en la estructura indicando que de la misma forma en que se incrementa la reactividad del amoniaco, la reactividad del potencial reductor del hidrogeno aumenta también.

Por su parte las reacciones de estado sólido en atmosfera de nitrógeno usando como precursores óxidos y nitruros con urea como agente nitrurante, dieron lugar a la formación de las ortoferritas pero no hubo nitruración. Esto indica que en este caso el amoniaco producido durante la descomposición de la urea no es lo suficientemente eficiente para promover el cambio de estado de oxidación del hierro para la formación del oxínitruro. Las pruebas usando urea y las ortoferritas como precursores en un molino de bolas de alta energía resultaron en la formación de fases de carbonatos debido a las colisiones de alta energía, indicando que la urea no es un adecuado agente nitrurante para esta técnica de síntesis. Adicionalmente una aproximación a la síntesis de los oxínitruros por el método de sol gel dio lugar a mezclas de óxidos secundarios con un alto contenido de residuos orgánicos; donde para obtener la estructura perovskita calcinaciones en atmosfera de oxigeno o aire alrededor de los 700 °C debieron ser realizadas, obteniendo las ortoferritas pero sin nitruración. Finalmente como un trabajo complementario y presentado como un anexo en este manuscrito, de los espectros de transmisión Mössbauer tomados a temperatura ambiente, se estimaron los factores relativos libre de retroceso F de los compuestos REFeO₃ (RE=La, Pr, Nd, Sm). Aplicando un método basado en la correcta determinación de las áreas subespectrales presentes en una mezcla de cantidades conocidas del compuesto bajo estudio y una muestra de referencia (α -Fe).

Palabras clave: Oxínitruro, Perovskita, Ortoferrita, Tierras raras, Auto-combustión

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Symbols Table

Latin Symbols

Symbol	Concept	SI Units	Definition
A	Area	m ²	$\iint dx dy$
Α	Lattice Parameter	Å	Figure 1-3
В	Unit cell diagonal	Å	Figure 1-3
С	Light speed	$\mathbf{m} \cdot \mathbf{s}^{-1}$	Eq. (2-3)
CS	Isomeric shift	$\text{mm} \cdot \text{s}^{-1}$	Table 3-3
CN	Coordination number	-	Table 1-1
D	Average crystal size	m	Eq.(3-1)
d	periodic distance of planes in a structure	Å	Eq. (2-1)
ϵ_0	Energy of absorption line	eV	Eq.(2-4)
E_D	Energy of radiation tuned by Doppler effect	eV	Eq.(2-3)
E_R	Energy of shift respect to absorption line	eV	Eq.(2-4)
E_{γ}	Energy of gamma radiation	eV	Eq. (2-3)
Н	Magnetic Field	Oe	DF
Ι	Current	А	Eq. (2-5)
n	Integer number	-	Eq.(2-1)
М	Metal element	-	Eq. (1-21)
MW	Molecular Weight	g·mole ⁻¹	Table 2-1
L	Length	m	DF
R	Resistance	Ω	Eq.(2-5)
R _A	Ionic radius of A cation	Å	Eq. (1-1)
R _B	Ionic radius of B cation	Å	Eq. (1-1)
RE	Rare Earth Cation	-	-
Ro	Ionic radius of oxygen	Å	Eq. (1-1)

Symbol	Concept	SI Units	Definition
$\overline{S_y}$	Function of the diffraction pattern		Eq.(2-2)
Т	Temperature	K	DF
T _{Room}	Room temperature	K	~300K
t	Goldschmidt tolerance factor	-	Eq. (1-2)
V	Volume	m ³	$\int dr^3$
V	Voltage	V	Eq.(2-5)
v	Velocity	$\mathbf{m} \cdot \mathbf{s}^{-1}$	Eq. (2-3)
$y_{i(Calc)}$	Calculated intensity	-	Eq.(2-2)
$y_{(Obs)}$	Experimental intensity	-	Eq.(2-2)
W_i	Corresponding weight for intensity	-	Eq.(2-2)
Z	Anion charge	-	Table 1-1

Greek Symbols

Symbol	Concept	SI Units	Definition
β	Full width at half maximum	-	Eq. (3-1)
θ	Diffraction angle	Degrees	Eq. (2-1)
3	Quadrupole splitting	$\mathbf{mm} \cdot \mathbf{s}^{-1}$	Table 3-3
λ	The wavelength of the radiation	m	Eq. (2-1)
μ	Octahedral factor	-	Eq. (1-3)
φ_e	Elemental stoichiometric coefficient	-	Eq.(2-15)
χ^2	Square Chi	-	Table 3-1

Sub index

Sub index	Concept
i	I-esime element
Х	Molar doping

Super index

Super index	Concept
n±	Charge
Ν	Exponents
Roman Numbers	Coordination

Acronyms

Acronym Concept

CRN	Carbothermal reduction and nitridation route
XRD	X-ray Diffraction
DSC	Differential Scanning Calorimetry
EDS	Energy-dispersive X-ray spectroscopy
ESC	Elemental stoichiometric coefficient
FC	Field Cooling
FWHM	Full width at half maximum
FT-IR	Fourier Transform Infrared Spectroscopy
GNP	Glycine-nitrate process self-combustion method
MS	Mössbauer Spectroscopy
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell
TGA	Thermogravimetric Analysis
VSM	Vibrating sample Magnetometry
ZFC	Zero Field Cooling

Abbreviations

Abbreviation	Concept
e.g.	For example
Et al.	And coworkers
a.u.	Arbitrary units

Introduction

Today the perovskite structure, with the general formula ABX_3 (with A alkaline metal cation, B metal cation and X anion), dominates the multifunctional ceramic area; being an appropriated crystallographic host for a big number of important materials in a wide range of applications [1]. Around 90% of the metallic elements of the periodic table are able to crystallize in oxides with this structure [2] and by changing the composition and/or stoichiometry of these compounds, it is possible to tune their physical and chemical properties in an intentional way.

As a result, with the objective to combine relevant and desirable characteristics of several elements, in the perovskite structure the cationic substitutions have been widely explored [3]. However, comparatively possible anionic substitutions have been left aside because they have the disadvantage of requiring synthesis methods less direct, more energetic and more difficult to control; as an effect of the highly stable metal-oxygen bond [4].

Among the possible anionic substitutions, a partial substitution of the oxygen crystalline positions by nitrogen has given origin to a emergent group of materials named oxynitrides[5], which in optimal cases may combine the advantages of oxides and nitrides [6]. This substitution is possible due to the nearby chemical, structural and electronic characteristics of the oxygen and nitrogen ions; such as polarizability, electronegativity, coordination number and ionic radio. This kind of substitution is very promising; since by this method, simply by adjusting the nitrogen content, it is likely to tune the valence states of cations, the bond covalency and the energy of the electronic states in the compounds [4].

Nevertheless, as a result of the high energy of the $N \equiv N$ bond and the unfavorable electronic affinity to form the N^{3-} anion, it is very difficult to achieve effective synthesis methods[7]. Therefore in this area, there are still some challenging tasks. For example, the synthesis of single crystal oxynitrides or the synthesis of potential structural compositions. Considering that the perovskite oxynitrides already synthetized are based only on electropositive metals in the B cation position.

In general, the main problem for the synthesis of oxynitrides with highly electronegative metals in the B cation position is related with the conventional nitridation method, where gaseous ammonia is used at high temperatures as nitriding agent. At these temperatures, the bond B-N is less stable and ammonia decomposes partially in hydrogen. Under these conditions when B is a highly electronegative transition metal, it is easily reduced by the hydrogen reduction potential, leading to collateral reactions like the formation of oxides and nitrides with lower oxidation states [4],[7]. However, this is not the unique problem for the synthesis of this kind of oxynitrides compositions, since the highly electronegative cations present lower oxidation states in comparison with electropositive metals. This is a disadvantage as it reduces considerably the possible ways of charge compensation in order to establish the electroneutral condition, which is lost due to the insertion of the extra negative charge of nitrate ion (N³⁻) with respect to oxygen ion (O²⁻).

In that sense, this work focuses in some of these cases, studying four oxide compounds of the rareearth orthoferrite family with the general formula REFeO₃ (RE = La, Nd, Pr, Sm), where the B cation position is occupied by the highly electronegative metal, iron (Fe). These compounds are orange to dark red and crystallize as distorted perovskite structures. Furthermore, they show interesting physical properties like a giant dielectric constant, an antiferromagnetic structure with parasitic ferromagnetism and photocatalytic activity, among others remarkable properties which have attracted much attention for use in potential applications, such as dielectric materials [8], [9], gas sensors [10], [11], SOFC cathodes[12], [13] and spin valves [14], [15].

The general objective of this work was to propound a methodology for the synthesis of the oxynitrides $REFeO_{3-x}N_x$ (RE = La, Nd, Pr, Sm) by evaluating several approximation routes. Additionally, if the compound syntheses could be achieved, perform the appropriate structural characterization and research about their magnetic and electrical properties.

As a first approximation to the synthesis of the oxynitrides $REFeO_{3-x}N_x$ (RE = La, Nd, Pr, Sm), and with the idea to use them as precursors for the nitridation, the synthesis of their respective oxides $REFeO_3$ (RE = La, Pr, Nd, Sm) was performed using the self-sustained combustion method GNP. Next, the characterization of the oxides was conducted, using XRD, EDS, Rietveld refinement and SEM to probe the purity of their phases, evaluate their nominal elemental composition and characterize their structures and morphology. Finally, in order to better understand these compounds and to perform a comparison of the properties of oxides and oxynitrides, a deeper characterization of the oxides was carried out. Therefore, the synthesized oxide compounds were studied using thermal analysis, FT-IR, Mössbauer spectroscopy, and magnetic and electric measurements.

At this point, the second part of this work began and the suitable nitridation procedure was considered. Moreover, different methods were evaluated, considering the tuning of the experimental set-up and the determination of the appropriated operation conditions in order to obtain the synthesis of the oxynitrides.

In this way, this work establishes a conceptual base to propose future research in the perovskite oxynitrides synthesis area, especially with high electronegative cations at structural position B, as well as eventually creating a starting point to pose and develop applications, in which the properties of the oxynitrides REFeO_{3-x}N_x (RE = La, Nd, Pr, Sm) could be exploited.

1. A Brief Review of Perovskite Oxynitrides

1.1 Perovskite Structure

The rare-earth orthoferrites REFeO₃ are a family of canted antiferromagnets with unusual magnetic properties[16]. These compounds crystallize in the *Perovskite* structure, which takes its name from the mineral CaTiO₃ (calcium titanate) discovered for the first time in 1893 in the Urals mountains by geologist Gustav Rose and named Perovskite in Honor to Lev Alexevich von Perovski, dignitary, mineralogist and military Russian[17]. The perovskite structure represented by the general formula ABX₃ is one of the most important structures in the technological area due to the fact that it covers insulators, piezoelectrics, ferroelectrics, metals, semiconductors, magnetic, and superconducting materials. This is a result of its wide versatility as a crystallographic host (see Figure 1-1); where A can be an alkaline cation, an alkaline earth or a lanthanide; B usually is a transition metal of mid-size and X is an anion, which is generally oxygen.





The ideal perovskite is an isometric structure with a very simple arrangement of ions characterized by the (strontium titanate) SrTiO₃. This compound crystallizes in space group $O_h^1 - Pm3m$, where the Ti atoms are located in the corners of a cube, the Sr atoms at the center of the cube and the oxygen atoms at the center of the twelve cube edges[1]. This is illustrated in Figure 1-2 where other forms used to represent the structure are also depicted (see Figure 1-2b and Figure 1-2c).



Figure 1-2: Ideal perovskite structure illustrated by the SrTiO₃ [1]

In this arrangement, Sr (A position) is surrounded by twelve equidistant oxygen neighbors while the Ti (B position) is surrounded by six, resulting in perfect TiO_6 octahedra with angles of 90°. These octahedra are united by their shared corner, creating an infinite network of chains, which extends in the three orthogonal directions.

The recreation of an edge view and a transversal cut of this ideal structure by applying the theoretical spherical atom model (where the atoms touch each other), is used to obtain a good approximation of the condition that the ionic radii of A,B and O should satisfy to form this structure.

For this purpose, r_A is defined as the ionic radius of the cation A, r_B as the ionic radius of the cation B and r_0 as the ionic radius of the oxygen. From Figure 1-3, it is easy to prove using the left subfigure (the edge view of perovskite structure) that the distance $r_A + r_0$ is equal to $a/\sqrt{2}$ (considering *a* as the lattice parameter) and from the transversal cut on the right, that the distance $r_B + r_0$ is equal to a/2.



Figure 1-3: Ideal perovskite structure in the spherical atom model.

In this way, by equating the value of *a* from the two relations, it can be obtained:

$$\sqrt{2}(r_{\rm A} + r_{\rm 0}) = 2(r_{\rm B} + r_{\rm 0}) \tag{1-1}$$

An important relation used by Goldschmidt in 1926 [18] to introduce a tolerance factor (t) for the formation and stability of the perovskite structure as a measurement of the deviation of the ideal situation. This factor is defined as:

$$t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}$$
(1-2)

Under the ideal conditions for the cubic perovskite, which actually is very unusual, this parameter should be one. However, this structure is stable even in much less symmetric conditions, finding in the literature t values ranging from 0.75 to 1.00, these values generate what is known as distorted perovskites structures. This is the case of the systems studied in this work, where the value of the tolerance factor (t) falls as the ionic radius of the A cation; when it becomes smaller in comparison with the space it must fill in the octahedra network (see Figure 1-2b). This means that the perovskite structure becomes distorted by ion displacements and the tilting of the octahedra to enhance the bonding of cations A in the big twelve coordinated cavities[19].

Nevertheless, the tolerance factor is a necessary but not sufficient condition for the formation of the perovskite structure [19] and the BO_6 octahedra plays an important role as the basic unit to the

formation of a perovskite. For this reason, another parameter known as the octahedral factor must be introduced:

$$\mu = \frac{r_{\rm B}}{r_{\rm O}} \tag{1-3}$$

This parameter guarantees the formation of the BO_6 octahedra and experimentally it has been found that it should be greater than 0,425 and with a maximum of around 0,6[19]. These two criterions, the Goldschmidt and the octahedral factor, govern the formability of perovskite structures and allow for estimating reasonably well; if the perovskite structure is stable under a specific elemental composition.

1.2 Perovskite Oxynitrides

The synthesis of new materials has been recognized as the element most essential in the technological advances[20], and no other structure has served so well to this purpose as the perovskite. Since the last century, this structure has dominated the multifunctional ceramic area due to its enormous versatility; where by in making the appropriated change in composition, one can modify the most significant electroceramic dielectric (BaTiO₃ and its relatives) phase in industry into metallic conductors, superconductors or the highest pressure phases in the earth [1]. For this reason, perovskite structure has attracted so much attention and the possible cationic substitutions have been very well studied [3][7] as shown in Figure 1-4 for the case of $BaTiO_3$.

However, not everything is done in perovskite structure and the anion substitutions which had been left aside previously, now are proving their value[7]. This is a value quite promising considering that in the perovskite formula the anionic element is the most abundant in composition and it is the base for the essential blocks of the structure, the octahedra BO_6 . Therefore, as is now well known in oxides, any stoichiometry defect or change of the anionic sublattice, affects considerably the structure and physic properties of compounds. Thus, normally to prevent these problems, the compounds are annealed under careful tailored temperature and amount of available oxygen conditions[21]–[24].



Figure 1-4: Crystal chemistry of multiple ion substitution in perovskite [25]

Nevertheless, what is a problem when it is not controlled, may be considered as an opportunity when it is intentional. This is how the controlled modification of the anionic part of the perovskite compounds have given origin to a group of emergent materials like carbides[26]–[28], halides[29]–[31] and nitrides[4], [5], [32]; where the oxygen ions in the structure are substituted partially or totally by other kind of anions.

This work focuses on one of these cases, the *oxynitrides*, which are compounds where the oxygen ions (O^{2-}) are partially replaced in their crystalline positions by nitride (N^{3-}) ions. This substitution is possible due to the proximity in the characteristics of these two ions, which is appreciable in Table 1-1.

Property	N ³⁻	O ²⁻
Anion charge (z)	-3	-2
Electronegativity	3.0	3.4
Atomic polarizability	1.10	0.80
Electron affinity $(A \rightarrow A^{z}/kJ \cdot mol^{-1})$	1736	601
Bond energy $A-A(kJ \cdot mol^{-1})$	941	499
Ionic radii (for CN=IV)	1.46	1.38
Coordination number (CN)	II-VIII	II-VIII

Table 1-1:Properties of nitrogen and oxygen ions [33]

Regardless of the nearby properties of the N^{3-} and O^{-2} ions, which allows for the substitution among each other in the same crystallographic sites; the slight differences in these ions lead to very interesting and useful changes which are listed below:

- 1. As nitrogen is less electronegative and more polarizable than oxygen, in oxynitrides the covalency of metal-anion bonds increases; as well as the valence band energy. This results in a narrower band gap for oxynitrides than for their corresponding oxides, which usually give rise to strong and different colors [4],[34]–[36].
- 2. The higher electrical charge of nitride leads to a larger crystal field splitting and the expansion of the electron cloud; which introduces changes in density, glass transition temperature, viscosity and refractive index. This represents improvements in hardness, acid-base properties, covalent character, reducing character and mechanical properties such as Young's modulus, chemical durability and a decrease in the thermal expansion coefficient and ease of crystallization[4],[37].
- 3. The higher electrical charge, also allows the formation of new compounds (not possible in oxides) by mixing some combinations of cations and transition metals with higher oxidation states[4],[7].

The first and second point above, confer a lot of the potential for applications such as dielectric materials[38],[39],[40], friendly environmental pigments[41],[42], photocatalytic materials[33][43], magnetic materials[44],[33],[9] and in many cases, advantages in some application in comparison to their respective oxides [7], [32].

On the other hand, the third point is very important since it represents not just an advantage, but also a requirement for the formation of the oxynitride. The third point also implies that the nitridation procedure must be accompanied by a charge compensation process due to the substitution of the O^{2-} ions by the N^{3-} ions. The possible mechanisms for this charge compensation in the perovskite structure ABO₃ are listed below.

1. In this case, the cationic network is not modified and three oxygen atoms are replaced by two nitrogen atoms (This case applies to nitrides)[32]:

$$2N^{3-}=3O^{2-}$$
 (1-4)

e.g.[45]:

$$Mn^{3+}Mo^{3+}O_3^{2-} \to Mn^{3+}Mo^{3+}N_2^{3-}$$
 (1-5)

2. Each nitrogen atom that is introduced is compensated by an oxidation of a cation generally B [7]:

$$N^{3-} + B^{(n+1)+} = 0^{2-} + B^{n+}$$
(1-6)

e.g.[46]:

$$La^{3+}V^{3+}O_3^{2-} \to La^{3+}V^{4+}O_2^{2-}N^{3-}$$
(1-7)

3. Generation of oxygen vacancies:

$$ABO_3 \to ABO_{3-3x/2}N_x \tag{1-8}$$

e.g.[47]:

$$BaTiO_3 \to BaTiO_{3-1.5x}N_x \tag{1-9}$$

 Cross-substitution of cations A and/or B maintains the same general stoichiometry: a)

$$A^{2+}BO_3 \rightarrow A^{2+}_{1-x}\hat{A}^{3+}_x BO_{3-x}N_x$$
 (1-10)

e.g. [48]:

$$Ca^{2+}Ti^{4+}O_3 \rightarrow Ca^{2+}_{1-x}La^{3+}_xTi^{4+}O_{3-x}N_x$$
 (1-11)

b)

$$AB^{4+}O_3 \rightarrow AB^{4+}_{1-x}\hat{B}^{5+}_xO_{3-x}N_x$$
 (1-12)

e.g. [49]:

$$Ca^{2+}Zr^{4+}O_3 \rightarrow Ca^{2+}Zr^{4+}_{1-x}Ta^{5+}_xO_{3-x}N_x$$
 (1-13)

5. Reduction of the number of anions:

a)

$$ABO_{3+x/2} \to ABO_{3-x}N_x \tag{1-14}$$

e.g. [50]:

$$LaTiO_{3.5} \rightarrow LaTiO_2N \tag{1-15}$$

b)

$$2(ABO_{3+x/2}) \rightarrow 2ABO_{3-x}N_x \tag{1-16}$$

e.g. [51]:

$$La_2 Zr_2 \ O_7 \ \rightarrow 2(La Zr O_2 N) \tag{1-17}$$

These charge compensation mechanisms are very important since they reveal the two possible routes to approaching the synthesis of oxynitrides with perovskite structure:

- The first one is represented by the Equations (1-6) and (1-8), mechanisms 2. and 3. respectively, where the precursors of the oxynitrides already have the perovskite structure.
- In the second route of approaching, represented by Equations (1-10) and (1-12); mechanism 4. and Equations (1-14) and (1-16); mechanism 5, the precursors to obtain the oxynitrides do not have the perovskite structure, which is formed during the nitriding reaction; either from the stoichiometric amounts of oxides, carbonates or nitrates precursors, mechanism 4, or from amorphous or lesser stable structures, mechanism 5.

In this work, the mechanism 4 is discarded, since it does not correspond with the desired stoichiometry. Meanwhile the mechanism 5 is discarded, due to the cations under study (RE^{3+} and Fe^{3+}) as a result of their oxidation states, they do not present known structures with higher anionic content. Therefore, the synthesis of the $REFeO_{3-x}N_x$ oxynitrides was attempted by starting from their respective perovskite oxides, anticipating possible mechanisms of charge compensation 2 and 3.

1.3 Nitridation methods

The perovskite oxynitrides are a relatively new materials family, which were reported for the first time by Marchand et al. in 1986 [5]. At first sight, this looks like a late report, since the substitution of O^{-2} by N^{-3} ions appears to be pretty logical; however, in practice there are very good reasons for this delay.

First, to perform the substitution it is necessary to provide a good source of nitrogen which has to be an effective nitriding agent during the entire reaction. Nonetheless, the ideal reagent (N₂) is not suitable for this purpose due to its triple bond ($N \equiv N$) that is one of the strongest bonds in nature with a enthalpy of dissociation of 226 kcal·mol⁻¹[32]. This is why more reactive, but also more dangerous, difficult to control and corrosive nitriding species, like NH₃ and NO, must be used in the nitridation process.

Second, due to the always greater reactivity of the elements for oxygen than for nitrogen, it is necessary to guarantee an atmosphere free of traces of moisture and oxygen[32], while ensuring high driving forces to conduct the nitridation. This is done in order to avoid the stagnation of the process and the reverse reaction[7].

Finally and very importantly, due to the high stability of the metal-oxygen bond, the nitriding reaction has to be performed at high temperatures[4].

Consequently, the nitriding substitution is far from being a trivial procedure and the mentioned facts make that the synthesis of oxynitrides require less direct, more difficult to control and more energetic methods than those for cationic substitutions[4].

In this context, the method that has been more extensively used and although it has limitations it has given the best results, is thermal ammonolysis.

1.3.1 Gas Phase Synthesis

1.3.1.1 Thermal ammonolysis

The thermal ammonolysis is a nitriding reaction to synthetize nitrides or oxynitrides where oxides or oxide precursors are treated with flow of gaseous ammonia (NH₃) under atmospheric pressure and temperatures among 900 and 1400 K [32]. The basic set-up for this process is presented in Figure 1-5.



In this reaction, the ammonia acts not only as a nitrogen source, but also as reducing agent, since over the 700K, it undergoes a partial decomposition in active nitriding species and molecular hydrogen[7] as it is further showed:

$$2NH_3 \rightarrow 2NH_2 + H_2 \tag{1-18}$$

$$2NH_2 \rightarrow 2NH + H_2 \tag{1-19}$$

$$2NH \to N_2 + H_2 \tag{1-20}$$

When this decomposition take place on the surface of the precursors, the nitriding species (NH₂, NH) react, insert the nitrogen into the structure while at the same time they remove the oxygen as water vapor (H₂O). This is shown in the general equation of the reaction which is presented below[32]:

$$MO_x + \frac{2x}{3}NH_3 \rightarrow MN_y + xH_2O + \left(\frac{x}{3} - \frac{y}{2}\right)N_2$$
 (1-21)

In this sense, the driving forces of the nitriding process are the free energy of formation of water and the entropy due to the high tempertures, which activates the diffusion of ions as in all solid reactions[7]. However, these temperatures are one of the problems of ammonolysis because over the 500K the ammonia is mostly dissociated into N_2 and H_2 , which are not effective nitriding sources, since the N_2 is inert gas and the H_2 just reduces the cations, leading to undesired sidereactions and competing with the formation of oxynitrides.

For this reason, the ammonolysis must be performed under non-equilibrium conditions, increasing the ammonia flow to high values (~ $20-180 \text{ ml} \cdot \text{min}^{-1}$) with the increasing of temperature [4], [7]. In this way it is possible to suppress in some extent the dissociation of the NH₃ before the contact with the sample; renew the active nitriding species over it and carry the water produced during the reaction out of the reactor to prevent the reverse reaction[7].

Nevertheless, despite the high flows of ammonia, the reaction slowly achieved the equilibrium:

$$NH_3 \leftrightarrow \frac{1}{2} N_2 + \frac{3}{2} H_2$$
 (1-22)

Which is a serious problem for the synthesis of those oxynitrides that have in position B high electronegative transition metals[4], [7].

Regardless, the reaction times depend on the nature of the precursors and the cations A and B. Another problem of ammonolysis is that generally these times are quite long, since to obtain pure and homogeneous phases, several ammonolysis steps with intermediate regrindings have to be done as an effect of the limited gas exchange between the solid precursors and the ammonia[7].

In order to improve and solve these problems of ammonolysis, some upgrades have been proposed to the basic set-up presented in Figure 1-5. One of them consists in using a rotatory reactor to increase the reaction surface while enhancing the exchange among the sample and ammonia[50]. Another interesting proposal is the idea to use a microwave field to induce an ammonia plasma (MIP), reducing in this way the reaction times while the reactivity is raised[52]. Despite these improvements, important issues like the kinetic of the ammonolysis is not understood yet, the conditions for the synthesis of oxynitrides are empirical and there are not synthesis methods for the growing of oxynitrides single crystals. Thus, research in new nitriding methods is quite important [7].

1.3.1.2 Thermal Ammonolysis in rotating tubes furnace

With the idea of solving the problem of the diffusion of ammonia in the solid precursors, rotating tubes and rotating cavities furnaces have been developed. These furnaces enhance the exchange rate between the solid and the ammonia; reducing the reaction times, increasing the homogeneity of the samples and avoiding the intermediate regrindings [53],[54],[55].

The design of these ovens is based on the rotary evaporators, but instead of the usual flask they rotate a quartz or alumina reactor. This reactor is placed in a furnace and cold ammonia gas is injected by a smaller inner tube directly onto the powder, which is effectively mixed by the rotation of the reaction cavity [7] (see Figure 1-6).





1.3.1.3 Ammonia Microwave-Induced Plasma (MIP)

Microwave radiation can be used to induce a plasma state in gases. A plasma is a high energetic gas containing ions, electrons and energetically exited particles. Microwave-induced plasmas (MIPs) are used extensively both for thin-film formation and surface modification and densification of ceramics [52], [56]. Bulk modification of solids using reactive gas plasmas have also been demonstrated [57], [58].

In oxynitrides, this method is quite promising since it offers the possibility to increase the reactivity of ammonia by inducing the plasma state [7]. As a result, the reactions time decrease, the synthetized phases have more homogeny and the reactions occurred at lower temperatures. Another advantage of this method, is that a MIP flow reactor could be set up starting of a domestic microwave oven (DMO) and in these devices the ammonia plasma can easily be generated as demonstrated in [52], [57], [59].
With the purpose of generating a MIP starting of a DMO, two possible designs have been suggested (see Figure 1-7 and Figure 1-8). The basic idea consisted of placing the sample in a sealed quartz tube with the desired atmosphere and to perform a vacuum under a microwaves field. The variations of the designs are related to the location and form of the quartz reactor tube in order to enhance the intensity of the plasma, among other concepts like how to guide the microwaves to the tube without them losing their congruence or how to refrigerate the system without dissipating its power.

Figure 1-7: Design proposed by Brooks et al. [59]

In this case, the reactor tube is in U-form and the ammonia comes in through one side and goes out through the other which at the same time goes to a vacuum. In this set-up, the tube is inserted to the DMO by the backside.



Figure 1-8: Design proposed by Houmes et al. [57]

In this set-up, the sample is located in the sailed side of a long tube where the vacuum is performed and the ammonia is carried to the sample by an inner tube of lower diameter. The two tubes come into the Microwave by the opposite side of the magnetron.



1.3.1.4 Thermal nitridation by annealing in nitrous (N₂O) and nitric (NO) oxide atmosphere

This method has been used in the semiconductors area for the nitridation of oxide targets and films of $SiO_2[60],[61], [62],[63]$. These materials are used as gate insulators in the structure of transistor (MOSFET) devices. The resultant oxynitrides are dielectrics with better diffusion barrier properties and higher dielectric constants[63]. In this area the ammonolysis is not suitable because it promotes the generation of hydrogen-related charge traps[61].

The annealing procedure is similar to the ammonolysis method, but in this case, the reaction atmosphere is NO or N_2O , where the nitriding agent for both cases is the NO[61]. However, when N_2O is used the nitrogen incorporation occurs simultaneously with nitrogen removal leading to compounds with low regularity. This phenomenon is due to the partial pressure of O_2 produced during the N_2O decomposition which reoxidizes the oxynitrides[63].

In this reaction it has been found that the nitrogen/oxygen ratio increases with temperature, as well as the amount of nitrogen in the oxynitrides, the depth of the nitrogen profiles and the width of the containing nitrogen areas. These are the reasons why typically the process is performed at high temperatures (T > 800 $^{\circ}$ C). This method is quite effective to obtain homogeny oxynitrides when it is used during the SiO₂ film growing[62].

On the other hand, in the perovskite oxynitrides area this synthesis route has been hardly used due to it having a lower reactivity than the ammonolysis. Nevertheless, the annealing by NO has the advantage of avoiding the reduction problems as a consequence of the hydrogen potential produced in the ammonia decomposition[60].

1.3.2 Solid state reaction synthesis

1.3.2.1 Carbothermal reduction and nitridation route (CRN)

In nature, generally the metals appear forming mineral compounds and the extractive metallurgy studies the different operations, phases and ways of treating those minerals in order to extract the free metals.

Among these metallurgic processes, one of the most extensively used in the case of oxides, is the carbon reduction procedure. In this process, the metal oxide is mixed with carbon and then heated to obtain a reductive molten where the oxygen of the oxides is removed by the formation of CO and CO₂. However this reaction has been harnessed not just in metallurgy, but also for the synthesis of nitrides and oxynitrides; since when oxygen is removed during the reduction the resulting compounds are high reactive and at high temperatures (1200° to 1500 °C) they can react with dinitrogen (N₂). This procedure is known as carbothermal reduction and nitridation route (CRN).

In practice, the procedure involves preparing a stoichiometric mixture of oxides with carbon, used as the precursor for synthesis of the oxynitrides. This mixture reacts in a horizontal alumina-tube reactor under nitrogen (N_2) gas flow. The carbon reduces the oxides removing the oxygen progressively, while the product then becomes more reactive and reacts with nitrogen to form the oxynitride [64].

e.g. RE₂AlO₃N[64]:

$$2RE_2O_3 + Al_2O_3 + 3C + N_2 \to 2RE_2AlO_3N + 3CO \uparrow \qquad (RE = Nd, Sm)$$
(1-23)

1.3.2.2 The reaction of binary nitrides with oxides

This method, also known as direct combination of elements, involves the direct mixture of the desired binary oxides and nitrides in the adequate stoichiometric ratios to form the required oxynitrides.

e.g. Re_2AlO_3N [65],[66] synthetized by a mix of RE_2O_3 and AlN in a N_2 at 1200 K.

The nitrides binary precursors may be obtain by amonólisis or CRN.

e.g.[32]:

$$Al_2O_3 + 2NH_3 \rightarrow 2AlN + 3H_2O\uparrow$$
(1-24)
$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO\uparrow$$
(1-25)

1.3.2.3 The reaction of oxides with solid ammonia sources

1.3.2.3.1 Reaction with Urea (CO(NH₂)₂)

In this method, urea is used as a solid nitrogen source in the oxynitrides synthesis. The urea is an organic compound with the chemical formula $CO(NH_2)_2$. The molecule has two $-NH_2$ groups joined by a carbonyl (C=O) functional group. This compound is an ideal nitriding precursor since the major product of its thermal decomposition is ammonia (NH₃)[67],[68], [69]:

a) At 408-493 K the urea decomposes in biuret and ammonia:

$$2CO(NH_2)_2 \xrightarrow{\Delta} H_2NCONHCONH_2 + NH_3$$
(1-26)

At 530.2 K the biuret decomposes in cyanic acid and ammonia:

$$H_2NCONHCONH_2 \xrightarrow{\Delta} NH_3 + 2HCON$$
 (1-27)

And the cyanic acid can reacts with water to produce carbon dioxide and ammonia:

$$HNCO + H_2O \leftrightarrow CO_2 + NH_3 \tag{1-28}$$

b) At 497-530 K the urea decomposes in ammonia and cyanic acid

$$CO(NH_2)_2 \xrightarrow{\Delta} NH_3 + HNCO$$
 (1-29)

The procedure is comprised of adding urea in high ratios to a stoichiometric mixture of oxide precursors (carbonates, oxides, halides, etc.). The resultant solid compound is taken to the furnace in an alumina boat where under N_2 atmosphere it reacts at high temperatures (~1200K) to form the ternary oxynitride [70],[71].

1.3.2.3.2 Reaction with Ammines (RNH₂)

This procedure is similar to the one used with urea, but in this case the nitrogen source is an ammine. This compound is an obvious nitriding compound since it results from the substitution of one or more of the hydrogens in the ammonia molecule. For this reason, these compounds can be at the same time the nitriding agent and have attached one of the cations for the oxide (generally and alkaline metal). This has the advantage of greater control over the reduction caused by the hydrogen produced during the decomposition of the ammonia molecule.

E.g. The Nitride TiN was synthetized by reaction of TiO_2 and Cyanamide (CN_2H_2) at under nitrogen atmosphere at 800 °C[72].

E.g. The oxynitride $Na_4MO_2N_2$ (M=Mo, W) was synthetized by the reaction of the respective oxide precursors with an excess of $NaNH_2$ in a stainless steel autoclave at ~500K[73].

1.3.3 Liquid-phase methods

1.3.3.1 Sol-gel Process

This method has been recently used to synthetize TiN oxynitrides. This process presents multiple variations, but basically consists of the formation of a gel precursor, which is then calcinated to obtain the desired products.

This gel can be formed by network growth from an array of discrete colloidal particles (method 1) or by formation of an interconnected 3-D network by the simultaneous hydrolysis and polycondensation of an organometallic precursor (method 2)[74]. In this case, the most used is method 2 where for the formation of the gel the is necessary to perform the following steps:

- *Mixing*: in this step liquid alkoxide precursors are hydrolyzed by mixing with water and a polycondensation reaction takes place resulting in liquid viscous network (sol).
- *Casting:* the sol is taken to a mold
- *Gelation:* with time, the condensed species becomes a three dimensional network
- *Aging:* consists of maintaining the cast object for a period of time completely immersed in liquid, for increasing the strength of the gel.
- *Drying:* the liquid is removed carefully from the interconnected pore network.
- Densification: heating the porous gel causes densification to occur
- *Calcination:* the gel is calcinated to obtain the desired products

For the synthesis of oxynitrides by this method. during the mixing step a compatible nitrogen source (NH₄Cl, NH₃, N₂H₄, NH₄NO₃ and HNO₃) is added in an adequate ph to avoid precipitation[75], [76].

1.3.3.2 Ammonothermal method

This method comes from the observation that ammonia is the solvent with the closest physical properties with respect to water. This suggests that analogue to hydrothermal growth (high pressure water solution), the growth of nitrogen-based compounds can be addressed by a high pressure ammonia solution. Recently, this method has become extremely important because it enables the synthesis of nitrides GaN single crystals [77],[78],[79].

The ammonothermal growth is part of the group of techniques named solvothermal growth where a liquid polar solvent, in this case ammonia (NH₃), is used to form metastable products with the solute (nutrient). Usually the reaction is carried on in a closed system to increase the solubility of the nutrient by inducing a supercritical state in the solvent (by applying high pressures and temperatures). Besides mineralizers that are frequently used or even essential to amplify the solubility of the nutrient, these materials speed up the crystallization process due to the fact that they reduce the molecular size of the species in a solution by the formation of complexes[80].

In the typical procedure, gaseous ammonia is inserted in an auto clave to react with the nutrient under the presence of a mineralizer, E.g. see Table 1-2.

Nitrides: Ammonothermal	Oxides: Hydrothermal
Ammmonia: $2NH_3 \leftrightarrow NH_4^+ + NH_2^-$	Water: $2H_2O \leftrightarrow H_3O^+ + OH^-$
AlN in ammonobase solution:	Al ₂ O ₃ in alkali water solution:
$AlN(nutrient) + NH_2^- + 2NH_3 \rightarrow Al(NH_2)_4^-$	$Al_2O_3(nutrient) + 20H^- + 3H_2O \rightarrow 2Al(OH)_4^-$
Mineralizer:	Mineralizer:
Acids: NH ₄ Cl, NH ₄ I, HCl	Acids: HNO ₃ , HCl, HI
Bases: KNH ₂ , NaNH ₂ , LiNH ₂	Bases: KOH, NaOH, LiOH
Salts: KI, NaCl, NH ₂ NH ₃ Cl	Salts: Na ₂ CO ₃ , KF, NaCl

 Table 1-2:
 Comparison of Dissolution-crystallization process in Hydrothermal and Ammonothermal solvents [80]

On the other hand, not only gaseous ammonia can be used as nitrogen solvent, molten flux variants using other nitrogen compounds have been used as usually is done in the hydrothermal method (see Table 2-1).

Ammonia System	Water system
$NaNH_2$	NaOH
$\mathrm{NH_4}^+$	H_3O^+
RNH_2	ROH
$R_2C=NH$	$R_2C=O$
$C(NH)(NH_2)_2$	Co(OH) ₂

Table 1-3:Analogous Compounds in the Ammonia and Water Systems[80]

R= an organic group or hydrogen

Particularly, the sodium amide $(NaNH_2)$ has been used with excellent results for nitridation of oxides [81], [82] and even in perovskite oxynitrides E.g. LaNbON₂ where NaNH₂ was used with a anhydrous liquid ammonia[83].

2. Experimental Methods

2.1 Characterization techniques

2.1.1 X-ray Diffraction (XRD)

The technique

The x-rays discovered by Wilhelm Röntgen in 1985 are electromagnetic radiation with a wavelength among 10^{-8} and 10^{-12} meters, which are produced usually during the collision of electrons against a Mo, Cu, Ni, Co or Fe target. The electrons used in the process generally come from a hot tungsten filament and are accelerated with energies of 102 eV.

Due to the wavelength of the x-rays matches with the order of the interatomic separations in a crystal (periodic arrangement of atoms or molecules), when they hit over them, they produce an analog phenomenon to the diffraction of the light when it hits a CD-ROM. Once the x-ray impinges a pair of parallel planes of a crystal lattice, each atom in the planes acts as a dispersion center, emitting secondary waves which interfere with each other and produce a characteristic pattern of diffracted waves with a greater intensity. The analysis of the specific distribution of the intensities diffracted, allows the representation of the structure where the x-ray hits [84].

The angles (θ) where the wave presents the highest intensities are determinated by the wavelength (λ) of the radiation and the periodic distance (d) of the planes in the structure, according with the Braggs law presented below:

$$n\lambda = 2d\,\sin\theta\tag{2-1}$$

This means that for two crystalline planes separated by a distance (d) where the x-ray radiation hits (see Figure 2-4), the condition for the constructive interfering is that the

difference between the ways of the scattered rays $2d \sin\theta$, must be a integer multiple of the wavelength of the radiation.



Figure 2-2: Schematic diagram of an x-ray diffractometer; T x-ray source, S specimen, C detector, and O the axis around which the specimen and detector rotate [85].



In Figure 2-5 is presented the geometry of a x-ray diffractometer, where a coherent and collimated x-ray beam is generated in point T and is directed to a sample in a flat plate S, which rotates around the perpendicular O axis. The intensities of the diffracted beams are detected by the counter C which also rotates around the O axis forming a 2 θ angle respect to S. This ensures that the imping and the reflection angles are always equal. As a result of the constant velocity of the counter, the measure returns a graph of the diffracted intensities as a

function of the angle 2 θ , in which the peaks correspond to the *hkl* planes of the material and the pattern is like a digital footprint of its structural phase and in this sense a way to identify it [85].

Experimental conditions

The X-ray diffraction patterns were taken using a Panalytical X PERT PRO MPD diffractometer with CuK α 1 = 1.5406 Å, operated at 45 kV and 40 mA. The diffraction patterns were recorded in an interval (2 θ) from 10^o to 90^o with a scanning step size of 0.013^o and 59s per step.



Figure 2-3: Panalytical X'PERT PRO MPD x-ray diffractometer

2.1.2 Rietveld Refinement

The technique

The Rietveld method is a technique for the characterization of crystalline structures, where applying the method of least squares, an experimental x-ray diffractogram is adjusted to a theoretical model based in structural, microstructural and instrumental parameters of the sample and the experimental measurement [86].

The minimized function is called residue and is given in the following equation:

$$S_y = \sum_i W_i \left(y_{i(Obs)} - y_{i(Calc)} \right)^2$$
(2-2)

In this function, $y_{i(Obs)}$ and $y_{i(Calc)}$ are the experimental and calculated intensities in the point i of the diffraction pattern, respectively, W_i is the corresponding weight given to this intensity, while the sum is over all the points of the diffraction pattern. S_y is a complex function which involves all the parameters that give rise to the diffraction pattern. The refinement seeks to find the optimal values of these parameters, so that S_y adopts the minimum possible value.

Experimental conditions

Rietveld refinement was performed using the software FullProf [87], 22 parameters were refined following a routine base in the refinement strategy of Ray Young [86].

2.1.3 Scanning electronic microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS)

The technique

In the scanning electronic microscopy (SEM), a collimated electron beam impinges over a point accurately focused on scanning a particular area of interest in a sample to form pictures in order to observe and characterize the material in scale since nanometers (nm) to micrometers (μ m). When the electron impinges, it interacts with a sample volume and in the process a set of signals are produced; secondary and backscattering electrons, characteristic x-rays and other photons of several energies which can be used to explore many characteristics of the sample (surface topography, crystallography, composition, etc.)[88].

The image signals of greatest interest the backscattered electrons and the secondary electrons which are emitted from a small chunk of the sample adjacent to the interaction point. The first ones give information of the surface, while the others allow the generation of tridimensional images. This with nearby resolutions to the size of the electron beam, that are in thanks to the large depth of field of the technique, are able to represent the relief of the sample for its topographical description[88].

The x-ray radiation emitted by the sample is another interesting signal, since energy is a characteristic for each element, which allows the qualitative and quantitative identification of the elemental composition of regions of $1\mu m$ of diameter and $1\mu m$ of depth under normal conditions[88].

The configuration of a scanning electronic microscopy and its optic is shown in Figure 2-4.



Figure 2-4: Scheme of the optics of an electron microscope [89]

Electron Microscopy Philips CM120 instrument operated with an acceleration voltage of 20 kV was used to study the morphology and to perform the microanalysis of the samples.

2.1.4 ⁵⁷Fe Mössbauer Spectroscopy (MS)

The technique

Mössbauer spectroscopy is based in the nuclear resonant absorption of gamma (γ) radiation known as the mössbauer effect and discovered in 1957 by Rudolf Mössbauer. This technique allows the characterization of the iron nucleus of the compound under study; the experimental procedure consisting of impinging over the sample (called absorber) with gamma radiation from a source of emitting excited nuclei (Mössbauer isotopes), which is looking for resonant absorption [90]. However, as the nucleus is not isolated, the resonant absorption may rupture by the interactions of the Mössbauer atom with its chemical environment, so as to achieve that the effect occurs in the γ radiation energy (E_{γ}) that is fitted generating a small Doppler shift by putting in relative motion with a velocity (v) the gamma source with respect to the absorbent[91]. Equation (2-3) shows how the E_{γ} is modulated while Equation (2-4) illustrates the condition for absorption, where E_D is the energy of gamma radiation tuned by the Doppler Effect, ϵ_0 is the energy of the absorption line, E_R the shift energy due to the environment of absorber and *c* the speed of light.

$$E_D = \frac{v}{c} E_{\gamma} \tag{2-3}$$

$$E_{\gamma} - E_D = \epsilon_0 - E_R \tag{2-4}$$

Experimental conditions

The Mössbauer spectra were obtained in a time-mode spectrometer working in constant acceleration transmission geometry with triangular reference signal at 300 K using a (10 mCi) 57Co/Rh source (see Figure 2-5). The calibration was carried out using α -Fe foil, the spectra were collected in 512 channels and fitted using the Recoil software in a nonlinear least squares fitting procedure assuming Lorentzian Mössbauer lines while the isomer shift value is quoted relative to that of α -Fe at 300 K.

Figure 2-5: Mössbauer set-up with a ⁵⁷Co source for the analysis of iron samples



2.1.5 Thermal Analysis

The technique

The thermal analysis involves a set of techniques, where the behavior and properties of materials are studied as an answer to the temperature change under controlled environmental conditions.

a) *The Thermogravimetric Analysis (TGA)* involves subjecting a material to a temperature profile under a controlled atmosphere while measuring the percentage change in its weight as a function of time or temperature. The technique can characterize materials exhibiting loss or weight gain due to processes of decomposition, oxidation or dehydration. Measurements are used primarily to determine the composition, purity of a material, predict thermal stability and kinetics of its chemical reactions[92].

In the process, the desired heating profile takes place in a closed oven in which the sample is located in a sampler holder attached to a microbalance. As the temperature varies the microbalance measures and the system records the weight change of the sample.

b) The *Differential Scanning Calorimetry (DSC)* measures the difference in the proportion of heat flow (mW = mJ \cdot sec⁻¹), as a function of time and temperature; to be delivered to a sample and an inert reference to both follow the same temperature program. In this way, by recording the heat flow applied to the sample and the reference which does not react and through an internal comparison, it is possible to identify the relative transitions of the sample under study, which are presented as incoming or outgoing heat flows of the material according if they are endothermic or exothermic reactions [93]. Also, by considering the temperature, the associated enthalpy and the shape of the data curve, it is also possible to determine the nature of the transition (glass transition temperature, point of melting, crystallization, oxidative induction time).

Thermogravimetric analysis and differential scanning calorimetry were carried out simultaneously in NETZSCH STA 409 CD equipment (see Figure 2-6). Samples were placed in an alumina pan in quantities of 5–8 mg and heated at 10K·min from room temperature up to 1200 K under N₂ atmosphere.

Figure 2-6: NETZSCH STA 409 CD equipment



2.1.6 FT-IR Spectroscopy

The technique

In Fourier transform infrared (FT-IR) spectroscopy, infrared radiation is passed through a sample, where according to the energy of the radiation, a part of it is absorbed by the sample and part of it is transmitted. The result is a spectrum of the molecular absorption and transmission, being a molecular fingerprint of the sample. As a fingerprint, no two unique molecular structures produce the same infrared spectrum; this makes infrared spectroscopy an excellent tool for various types of analysis, such as identifying unknown materials, the determination of the quality or consistency of a sample and the detecting of the constituents present in a compound[94].

FT-IR spectra were obtained by diluting the samples in KBr (1g of sample: 100 g of KBr), using a Shimadzu 8400S from 400 to 4000 cm⁻¹ and a spectral resolution of 2 cm⁻¹(See Figure 2-7).



Figure 2-7:Shimadzu 8400S

2.1.7 Vibrating sample magnetometry

The technique

Vibrating sample magnetometry (VSM) measures the magnetization of a sample based on Faraday's law, which states that a time variable magnetic field induces an electromagnetic force (FEM). In this procedure, the magnetization is measured by swinging the sample under the presence of a static magnetic field to generate a time variable magnetic field, which induces an electrical current. From this signal, it is possible to calculate the magnetization value by removing the oscillation frequency of the sample. This technique allows to determine the magnetiz properties of materials and devices, such as saturation magnetization, remanent magnetization, coercive field and maximum energy product $(B \cdot H)_{max}$, by performing a hysteresis loop[95]. Additionally, by using a cryostat to perform measurements of magnetization while cooling, under magnetic field (FC) or without magnetic field (ZFC), it is possible to study using this technique how the magnetic behavior of materials varies with the temperature and their different magnetic transitions.

Magnetics measurements were performed using a Quantum Design PPMS SQUID magnetometer (see Figure 2-8), the M-H curves were taken at room temperature and since -10 KOe to 10KOe and the FC and ZFC curves were performed since 2-300K and under a field of 2KOe.



Figure 2-8: Quantum Design PPMS SQUID

2.1.8 Electrical Measurements

2.1.8.1 Polarization Loop

Experimental conditions

For the characterization of the ferroelectric behavior of the samples and their electrical properties, a Radiant Technologies precision LC test system (P loop) was used. For this purpose, cylindrical pellets of 7 mm in diameter and 1 mm thick were pressed at 300 MPa in uniaxial disc. These discs were fabricated from the grounded powder treated at 900 °C and were sintered at 1200 °C for 12 h in air (see Figure 2-9). The measurements were taken using a sample holder, which forms a capacitor by pressure. In this way, a Pt bottom electrode was connected to the drive of the precision LC and the Au top electrode to the drive of the precision LC (see Figure 2-10).

Figure 2-9: Cylindrical pellets of the Rare-earth orthoferrites used in the electrical measurements



Figure 2-10: Experimental set-up for the recording of polarization Loops



a) Radiant Technology Precision LC



b) Electrodes and sample holder

2.1.8.2 V vs I Curves

The technique

For plotting the V vs I curves the four corners method is widely used. In this method, four ohmic contacts are welded to the sample and two contacts apply a current while the other two corresponding contacts measure the voltage. Adjusting this data using Ohm's law, it is possible to calculate the resistivity of a compound. Eq. (2-5) shows Ohm's law where V is voltage, R is resistance (related with resistivity) and I is current.

$$V = RI \tag{2-5}$$

For these measurements, the pellets pressed for the P loops were used. Using silver paint four ohmic contacts were welded using a clover pattern. The sample was fed using a Power source KEITHLEY-236 while a Nanovoltimeter KEITHLEY-181 measured its voltage response. The system was controlled and the data were collected using a Labview interface (see Figure 2-11). The step current of the measurements was 1E-10 A.

Figure 2-11: Set-up for the measurements of the V vs I curves



a) Contacts in the samples



 a) Power source KEITHLEY -236, Nanovoltimeter KEITHLEY -181 and data processing system

2.2 Synthesis Procedures

2.2.1 GNP self-sustained combustion method

The Glycine-nitrate process (GNP) is a self-combustion wet method, usually used to synthesize polycrystalline multi-component oxide nanopowders. This method is based in a strong redox reaction of ion precursors with a fuel to promote the ignition of a high exothermic self-sustained combustion [96]. In the process, as its name makes mention, an aqueous solution is prepared using

nitrates as precursors, while at the same time being the source of cations and the oxidant agent. Meanwhile, the fuel is the Glycine amino acid, which also complexes the cations increasing their solubility and preventing their selective precipitation as water is evaporated. This ensures the chemical homogeneity of the final oxides and the absence of segregated phases in them [97]. For this report, the mechanism of complexation for the cations RE^{3+} in the Glycine molecule is in Figure 2-12 and takes place in the amino group. This mechanism is the same for the Fe⁺³ cations due to both having the same oxidation state.

Figure 2-12: Complexation process of the RE³⁺ cations in the Glycine molecule [97]



When the solution of the complexed cations is heated, the water excess is evaporated forming a viscous precursor which makes ignition over the 450K to produce the desired oxides. The resulting compounds are fine powders due to the large amount of gases expelled as coproducts in the decomposition of the glycine. These oxides usually present low values of remaining carbon due to the high temperatures of the reaction [98].

For this report, the general formula for the reaction is the following:

$$RE(NO_3)_3 + Fe(NO_3)_3 + NH_2CH_2COOH \rightarrow REFeO_3 + NO_x \uparrow + CO_x \uparrow + H_2O \uparrow + C$$
(2-6)

From the formula, it is clear that to prepare one mole of $REFeO_3$ it is necessary to use one mole of rare-earth nitrate and one mole of iron nitrate. With this in mind, the stoichiometric calculations to synthetize 0,01 mole of each orthoferrite REFeO₃ (RE = La, Pr, Nd, Sm) using the reactants of Table 2-1 are presented below.

Reactants	Name	Brand	Presentation	Density	Oxide	MW (g/mole)
H ₂ NCH ₂ CO ₂ H	Glycine	Merck	Powder	-	-	75,1
<i>Fe</i> (NO ₃) ₃ · 9H2O	Iron nitrate	Merck	Powder	-	-	404,00

Table 2-1: Reactants for the nitrate-glycine self-combustion synthesis

Reactants	Name	Brand	Presentation	Density	Oxide	MW (g/mole)
La(NO ₃) ₃ · 6H2O	Lanthanum nitrate	Merck	Powder	-	-	433,01
Pr(NO ₃) ₃ · 6H2O	Praseodymium nitrate	Rhodia	Solution	0,500 g/ml	Pr_6O_{11}	1021,45*
<i>Nd</i> (NO ₃) ₃ · 6H2O	Neodymium nitrate	Rhodia	Solution	0,519 g/ml	Nd_2O_3	336,48*
<i>Sm</i> (NO ₃) ₃ · 6H2O	Samarium nitrate	Rhodia	Solution	0,369 g/ml	Sm_2O_3	348,72*

^{*}Molecular Weight of the oxide.

• Calculation of the grams corresponding to 0,01 mole of the iron nitrate powder:

$$0,01 \text{ mole Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} \times \frac{404,00 \text{ g}}{1\text{ mole Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}} = 4,040 \text{ g Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} \quad (2-7)$$

• Calculation of the grams corresponding to 0,01 mole of the lanthanum nitrate powder:

$$0,01 \text{ mole } \text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} \times \frac{433,01 \text{ g}}{1 \text{ mole } \text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}} = 4,330 \text{ g} \text{ La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} \quad (2-8)$$

• Calculation of the milliliters corresponding to 0,01 mole of the praseodymium nitrate solution:

$$500 \ \frac{g}{L} \Pr_6 O_{11} \times \frac{1 \text{ mole } \Pr_6 O_{11}}{1021,45 \text{ g}} \times \frac{6 \text{ mole } \Pr}{1 \text{ mole } \Pr_6 O_{11}} = 2,940 \ \frac{mole}{L} \Pr$$
(2-9)

$$0,01 \text{ mole } \text{Pr} \times \frac{1000 \text{ ml}}{2,94 \text{ mole } \text{Pr}} = 3,401 \text{ ml}$$
(2-10)

• Calculation of the milliliters corresponding to 0,01 mole of the Neodymium nitrate solution:

519
$$\frac{g}{L}$$
 Nd₂ $O_3 \times \frac{1 \text{ mole } Nd_2O_3}{336,48 \text{ g}} \times \frac{2 \text{ mole Nd}}{1 \text{ mole } Nd_2O_3} = 3,080 \frac{mole}{L}$ Nd (2-11)

$$0,01 \text{ mol Nd} \times \frac{1000 \text{ ml}}{3,08 \text{ mol Nd}} = 3,246 \text{ ml}$$
(2-12)

• Calculation of the milliliters corresponding to 0,01 mole of the samarium nitrate solution:

$$369 \frac{g}{L} Sm_2 O_3 \times \frac{1 \text{ mole } Sm_2 O_3}{348,72 \text{ g}} \times \frac{2 \text{ mole } Sm}{1 \text{ mole } Sm_2 O_3} = 2,116 \frac{mole}{L} Sm$$
(2-13)

$$0,01 \text{ mol Sm} \times \frac{1000 \text{ ml}}{2,12 \text{ mol Nd}} = 4,716 \text{ ml}$$
 (2-14)

Now, in order to calculate the glycine amount necessary to complete the combustion of all elements, we have to take in account the elemental stoichiometric coefficient (ESC) or equivalence ratio of a mixture defined as:

$$\varphi_{e} = \frac{Oxidizer}{Fuel} = \frac{\sum (Molar \ Coefs. \ of \ oxidizing \ elements)(Valency)}{(-1)\sum (Molar \ Coefs. \ of \ reducing \ elements)(Valency)}$$
(2-15)

Where oxygen is the only oxidizing element; carbon, hydrogen, and metal cations are reducing elements and nitrogen is neutral. Oxidizing elements have positive valencies and reducing elements have negative valencies [99]. According to this, for this report the oxidizers are the nitrates $RE(NO_3)_3$ and $Fe(NO_3)_3$, while the fuel is the glycine.

In this way the stoichiometric coefficient for REFeO₃ is:

$$\varphi_e = \frac{[1Re(-3) + 3N(0) + 90(2)] + [1Fe(-3) + 3N(0) + 90(2)]}{(-1)[2C(-4) + 1N(0) + 5H(-1) + 20(2)]}$$
(2-16)

$$\varphi_e = \frac{Oxidante}{Combutible} = \frac{3mol}{9mol} = 3,\hat{3}$$
(2-17)

This means that for the synthesis of 0,01 mole of REFeO₃ it is necessary to use 0,03 mole of Glycine. However, in it was found in this experiment, that despite this amount of glycine ensuring the total combustion of the organic material, it was necessary to be very careful with the content of water of the solution and the speed of evaporation, otherwise oxides of secondary structure appeared that were associated with the precipitation of their respective cations. For this reason, it was decided to work with a higher content of glycine using the ratio $NO_3/NH_2 = 1$ to calculate this amount; because even with this it means more residual carbon guarantees the complete complexation of the cations.

In this way, where in the reaction there is 0,03 mole of NO_3 for each nitrate (Rare earth and Iron) 0,06 mole glycine should be used to obtain the ratio $NO_3/NH_2 = 1$.

0,06 mol Gly
$$\times \frac{75,1g}{1mol Gly} = 4,506$$
 g de Gly (2-18)

After this calculation, the syntheses of the orthoferrites REFeO₃ (RE = La, Nd, Pr, Sm) was completed, preparing aqueous solutions with 50ml of water and the nitrates of Table 2-1 in the adequate stoichiometry to obtain 0,01 mole of the desired oxide. Glycine $H_2NCH_2CO_2H$ was added at the required amount to obtain the molar ratio of $NO_3/NH_2 = 1$ and the resulting solutions were slowly evaporated at ~400K until vitreous gels were obtained. The gels were heated up to around 550 K when an auto ignition reaction and rapid combustion takes place, producing powdered precursors which may still contains carbon residues (see Figure 2-13).

Figure 2-13: Glycine-nitrate self-sustained combustion synthesis of orthoferrites REFeO₃ (RE = La, Pr, Nd, Sm)



a) Vitreous gel precursor



b) Ignition of the reaction



c) Heat wave propagation



d) Rapid self-sustained combustion



e) Highly porous powders



f) Precursors for calcination

The precursors obtained from the combustion reaction were taken for calcination at 900 K for 10 h, to eliminate all the remaining carbon (if there was any) and to promote the crystallinity. The whole process of synthesis is summarized step by step in Figure 2-14.

Figure 2-14: Blocks diagram of the syntheses process of the orthoferrites REFeO₃ (RE = La, Nd, Pr, Sm) by the glycine-nitrate self-combustion method



2.2.2 Ammonolysis Procedures

Experimental conditions

For the ammonolysis procedures, samples of 200 mg were placed in an alumina boat and taken to the furnace. The samples were heated under a $30\text{ml}\cdot\text{min}^{-1}$ nitrogen flow at a rate of $10\text{K}\cdot\text{min}^{-1}$ to their target temperature; then the quartz tube was evacuated and refilled with anhydrous ammonia (Indura 99.9%) flow of $200\text{ml}\cdot\text{min}^{-1}$ to start the nitriding reaction. After the treatment was completed, the furnace was switched off and allowed to cool down. When the temperature was below 250 °C, the ammonia flow was changed to nitrogen in order to cool to room temperature. The experimental set-up is shown in Figure 2-15.



Figure 2-15: Ammonolysis Set-up

2.2.3 Ammonia Microwave-Induced Plasma (MIP)

Set-up and experimental conditions

The microwave set-up is based on an Electrolux EMDN2363ML6, 2.45 GHz, 900W, DMO. The design used for the system was suggested by Houmes et al. [57] and was developed using the improvements suggested by Aguiar[100].

Among these improvements, the most important are:

- c) A brass wave guide for focusing the microwave radiation in an area of large electrical field intensity where the plasma is more powerful.
- d) To prevent reflected power damaging the magnetron and to keep the waveguide from overheating, water is circulated through copper piping placed around the waveguide and connected to a dummy load vessel placed out of the DMO.

For the procedures using this method, a (Indura 99.9%) ammonia flow was controlled by a mass flow controller SmartTrak 100 that was used to adjust a pressure of 50 mbar. The experimental set- up is shown in Figure 2-16.







2.2.4 Urea Procedures

2.2.4.1 Reaction using oxide precursors

For this synthesis, the general approximation way involves the formation of the perovskite structure during the reaction. For this reason, a stoichiometric mixture of the precursors; lanthanum oxide, hematite and urea were prepared in a ratio oxides to urea of 1:1: 24 and according to literature [70]. The oxides used for this purpose were activated by calcination under oxygen flow at

1173K by 2h and after were mixed in an agate mortar under absolute alcohol (isopropanol) as medium for 1h (see Figure 2-17). The mixture was dried and heated under nitrogen (N_2) atmosphere at a rate of 10 K/min up to 1223 K and held at that temperature for 1 h. The expectation was that the following reaction would take place:

$$RE_2O_3 + Fe_2O_3 + 2NH_3 \xrightarrow{\Delta} 2REFeO_2N + 2H_2O \uparrow + H_2 \uparrow$$
(2-1)

After the reaction, the temperature was lowered to room temperature in a nitrogen atmosphere and the samples were collected for analysis.



Figure 2-17: Stoichiometric mixture of oxide precursors with urea

2.2.4.2 Reaction Using Nitrate precursors

For this variant of the previous procedure, the same treatment conditions have been used, simply that instead of using oxides as precursors, the stoichiometric mixture of the precursors where the nitrates of the respective cations.

Figure 2-18: Urea Reaction using nitrate precursors



a) Stoichiometric mixture of nitrates precursors



b) Precursor mix in an alumina boat for the thermal treatment

2.2.4.3 Reaction by High Energy Ball Milling (HEM)

For this reaction a mixture of 1g PrFeO₃ with urea excess in a ratio 1:24 was prepared. The mix was placed into an oxide zirconia jar of 45ml of volume with ten 1cm of diameter oxide zirconia balls (see Figure 2-19). The jar atmosphere was purged with N_2 and then a treatment of 48h at 800 rpm into the high energy ball milling Micro mill pulverisette 7 premium line was performed. After a complete reaction occurred, the recovered material was taken for analysis.

Figure 2-19: Micro mill pulverisette 7 premium line

Planetary ball milling a)

c) Zirconium oxide - ZrO_2 balls of 1cm of diameter

2.2.5 Sol-gel test

A clear sol was prepared by adding stoichiometric amounts of the iron and rare-earth nitrates to 100ml of nitric acid (HNO₃). After, ammonium hydroxide (NH₄OH) was added drop wise to the acid solution until the desired pH was reached (~9). The resulting suspension was mechanically stirred at room temperature for 5h and after at least 12h of decantation, the liquid was removed. The precipitate was subsequently washed twice with a 0.23M solution of NH₄OH and then dried in an oven at 100°C. The resulting gel was calcinated during 1h at 500 °C under air atmosphere by heating at a rate of 5 °C/min[75].





b) Zirconium oxide - ZrO₂ 45ml Jars



3. Orthoferrites Results

3.1 X-ray diffraction analysis and Rietveld refinement

The crystal structure and phase purity of the rare-earth orthoferrite compounds $REFeO_3$ (RE= La, Pr, Nd, Sm) were studied by X-ray diffraction. The X-ray diffraction patterns of the samples after calcinations present well-defined peaks. All diffraction lines for these structures match with JCPDF cards (see Figure 3-1). In Figure 3-1it can be observed that no segregated phases were found, indicating that the auto combustion synthesis method produce single phase and crystalline compounds.







(b) Orthorhombic distorted structure of the refined PrFeO₃ compound

The structure of the **REFeO**₃ (RE= La, Pr, Nd, Sm) phases were determined by Rietveld refinement of X-ray diffraction data (see Figure 3-2). The four compounds were fitted in the space group *Pbnm* with an orthorhombic symmetry, where the iron atoms are octahedral coordinated (FeO₆) and the Rare-earth (RE) atoms are located in the interstices, this is clear in Figure 3-1.b where the refined structure of PrFeO₃ is depicted.





In this structure, the atomic position of the rare-earth atom is displaced from its ideal cubic position generating the octahedral tilted around the b and c orthorhombic axes, this phenomena is more evident in the Fe–O–Fe bond angles that are lower than the ideal value of 180^{0} [101]. To a large extent, the degree of tilting is determined by the size of the RE ions: hence, the larger the RE ion, larger the tilting and the Fe–O–Fe bond angle approaches to 180^{0} [102]. This is clear in Table 3-1 where the refined structural parameters, selected bond lengths and bond angles are summarized. As shown, the cell volume increases with the cell parameter c associated with the elongation of the ideal cubic cell, while the Fe-O-Fe angle decreases with the RE ion radii as was expected. In the same way is clear that the R_{WP} factors are close to the R_{exp} factors, this results in calculated χ^2 values near to one. These values, for the number of counts collected in the diffractograms around 30.000), are a good indicator that the model calculated is well adjusted to the experimental diffractograms as is shown in the residues function in the Figure 3-2.

The average crystal sizes reported were estimated from X-ray line broadening using Debay-Scherrer's equation:

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$
(3-1)

Where λ is the wavelength of the X-ray radiation (0.154056 nm), β is the full width at half maximum (FWHM) intensity and θ is the diffraction angle. In this way, it can be estimated that the average crystallite size will be among 55 and 76 nm to the four compounds.

Table 3-1:Refined structural parameters of orthoferrites REFeO3 (RE= La, Pr, Nd, Sm)
phases obtained by self-combustion method.

Compound	Compound LaFeO ₃ PrFeO ₃ NdFeO ₃		NdFeO ₃	SmFeO ₃
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
er ystar system	ormonioniole	ormonioniole	ormornomole	ormornomore
Space group	<i>Pbnm</i> (no. 62)	<i>Pbnm</i> (no. 62)	<i>Pbnm</i> (no. 62)	<i>Pbnm</i> (no. 62)
	a= 5.55050(6)	a= 5.48390(6)	a= 5.45361(6)	a= 5.40297(6)
Lattice Parameters (Å)	b= 5.56212(7)	b= 5.57395(7)	b= 5.58538(7)	b= 5.59128(7)
	c= 7.86486(8)	c= 7.78816(8)	c= 7.76401(8)	c= 7.71339(8)
Cell Volume (Å ³)	242.80830	238.06070	236.49550	233.01770

Compound	LaFeO ₃	PrFeO ₃	NdFeO ₃	SmFeO ₃
Re (x, y, 0.25) (4c)				
X	0.0039(13)	0.99052(13)	0.98843(13)	0.98803(13)
Y	0.0287(14)	0.04282(14)	0.04789(14)	0.05437(14)
Fe (0, 0.5, 0) (4b)	-	-	-	-
O1 (x, y, 0.25) (4c)				
X	0.072(15)	0.08313(15)	0.08900(15)	0.09844(15)
Y	0.492(16)	0.48680(16)	0.48247(16)	0.46299(16)
O2 (x, y, z) (8d)				
X	-0.28090(17)	0.72204(17)	0.70736(17)	0.71561(17)
Y	0.28150(18)	0.28603(18)	0.29133(18)	0.29103(18)
Z	0.03940(19)	0.04361(19)	0.04262(19)	0.04680(19)
R factors (%)				
R _p	22.29	23.17	22.91	27.84
$\mathbf{R}_{\mathbf{wp}}$	13.52	12.58	12.91	14.03
R _{exp}	7.61	8.97	8.27	12.00
χ ²	3.16	1.96	2.44	1.37
Bond lengths (Å)				
$Fe-O_1 \times 2$	1.9941	2.0010	2.0032	2.0110
Fe–O2×2	1.9556	1.9650	2.0037	1.9638
FeO2' × 2	2.0474	2.0347	2.0090	2.0335
Bond angles (⁰)				
Fe–O ₁ –Fe	160.80650	153.31558	151.37822	147.02716
Fe-O ₂ -Fe	157.90849	155.63918	153.15858	153.08739
Average crystal size (nm)	55.324	72.087	75.279	69,900

3.2 Surface morphology and elemental compositions

Scanning electron micrographs for REFeO₃ (RE= La, Pr, Nd, Sm) perovskites synthesized by selfcombustion method are depicted in Figure 3-3. These results are in good agreement with the inference that combustion method gives rise to porous material and open flakes type morphology. Theses macro-porous are formed due to the rapid evolution of gases during the auto-combustion process. The BET specific surface area for REFeO₃ perovskite are around 10 m²/g where occasionally CO₂ molecules are trapped due to the base nature of the lanthanides [103].

Figure 3-3: SEM micrographs at 500x and 1500x of orthoferrites phases obtained by selfcombustion method. (a) LaFeO₃, (b) PrFeO₃, (c) NdFeO₃ and (d) SmFeO₃.





Elemental composition of the materials was estimated using EDX and atomic absorption analysis. The atomic percentage of La, Pr, Nd, Sm, Fe and oxygen are listed in Table 3-2. In this table it can be observe that RE/Fe ratio was almost equal to unity for all perovskites, indicating the incorporation of the elements on the structure and confirming the absent of residual oxides.

Somula	Nomi	Nominal atomic composition				
Sample	Re	Fe	0	RE/Fe		
LaFeO ₃	21.53	22.48	55.99	0.96		
PrFeO ₃	22.85	23.00	54.15	0.99		
NdFeO ₃	22.33	23.69	53.98	0.94		
SmFeO ₃	22.21	23.17	54.62	0.96		

Table 3-2:Elemental composition of orthoferrites $REFeO_3$ (RE = La, Pr, Nd, Sm) phases
estimated from EDS.
3.3 FT-IR analysis

The FTIR spectra of REFeO₃ (RE= La, Pr, Nd, Sm) orthoferrites are compared in Figure 3-4. Infrared data spectra were fitted by using the Lorentzian and/or Gaussian functions. All FTIR spectra show a well-defined absorption bands typical of perovskite oxides ABO₃ [104]. Due to the fact that the Fe–O bonds of the FeO₆ octahedral units are undoubtedly stronger than those of the 12-coordinated RE(III)–O units, one may predict that the FeO₆ units dominate the spectroscopic behavior. The bands in the low-wavenumbers region (250–500 cm⁻¹) correspond to the deformational modes of the octahedra. Bands associated to a RE(III)–O stretching motion can also appear in this region [105], and bands in the 500–730 cm⁻¹ region are assigned to the stretching modes of the FeO₆ octahedra. FT-IR spectra of REFeO₃ present intense bands around ~550 cm⁻¹ with a shoulder at ~570 cm⁻¹. The main band can be assigned to asymmetric stretching vibration of Fe–O bonds in the FeO₆ octahedra [105], which involves internal motion of a change in Fe–O bond length, whereas the shoulder can be assigned to the symmetric stretching vibration of these octahedra.





3.4 Thermal events analysis

The thermal stability of $REFeO_3$ (RE= La, Pr, Nd, Sm) compounds was studied with TGA/DSC (see Figure 3-5). The TGA curves are very similar and present a continuous negative slope where it is difficult to determine the events that take place while it is heating. Nevertheless, in the inset that shows the DSC curve for NdFeO₃ (representative for the four compounds), it is easy to observe three events; the first one around 100 °C and associated with the dehydration of the samples, the second one between 200 °C and 400 °C is related to the release of absorbed gases from the environment like CO and CO₂ due to the highly porous nature of the compounds and finally the third one, that begins around 400°C is attributed by Mizusaki et al. [106] to the formation of oxygen vacancies. After, the variations among the curves slopes are related to the differences in the vacancies formation enthalpies [107].

Figure 3-5: Orthoferrites **REFeO**₃ (RE= La, Pr, Nd, Sm) TGA curves in N₂. Inset shows DSC curve for NdFeO₃.



 X^2

3.5 Mössbauer spectroscopy characterization

Mössbauer spectra at room temperature were recorded and fitted using Recoil software[108] as structural and magnetic complementary characterization, all orthoferrite compounds spectra were adjusted in a sextet pattern with values of isomeric shift and quadrupole interaction which are in good agreement with the crystallographic structure and the stoichiometry of the compound, where the iron atoms are in equivalent sites with a $3d^5$ configuration, in a octahedral coordination and with an oxidation state Fe⁺³ Table 3-3.

obtained by self-combustion method.					
Site Parameters	LaFeO ₃	PrFeO ₃	NdFeO ₃	SmFeO ₃	
CS [mm/s]	0.3657	03597	0.3603	0.3596	
ε [mm/s]	-0.0349	-0.0151	-0.0098	-0.0467	
H [T]	52.179	51.340	51.112	50.082	
A [counts·mm/s]	191200	723000	1088000	502000	
W ₃ [mm /s]	0.152	0.195	0.203	0.213	
A_1/A_3	2.81	2.83	2.80	2.96	
A_2/A_3	1.85	1.85	1.85	1.97	
W_1/W_3	1.21	1.13	1.075	1.19	
W_2/W_3	1.08	1.06	1.018	1.10	

Table 3-3:Hyperfine Mössbauer ⁵⁷Fe parameters at Troom for the **REFeO**₃ orthoferrites
obtained by self-combustion method.



1.79733

1.6250

1.18182

0.744167



The high and similar values of the magnetic field for the four samples imply that these kind of compounds have a magnetic behavior at room temperature and this case is due to the magnetic interactions of the two different types of magnetic ions: Fe³⁺ and RE³⁺. The competition of Fe–Fe, RE–Fe and RE–RE interactions in different magnetic networks leads to an antiferromagnetic behavior [14], which is confirmed in the Mössbauer spectra fitted in a sextet pattern characteristic for this magnetic structure.

3.6 Magnetic measurements

As shown in Figure 3-7, the obtained M-H curves for the orthoferrite compounds are very similar in magnitude and shape and although the PrFeO₃ shows a soft hysteresis shape and with NdFeO₃ and SmFeO₃ presenting small values of spontaneous magnetization and coercive field, there is not a saturation value in the curves for the magnetization in the range of measurements and the magnetization still has the tendency to increase in all, which is characteristic of antiferromagnetic compounds. Another point to consider about the curves, is that the moment values are considerably lower than those reported in earlier literature [109],[110]. However, they are in good agreement with those reported in compounds synthetized by other combustion methods [111] where they attribute this phenomena of the large surface to the volume ratio of the nanocrystalline powders.





Figure 3-8 shows the dependence of the M-H curve in respect to temperature for $LaFeO_3$, from room temperature to 5K. Even at low temperatures, although the magnetization increases, the general behavior still persists and there is not saturation, while the spontaneous magnetization is almost null as well as the coercive field; which is a typical behavior for antiferromagnetic compounds.





ZFC and FC curves were performed to understand better the magnetic behavior of the compounds. In Figure 3-9, the ZFC curves show for the compounds a small moment of magnetization at 2K with zero field applied, which could be attributed to a spin canting effect that this family of compounds presents as a result of the distortion in the perovskite ideal structure. The magnetic order is affected avoiding the total cancellation of the magnetic moments and this results in a weak net ferromagnetism. Additionally, there is a competition among the sublattice of Fe³⁺ and RE³⁺ and below a determinate temperature of around 35 K the magnetics moments of the ferromagnetic Re sublattice become greater than those of the antiferromagnetic Fe sublattice becomes prominent again and the compound returns to its antiferromagnetic behavior. Moreover, there is a competition

among the sublattice of Fe^{3+} and RE^{3+} and below a determinate temperature of around 35 K, the magnetics moments of the ferromagnetic Re sublattice become greater than those of the antiferromagnetic Fe sublattice and this is shown by the ZFC curve. However, again when the temperature increases in FC the Fe sublattice becomes prominent again and the compound returns to its antiferromagnetic behavior. This is clear for PrFeO₃, NdFeO₃ and SmFeO₃ however for LaFeO₃ it is not the case and Anhua Wu et al. explain this as the result of magnetic frustration or glassy behavior [112]. Finally, it is easy to appreciate in Figure 3-9 the reversibility of the ZFC and FC curves for the PrFeO₃ and SmFeO₃ while around the 175K appears an anisotropy for NdFeO₃ which to be understood, will require further measurements.



Figure 3-9: ZFC and FC curves for REFeO₃ (RE= La, Pr, Nd, Sm) orthoferrite at 2KOe since 2 to 300K

3.7 Polarization Measurements

Polarization measurements of the rare-earth orthoferrite REFeO₃ (RE= La, Pr, Nd, Sm) were performed. The results for the hysteresis polarization loops are depicted in Figure 3-10 where it is easy to observe that the four samples show a typical ferroelectric loop and clearly the behavior is much more intense in LaFeO₃. Although the samples do not saturate, this is solely due to the absence of thermal activation for the low frequencies, but the loop implies the spontaneous polarization[113].



Figure 3-10: Hysteresis polarization loop for Rare-earth Orthoferrites at 50 Hz and applied field of 300V

To explore deeply the behavior of the $LaFeO_3$ orthoferrite, measurements of this composition where recorded at different fields and frequencies trying to determine if the answer of the compound was associated with electronic or molecular polarization.

The results are plotted in Figure 3-11. From the left side of Figure 3-11 it is shown that in spite of the area of the curve increasing with the field even at very high value like 1000V, the LaFeO₃ orthoferrite does not saturate. Meanwhile in the graph on the right side, it can be appreciated the big effect of the frequency in the measurements and it is clear that the polarization decreases

considerably with the increase of the frequency. These two results point to the polarization of the oxide that can be majorly attributed to the formation of dipoles associated with the molecules or even the grain frontiers.



Figure 3-11: Hysteresis polarization loops of LaFeO₃

3.8 V vs I Curves

According to section 2.1.8.2, the V vs I curves for the Rare-earth orthoferrites were recorded and the data was plotted and adjusted using a linear fit for comparison to Omh's law. The resulting curves and fittings are depicted in Figure 3-12.





a) V vs I Curves of LaFeO₃ with the values of its adjustment



d) V vs I Curves of SmFeO₃ with the values of its adjustment

The information of the pellets used in the measurements and the slopes resulting from the fitting are shown in Table 3-4. Noticing that in this case, by the Ohm's law, the slopes are analogue to

the resistance and with the geometric characteristics of the pellets the resistivity is calculated using the following equation.

$$\rho = R \frac{S}{L} \tag{3-2}$$

Sample	Cross Section (cm ²)	Length (cm)	Resistance (Ohm)	Resistivity (Ohm*cm)
LaFeO ₃	2.64E-01	0.065	2.76E+05	1.12E+06
PrFeO ₃	3.04E-01	0.109	9.67E+04	2.70E+05
NdFeO ₃	3.06E-01	0.112	1.78E+06	4.87E+06
SmFeO ₃	3.06E-01	0.112	9.59E+05	2.62E+06

Table 3-4:Resistance and resistivity values of the rare-earth orthoferrite compounds

From the results, it is clear that these compounds are high insulators with resistivities to the order of $M\Omega^*$ cm. Where comparatively NdFeO₃ shows the highest resistivity of the four compounds, follow by the SmFeO₃. This is easy to see in Figure 3-13 where LaFeO₃ is not included due to its pellet that had a lower length than the others.

Figure 3-13: V vs I for the PrFeO₃, NdFeO₃ and SmFeO₃



4. Oxynitrides Results

4.1 Thermal Ammonolysis

The first approach to the synthesis of the REFeO_{3-x}N_x (RE = La, Nd, Pr, Sm) oxynitrides, was performed by the thermal ammonolysis method which is the most extensive method used in the synthesis of oxynitrides due to its nitriding high efficiency. In this sense when this reaction take place oxygen ions O^{-2} in the structure are replaced by N⁻³ ions and the following charge compensation mechanisms can occurs:

 Each nitrogen anion (N³⁻) introduced in the structure is compensated by an oxidation of one of the cations, generally B:

$$N^{3-} + B^{(n+1)+} = O^{2-} + B^{n+}$$
(4-1)

• Generation of oxygen vacancies in the structure:

$$ABO_3 \to ABO_{3-3x/2}N_x \tag{4-2}$$

These mechanisms would result in compounds with the formulas (4-3) and (4-4) respectively.

. _ _

$$RE^{3+}Fe^{3+}O_3^{2-} \to RE^{3+}Fe^{4+}O_2^{2-}N^{3-}$$
 (4-3)

$$REFeO_3 \rightarrow REFeO_{3-1.5x}N_x$$
 (4-4)

In these mechanisms, the perovskite structure is preserved during the nitriding process. For this reason the precursors for the synthesis of the REFeO_{3-x}N_x (RE = La, Nd, Pr, Sm) oxynitrides by thermal ammonolysis method are their respective oxides the orthoferrites REFeO₃ (RE = La, Nd, Pr, Sm); which were synthetized and characterized in the previous chapter.

In order to perform the ammonolysis procedures, the samples were placed in an alumina boat and taken to the furnace. To generate vacancies in the compounds to favor the nitriding process, the samples were heated under a $30\text{ml}\cdot\text{min}^{-1}$ nitrogen flow at a rate of $10\text{K}\cdot\text{min}^{-1}$ to their target temperature, where the quartz tube was evacuated and refilled with anhydrous ammonia flow.

With the idea to determine the behavior of the compounds, tests were performed at intermediate temperatures, short times and high ammonia flow according with literature. These treatments are summarized in Table 4-1 in the order they were realized.

Sample	Temperature [°C]	Time [h]	Ammonia Flow[ml·min ⁻¹]
	900	12	200
LaFeO ₃	900	6	200
	800	12	200
	800	6	200

 Table 4-1:
 Ammonolysis tests for LaFeO₃ preheated in N₂

After the first treatment performed at 900°C for 12h, the sample was characterized by the X-ray diffraction technique in order to determine the effect on the structure. From the X-ray diffractogram presented in Figure 4-1-a), it was found that during the reaction with NH₃ the LaFeO₃ structure collapse, producing impurity phases like metallic iron, hematite, magnetite and lanthanum oxide. The last one reacts after the process with the moisture and produces the corresponding hydroxide.

This phenomenon gives a clue about what is happening during the nitridation; since before the reaction the iron in the perovskite structure is in form of Fe^{+3} ion and at the end of the process the iron take place in magnetite and α -iron structures. For this to happen the iron had to be reduced to a mix of its oxidation states Fe^{+3} and Fe^{+2} in magnetite and to Fe^{0} in the α -iron.

This means during the reaction the iron undergoes a reduction process which could be attributed to the reduction potential produced during the partial decomposition of ammonia in hydrogen. This process compete with the nitriding procedure promoting collateral reactions like the formation of secondary oxides, metals and worst still, the destruction of the perovskite structure.

In this sense, the next step was searching for conditions where the structure was more stable and the nitriding reaction could take place without generate collateral reactions. This is the reason why the next tests were performed every time at lower times and temperatures; as is easy to see in the subsequent treatments of Table 4-1. The results of x-ray diffractograms for the resulting samples are shown below.



Figure 4-1: X-ray diffractograms of ammonolysis exploratory tests for LaFeO₃

For the previous treatments comparing with LFO 900°C by 12h, it can be suggested that:

- **LFO 900°C 6h:** The structure still is lost and the iron is reduced. However, in this occasion the time of the treatment is not enough to achieve the metallic iron.
- LFO 800°C 12h: This time not all the perovskite structure is lost but the iron still is reduced.

• LFO 800°C - 6h: In this case reduction of iron is not appreciable but the hydrogen reacts with the lanthanum to form lanthanum oxide.

At this point, where part of the structure is preserved, the most important point to consider is the efficacy of the nitridation process since it is not needed just preserving the structure but also introducing the nitrogen in the network. For this reason, more tests were conducted at a lower temperature, 700 °C, but at the same time exploring longer times. The treatments are in Table 4-2 and the X-ray diffractograms of their results are plotted in Figure 4-2.

Temperature Time **Ammonia Flow** Sample [°C] $[200 \text{ ml} \cdot \text{min}^{-1}]$ [h] 700 12 200 LaFeO₃ 700 200 6 700 3 200

Ammonolysis for LaFeO₃ at low temperatures (preheated in N₂)



Figure 4-2: X-ray diffractograms of ammonolysis for LaFeO₃ at 700 °C

Table 4-2:



This last result for the treatment at 700 °C for 3h, show the reduction of the iron and the formation of the lanthanum oxide still remain. While even at these relatively low temperatures and short times the structure is already affected and nitridation signs like color change, which is common in oxynitrides with respect to oxides, does not appear.

At this point is really important to highlight that similar results appeared for the other three orthoferrites.

Considering that usually an ammonolysis procedure lasts at least eight hours and until 72h or more as it is reported elsewhere [4], [7] the behavior of the compound is quite far from the typical cases. According to the literature, this phenomenon is due to the high electronegativity of iron compared with the more electropositive cations normally used in oxynitrides[4], [7]. This electronegativity increases the reactivity of the compound with the reduction potential of hydrogen resulting in reduced compounds even at low temperatures and very short times (3h).

In this sense, due to the nature of the compounds, the thermal ammonolysis method is inadequate for the nitriding process in the particular case of iron oxides with perovskite structure. Therefore it is necessary to look for other synthesis methods with lower reaction temperatures but at the same time with highly reactive nitriding species able to incorporate themselves in the structure.

4.2 Ammonia Microwave-Induced Plasma (MIP)

The ammonia microwave-induced plasma (MIP) was the first alternative route considered for the synthesis of oxynitrides. This method consists in mating a magnetron to the quartz reactor in order to induce the plasma state in ammonia. Therefore this method was quite promising since it takes place at lower temperatures (around the 550 °C) and the nitriding species produced in the ammonia decomposition are more reactive due to the plasma state.

The set-up and experimental conditions for these tests are described in section 2.2.3. The treatments that have been explored for the orthoferrites are shown in Table 4-3 for the $PrFeO_3$ case, where intermediate regrindings were perform each half hour.

Sample	Time [h]	Power [W]
	1	800
PrFeO ₃	2	800
	3	800

Table 4-3:Nitriding tests by ammonia MIP for PrFeO3

For the treatments of 1h and 2h there was any visible change as well as any variation in the x-ray diffractogram with respect to the $PrFeO_3$ precursor. Meanwhile for the treatment of 3h the reduction phenomena due to the hydrogen potential take place. The diffractogram for this treatment is depicted in Figure 4-3, where segregated phases of Pr_7O_{11} and hematite appear.

Figure 4-3: X-ray diffractograms of nitriding tests by ammonia MIP for PrFeO₃ treated 3h



Similar results were obtained for these treatments using the other three orthoferrites (see Figure 4-4).



Figure 4-4: X-ray diffractograms of nitriding tests by ammonia MIP during 3h

In these results the reduction process is evident and once again the formation of metallic iron and the secondary rare earth oxides take place. This implies that despite of the lower temperatures of this route with respect to thermal ammonolysis this method also promote the reduction of the iron resulting in collateral reactions due to its high electronegativity and the difficulty to effectively control the reducing character of ammonia plasma related with the formation of ionized hydrogen. Therefore this method also is inadequate for the nitriding process in the particular case of iron oxides with perovskite structure and in order to have a higher control of the reduction potential during the nitriding reactions it is necessary consider synthesis methods where the state of the nitrogen source is solid and not gaseous.

4.3 Urea as Nitridation agent

With the aim to avoid reductive collateral reactions due to uncontrolled reduction potential in the reaction, solid ammonia sources were considered to perform the synthesis of the oxynitrides.

Among the possible solid ammonia sources, the better explored is the route using urea $(CO(NH_2)_2)$ as it was reviewed in section 1.3.2.3.1. At temperatures over the 530 K, urea decomposes in ammonia and cyanic acid, which can also produce ammonia when reacts with water.

For this synthesis, the general approximation way involves the formation of the perovskite structure during the reaction. For this reason, a stoichiometric mixture of the precursors; lanthanum oxide, hematite and urea was prepared in a ratio oxides to urea of 1:1: 24 and a according to literature [70], the mixture was heated under nitrogen (N_2) atmosphere at a rate of 10 K/min up to 1123 K and held at that temperature for 1 h. It was expected that the following reaction would take place:

$$RE_2O_3 + Fe_2O_3 + 2NH_3 \xrightarrow{\Delta} 2REFeO_2N + 2H_2O \uparrow + H_2 \uparrow$$

$$(4-5)$$

After the reaction, the temperature was lowered to room temperature in a nitrogen atmosphere and the samples were collected for analysis. The X-ray diffractogram of the sample of lanthanum is plotted in Figure 4-5.



Figure 4-5: X-ray diffractogram of the oxide mix precursor treated with Urea

From Figure 4-5, it is clear that a big part of the iron oxide (the hematite) in the precursor mixture has been reduced to its free metal during the treatment with urea and just a small amount of the precursor have adopted the perovskite structure.

Additionally, although with further heat treatments the percentage of precursor forming the perovskite structure increase, these kind of procedures are not quite relevant since at the same time segregated phases of secondary lanthanum compounds due to the reduced iron were continually observed.

With the idea to avoid this behavior by increasing the rate of crystallization, the diffusivity of the ions and reducing the interaction of the precursor with the reduction potential before the perovskite formation; a second reaction without changing the treatment but using nitrates as precursors instead of oxides was considered.

The X-ray diffractogram of the product of this second procedure is plotted in Figure 4-6. Figure 4-6 clearly shows the perovskite structure was formed without any other segregated phase and for this reason the sample was taken for further analysis.



Figure 4-6: X-ray diffractogram of the nitrate mix precursor treated with Urea

As a first way to explore the possible content of nitrogen in the structure of the LaFeO₃ phase synthetized by the nitrate mixture precursor treated with urea, the FT-IR spectrum of the sample was recorded and the result is plotted in Figure 4-7. In this figure is easy to see the two characteristic bands of orthoferrites around the 650 and 350 cm⁻¹; however, there is not presence of new obvious bands, just very small irregularities in the baseline around the 1070 cm⁻¹[114]. This

result is interesting since could be associated with stretching vibration modes of Fe–N bonds in the $FeO_{6-x}N_x$ octahedra. For this reason the sample was studied by CHN elemental analysis to determine the possible presence of nitrogen; the results are presented in Table 4-4.



Figure 4-7: FT-IR spectrum of the nitrate mix precursor treated with Urea

Table 4-4:CHN elemental analysis of the sample $LaFeO_{3-x}N_x$ (Urea)

Sample	%C	%H	%N
LaFeO _{3-x} N _x (Urea)	0,26	0,07	0,00

From Table 4-4, it is shown that there is not nitrogen content in the samples and the possible bands of the FT-IR spectrum can be associated with other organic compounds produced during the decomposition of the urea.

In this case, the absence of the reduction phenomenon may be attributed to the reaction of the nitrate groups $(NO_3)_3$ with the products of the decomposition of the urea neutralizing the nitriding potential of ammonia. At this point, it is worth mentioning that usually urea is used as an oxidizer in the self-combustion synthesis of oxides where nitrates are used as precursors. However, in this reaction it was expected that due to the high ratio of urea/nitrates the excess of urea perform the nitriding reaction.

Thus it can be concluded that this synthesis route was not effective in this particular case since for the formation of oxynitrides is required not just the formation of the perovskite structure but also the change of oxidation state of iron Fe^{3+} to Fe^{4+} and this process only takes place in highly

oxidative atmospheres or oxide-reducing atmospheres as ammonolysis. Therefore, a possible solution implies a method in which the nitrogen insertion in the structure occurs in a more direct way so the change in the oxidation state of the iron can be forced.

In this regard, a last procedure was performed using urea, but this time a method was used where the reaction would take place just in solid state. Due to that purpose, the High-Energy Ball Milling (HEM) process was selected. Furthermore, with the objective to avoid the reduction of iron as much as possible, it was decided to use as a precursor the orthoferrite (with the perovskite structure) instead of the mixture of the secondary oxides which are more reactive.

For this reaction, a mixture of 1g PrFeO3 with urea excess in a ratio 1:24 was prepared. The mixture was placed into a tungsten vessel with zirconia balls under N2 atmosphere and then was treated into the high energy ball milling for 48H at 800 rpm. The reaction expected was the following:

$$PrFeO_3 + NH_3 \xrightarrow{\Delta} PrFeO_2N + H_2O \uparrow + \frac{1}{2}H_2 \uparrow$$
(4-6)

After a complete reaction, the recovered material was taken for analysis and the X-ray diffractogram is depicted in Figure 4-8.



Figure 4-8: The X-ray diffractogram of PrFeO₃ Sample treated with Urea in High energy ball milling

From Figure 4-8, it is shown that after the treatment of 48h in the high energy ball milling the perovskite structure of the precursor is conserved and there are not any segregated phases, just a higher background due to the amorphous inorganic compounds produced during the reaction of the Urea. Therefore, the sample was taken for further analysis to determine the presence of nitrogen in the structure. For this purpose the FT-IR spectrum of the sample was recorded and is presented in Figure 4-9.



Figure 4-9: FT-IR spectrum of PrFeO₃ Sample treated with Urea in High energy ball milling

In this spectrum it is clear that several new bands appear, where the most intense is located exactly in the nitrogen species area around the 1600 and 1400 cm⁻¹. However, before studying the possibility of removing the other inorganic compounds associated with the other bands in the spectrum, it was desired to determine if the nitrogen content was inside the perovskite structure. For this purpose, the Mössbauer spectrum of the sample was recorded and the result is plotted in Figure 4-10.



Figure 4-10: Mössbauer spectrum of PrFeO₃ Sample treated with Urea in High energy ball milling

Table 4-5:Hyperfine parameters of the adjusted Mössbauer spectrum for the PrFeO3 Sample
treated with Urea

Site Parameters	PrFeO ₃	Doublet
CS [mm/s]	03597	1.09
ε [mm/s]	-0.0151	2.10
H [T]	51.340	-
A [counts·mm/s]	723000	33400
Site Populations [%]	74.5	25.5
X^2	0.79	1744

From the Mössbauer spectrum, the characteristic sextet of orthoferrites with iron in oxidation state Fe^{3+} (magenta line) and a new iron site adjusted in a doublet (green line) is shown. However, this site could not be associated with site characteristics of Fe^{4+} which is characterized by the ferrates Na₂FeO₃, K₂FeO₃, BaFeO₃[115] besides its isomer shift of 1.09 mm/s, its quadrupole splitting of 2.10 mm/s and its shape are characteristic of the iron carbonates (-FeCO₃)[116], [117]. This result indicates that for the method of high energy ball milling, urea is not a correct nitriding agent

since its molecule contains carbon which is a reducing agent and promotes collateral reaction as the carbonates formation.

In this vein as a possible solution to these problems, a method of wet synthesis that has been used for the synthesis of secondary oxynitrides was evaluated. This method has the advantage of working at lower temperatures and with free carbon precursors.

On the other hand and an option to consider for the nitridation using the high energy ball milling, is to perform the reaction under atmosphere of anhydrous ammonia (NH₃), which has been explored in the nitridation of free metals [118], [119], [120]. Ammonia seems to be a more logical nitriding agent; however, in this case urea is preferred to avoid the reductive potential of hydrogen; something that is not a problem in the case of free metals which have a null oxidation state.

4.4 Sol-gel Process

Based on the preparation of oxynitrides of TiO2 [75], [76] and the preparation of orthoferrites by sol-gel [111], a methodology was proposed to try to perform the synthesis of the perovskite oxynitrides.

A clear sol was prepared by adding stoichiometric amounts of the iron and rare-earth nitrates to 100ml of nitric acid (HNO₃). Then ammonium hydroxide (NH₄OH) was added drop wise to the acid solution until the desired ph was reached (~9). The resulting suspension is mechanically stirred at room temperature for 5h and after at least 12h decantation, the liquid is removed. The precipitate is subsequently washed twice with a 0.23M solution of NH₄OH and then dried in an oven at 100°C. The resulting gel was calcinated during 1h at 500 °C under air atmosphere by heating at rate of 5 °C/min[75]. The x ray diffractogram of the resulting sample is presented in Figure 4-11.a. As it is clear the compound was highly amorphous, a further treatment of 12h at 700 °C under N₂ atmosphere was performed. The results are depicted in Figure 4-11.b, where it can be seen that even after this treatment the perovskite structure is not completely formed. Thus, a third treatment was performed; calcination under air atmosphere at 700 °C by 4h and finally the structure was formed as is shown in Figure 4-11.c. However, the CHN measurements shown there did not include any nitrogen content see Table 4-6.





Table 4-6:CHN elemental analysis of the sample $PrFeO_{3-x}N_x$ (Sol-gel)

Sample	%C	%H	%N
PrFeO _{3-x} N _x Sol-gel	0,15	0,04	0,00

According to these results, in spite of sol-gel process and other wet routes have proved their efficacy for the synthesis of titanium nitrides and oxynitrides; in the case of ternary oxynitrides as perovskite type, they are inadequate. This is because for these structures the formation energies are greater and in order to obtain a homogenous phase and completely remove the organic matrix more aggressive thermal treatments are needed and in these the possible nitrogen content is removed.

5. Conclusions and Outlook

5.1 Conclusions

According with the XRD, FTIR and EDS measurements pure and homogeneous phases of the orthoferrites REFeO₃ (RE=La, Pr, Nd, Sm) were synthetized by the self-sustained combustion method. These compounds crystallize as distorted perovskite structures in the orthorhombic Pbnm system due to the size of the rare-earth cations; which is related in an inverse way with the grade of distortion of the network.

The characteristic distorted perovskite structure confers to the orthoferrite compounds interesting magnetic properties like an antiferromagnetic structure with a parasitic ferromagnetism behavior; which is shown in the M vs H curves and in the M vs T measurements under FC and ZFC. In these curves small irreversibilities were found, however for better understanding of this comportment a deeper characterization must be realized since may be associated with grain size effects or spin glass phenomena.

The synthetized orthoferrite compounds shown a ferroelectric behavior and according to the polarization measurements under different frequencies looks to be associated with grain-grain interfaces. The highest intensity of this behavior was found for the case of $LaFeO_3$, however the hysteresis loops are quite narrow and saturation was not achieved under the measurement range. Nevertheless the ferroelectric behavior was confirmed in the V vs I curves where the ohmic behavior of the compounds was manifest and allows the calculation of the resistivity for the compounds, which is in the order of megaohms.

The thermal ammonolysis of the orthoferrites REFeO₃ (RE=La, Pr, Nd, Sm) is not a suitable procedure for the synthesis of the oxynitrides REFeO_{3-x}N_x (RE=La, Pr, Nd, Sm); due to the iron in the structure is reduced even at low temperatures and short reaction times by the reduction potential of hydrogen produced during the ammonia decomposition. This behavior is attributed to

the high electronegativity of the iron in comparison with the B transition metals in the oxynitrides already synthetized.

The nitridation by ammonia microwave-induced plasma (MIP) does not solve the reduction problem of the iron despite of its lower reaction temperatures, since is very difficult to control the reducing character in the ammonia plasma related with the formation of ionized hydrogen.

Methods where the amount of reducing agent in the reaction can be controlled seems to be the better approximation for the synthesis of the rare-earth oxynitrides REFeO_{3-x}N_x (RE=La, Pr, Nd, Sm). However, solid state reactions under nitrogen atmosphere using oxide or nitrides precursors and urea as nitriding agent were not effective in our particular case, since for the formation of the oxynitrides the reaction must promote the change in oxidation state of the iron from Fe³⁺ to Fe⁴⁺. This process takes place in high oxidative atmospheres or oxo-reductive atmospheres like in the ammonolysis.

High energy ball milling is a method quite interesting for the synthesis of rare-earth oxynitrides $REFeO_{3-x}N_x$ (RE=La, Pr, Nd, Sm), since the nitridation process is due to the high energetic collisions among the balls and the reactants for this reason is more direct. In these sense urea is not an adequate nitriding agent for this synthesis technique since its molecule have carbon, which as reducing agent promotes collateral reactions like the formation of carbonates.

Wet routes like sol gel have been used for the synthesis of secondary oxynitrides however in this case for the rare-earth oxynitrides $REFeO_{3-x}N_x$ (RE=La, Pr, Nd, Sm), which have a ternary structure this method is not effective since to obtain the formation of the perovskite structure and the total elimination of the inorganic matrix; calcinations under oxygen or air atmosphere around the 700 °C had to be performed but in the process the possible nitrogen in the structure is lost.

5.2 Outlook

The synthetized rare-earth orthoferrites (RE=La, Pr, Nd, Sm) are a group of materials quite interesting considering their antiferromagnetic, insulator and ferroelectric nature as is shown in this

work (among other characteristics). For this reason is very worth continue exploring the possible synthesis of their respective oxynitrides since the incorporation of nitrogen in its structure could improve their already wonderful properties.

In this sense, it would be a good idea to try compositions where the rare-earth precursor has the oxidation state (IV) like Pr^{4+} or Ce^{4+} in order to make easier the incorporation of nitrogen since the iron does not have to change during the nitriding process from Fe^{3+} to Fe^{4+} .

Synthesis methods where the amount of reducing agent can be controlled, like in solid sources of nitrogen, should be consider in order to avoid the problem of the reduction of iron in the structure due to its high electronegativity. In particular gaseous ammonia should be avoided since the reduction potential of hydrogen produced during its decomposition is very difficult to control.

Among these procedures the ammonothermal synthesis which provides a higher control of the synthesis variables or the nitridation using nitric oxide (NO) which does not have an aggressive reducing agent are quite promising. In the other hand the solid state synthesis at high pressures or by high energy ball milling could be also considered, as long as it is provided a solid or liquid nitrogen source free of carbon or other undesired elements.

A. Annex: Relative Recoilless F-factor in REFeO₃ (Rare-earth = La, Pr, Nd, Sm) orthoferrites synthetized by selfcombustion method

ABSTRACT

From the transmission Mössbauer spectra recorded at room-temperature, a relative recoilless Ffactor of the REFeO₃ (RE =La, Pr, Nd, Sm) compounds were estimated. Applying a method based on the correct determination of the two subspectral areas present in a mixture of known amounts of the compound under study and a standard sample (α -Fe), the F-factor values were calculated. The procedure was repeated three times for different amounts of the compounds. The obtained spectra were thickness-corrected and fitted using the commercial software Recoil. The relative recoilless F-fractions for the REFeO3 (RE= La, Pr, Nd, Sm) with respect to α -Fe were calculated to be 1.30±0.02, 1.08±0.04, 1.15±0.05, 1.18±0.08 respectively. These results compare reasonably well with the values predicted by the Debye model and the reported Debye temperatures for these compounds.

1. Introduction

The rare-earth orthoferrites REFeO₃ are a family of oxides with distorted perovskite structure which show unusual and interesting magnetic properties [16],[121]. These materials are canted antiferromagnets and have attracted much attention first, for their special antisymmetric exchange interaction which results in weak ferromagnetism[122], and second, for the idea to use them for potential applications in spin valves [14], [123]; as they show spin reorientation phenomena induced by temperature or by an applied magnetic field[124].

For these interesting magnetic properties, most of Mössbauer spectroscopy studies of orthoferrites have been focused on the comprehension of their weak ferromagnetism and the temperature dependence of the sublattices magnetization[102]. Leaving aside one of the potential applications of the technique in the case of iron oxides; where due to the compounds being magnetically ordered over a wide range of temperatures and that their Mössbauer parameters differ considerably between the individual species, the technique is frequently used for the unequivocal distinction and detection of minor amounts and also often a quantification of iron oxides in systems of complex compositions, taking advantage of the insensitivity of Mösssbauer spectroscopy to all isotopes except that under interest [125]. This could be a useful application of the technique for these compounds due to the actual crisis of rare earth elements[126] and the tendency to recycle them[127].

However, to properly do a Mossbauer sub-spectral, areas of the quantitative characterization of a sample in which there are present two or more iron compounds, it is necessary to take into account the recoil-free fraction (f) of each one of them.

This parameter is define as the probability of a nucleus in a specific environment at a given temperature, to present absorption and emission of gamma rays without recoil [90] and it must be considered since in the Mössbauer spectrometry the nucleus is used as a probe to get information of the different fields which are interacting with it. In that sense, according to the state of the nucleus every compound has an inherent predisposition to show recoil-free events and a specific answers to the stimulus. This phenomenon is reflected in a difference among the intensities of their sub-spectral areas that affect the accuracy of the calculations.

Nevertheless, calculating the recoil-free fraction (f) is not an trivial procedure, at least not by using the usual method, the Debye theory; because it implies determining the Debye temperature of the compound by finding the dependence of its isomer shift (δ) or its subspectral area (A) with respect to temperature, which is a procedure very sensitive and with an inherent wide experimental error [128]. As a solution for this problem, a recent method introduced the relative recoilless fraction (F), which is defined as the ratio of the recoil free fractions of two different compounds; makes it possible to find the recoil free fraction of a compound without using the Debye approximation; just by starting of a known recoil free fraction of a reference compound. This is very useful since first it makes it easier to perform the accurate conversion of the sub-spectral areas to the relative atomic, molecular, or weight fractions of each compound[128] and second it allows to correlate direct or indirectly (using the same reference for two different iron phases) the predisposition to show the Mössbauer effect of each compound and evaluate the physic phenomena behind of this relation according to their characteristics.

In this sense, the objective of this work was find the room-temperature relative recoilless Ffactor of four oxide compounds of the rare-earth orthoferrite family REFeO3 (RE =La, Pr, Nd, Sm) with respect to α -iron which is commonly used as reference for these calculations.

2. Theory

Using the Debye approximation the probability of recoil-free emission or absorption events (f) can be described by the following equation:

$$f = exp - \left\{ \frac{3E_0^2}{k_B M \theta_D c^2} \left[\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x dx}{e^x - 1} \right] \right\}$$
(5-1)

Where E_0 , k_B , M, θ_D , c, T and x are Gamma ray energy, Boltzmann's constant, the mass of the iron ⁵⁷Fe nucleus, the Debye temperature, speed of light, temperature and $\hbar\omega/k_BT$, respectively.

As shown in equation (5-1), this parameter is related closely with the strength of the atomic bonding and the vibrations in the solid in which the Mössbauer nucleus is embedded [129] and it is clear that as the Debye temperature of the crystal becomes higher, the recoil-free fraction (f) is higher too[91]. This means that at a given temperature the probability of a compound to show recoil-free emission or absorption events increases with the increasing of bond strength [130].

As already mentioned, in practice using the Debye approximation to calculate the recoil free fraction (f) is complicated due to firstly, performing several spectra under different temperatures, secondly, adjusting the temperature dependence of the isomer shift (δ) or of the subspectral area (A), to calculate the Debye temperature and finally to use it in Equation (5-1). In comparison, in order to determine the relative recoilless fraction (F) the procedure is easier, since F is defined as the ratio of the recoil free fractions of two different materials. The method derives an expression for F from the ratio of the two Mössbauer sub-spectral areas, when the thin absorber condition is satisfied, these areas are proportional to the product of the number of

⁵⁷Fe atoms and the recoil-free fraction (f) of each one of them [129]. In this way it can be had that:

$$\frac{A_a}{A_r} = \frac{f_a N_a}{f_r N_r} \tag{5-2}$$

$$F_a = \frac{f_a}{f_r} = \frac{A_a N_r}{A_r N_a} \tag{5-3}$$

Where F_a is the relative recoilless fraction of the compound *a* with respect to a reference *r* and f_i , A_i , N_i are recoil free fraction, the Mössbauer sub-spectral area and the total number of ⁵⁷Fe atoms in each iron compound, respectively. N_i in each one of the compounds, can be estimated as follows:

$$N_i = \frac{am_i O_i N_0 N_{i,m}}{M W_i} \tag{5-4}$$

Where *a*, m_i , O_i , N_0 , $N_{i,m}$ and MW_i are an abundance of ⁵⁷Fe (a = 0.0217), mass of the compound, occupancy fraction, Avogadro's constant ($N_0 = 6.022 \times 10^{23} \text{ mol}^{-1}$), number of iron atoms per unit formula and the molecular weight, respectively. In this case, the final expression for the F-factor REFeO₃ (RFO) orthoferrites relative to alpha-iron (α – Fe) as a function of their sub-spectral areas, was obtained by replacing equation (5-4) in (5-3) thus:

$$F_{\rm RFO} = \frac{m_{\alpha \, \rm Fe} A_{\rm RFO} O_{\alpha \, \rm Fe} N_{\alpha \, \rm Fe,m} M W_{\rm RFO}}{m_{\rm RFO} A_{\alpha \, \rm Fe} O_{\rm RFO} N_{\rm RFO,m} M W_{\alpha \, \rm Fe}}$$
(5-5)

Where $M_{\alpha Fe}$, $O_{\alpha Fe}$, $N_{\alpha Fe,m}$ and $MW_{\alpha Fe}$ are the mass, occupation fraction, ⁵⁷Fe atoms presents by unitary formula and molecular weight of the alpha-iron, respectively. M_{ReFO} , O_{RFO} , $N_{RFO,m}$ and MW_{RFO} are the mass, occupation fraction, ⁵⁷Fe atoms present by unitary formula and molecular weight of the orthoferrite RFO, respectively. $A_{\alpha Fe}$ and A_{RFO} are alpha-iron and the orthoferrite sub-spectral areas, respectively.

Now assuming the values for the occupation fractions of the alpha-iron and the orthoferrites are one, considering the ⁵⁷Fe atoms present by unitary formula of the alpha-iron and the

orthoferrites are also one and doing the substitution in equation (5-5) with the molecular weights of the compounds (see Table 5-1); it is obtained four simple formulas to determine the F factor of the orthoferrites relative to alpha-iron which only depend of the experimental masses and the fitted Mössbauer sub-spectral areas.

Table 5-1: α-iron and rare-earth orthoferrites molecular weights

Compound	α-Fe	LFO	PFO	NFO	SFO
MWn	55 847	242 751	244 753	248 085	254 205
(g/mole)	55,017	212,731	211,755	210,005	25 1,205

$$F_{\rm LFO} = \frac{m_{\alpha \, Fe} A_{\rm LFO}(242,751 \, \text{g/mole})}{m_{\rm LFO} A_{\alpha \, Fe}(55,847 \, \text{g/mole})} = 4,347 \left(\frac{m_{\alpha \, Fe} A_{\rm LFO}}{m_{\rm LFO} A_{\alpha \, Fe}}\right)$$
(5-6)

$$F_{PFO} = \frac{m_{\alpha Fe} A_{PFO}(244,753 \text{ g/mole})}{m_{PFO} A_{\alpha Fe}(55,847 \text{g/mole})} = 4,383 \left(\frac{m_{\alpha Fe} A_{PFO}}{m_{PFO} A_{\alpha Fe}}\right)$$
(5-7)

$$F_{\rm NFO} = \frac{m_{\alpha \, \rm Fe} A_{\rm NFO}(248,085 \, {\rm g/mole})}{m_{\rm NFO} A_{\alpha \, \rm Fe}(55,847 {\rm g/mole})} = 4,442 \left(\frac{m_{\alpha \, \rm Fe} A_{\rm NFO}}{m_{\rm NFO} A_{\alpha \, \rm Fe}}\right)$$
(5-8)

$$F_{SFO} = \frac{m_{\alpha Fe} A_{SFO}(254,205 \text{ g/mole})}{m_{SFO} A_{\alpha Fe}(55,847 \text{g/mole})} = 4,552 \left(\frac{m_{\alpha Fe} A_{SFO}}{m_{SFO} A_{\alpha Fe}}\right)$$
(5-9)

3. Experimental

The Mössbauer spectra were obtained in a time-mode spectrometer working in constant acceleration transmission geometry with triangular reference signal at 300 K using a (10 mCi) 57Co/Rh source. The calibration was carried out using α -Fe foil, the spectra were collected in 512 channels and fitted using the Recoil software in a nonlinear least squares fitting procedure assuming lorentzian Mössbauer lines while the isomer shift value is quoted relative to that of α -Fe at 300 K.

3.3 F- Factor samples preparation

In order to calculate the relative recoilless fraction of REFeO₃ compounds with respect α -iron, absorbers were prepared as a homogenous mixture of the sample, the reference and sugar that were added to fill the entire sample holder. To estimate an error for the calculation of the (F) factors, the procedure was repeated three times for the different amounts of the compounds as reported in Table 5-2. With the purpose of choosing correctly the amounts of samples to prepare the absorber, the ideal thickness, defined as the absorber thickness that gives the largest signal to noise ratio in a given time [131], was calculated for each one of the samples and the reference using the equation:

$$t_{ideal} = \frac{1}{\sum_{i} m_{i} \mu_{e,i}}$$
(5-10)

Where m_i represents the mass fraction of the i-element in the absorber and $\mu_{e,i}$ is the electronic mass absorption coefficient for the 14.4 keV Mössbauer γ -rays of the i-element. In this way the calculated t_{ideal} for α -Fe was found to be 15.625mg/cm² and considering the holder diameter their respective ideal mass 19.79 mg the respective values for the orthoferrite compounds are collected in Table 5-2. Another concept taken into account in this point is the thin absorber thickness, t_{thin} , defined as the largest thickness where thickness effects are negligible. However, to satisfy this condition the dimensionless thickness version of the thin absorber thickness must be $t_{a.thin} \ll 1$. This parameter is given by:

$$t_i = f_i n_i \sigma_0 = \frac{f_i N_i \sigma_0}{A} \tag{5-11}$$

Where σ_0 (2,4 × 10⁻¹⁰ cm⁻¹) is the cross section at resonance for the mössbauer transition and n_i is the total number of ⁵⁷Fe atom of the *i* compound in the area of the holder. Now considering Eq. (5-4) it is obtained:

$$t_i = \frac{f_i N_0 m_i a O_i N_{i,m} \sigma_0}{M W_i A}$$
(5-12)

According to this equation, to calculate the dimensionless thickness it is necessary to know the value of (*f*) factor; for this reason it is difficult work under this condition and was attempted satisfied by taking all the masses for the measurements under their respective ideal masses ($m_{REFeO3} < m_{REFeO3,ideal}$ and $m_{\alpha-Fe} < m_{\alpha-Fe,ideal}$) and calculated the dimensionless thickness for the absorbers with the results for the *f*-factors found using the spectra with thickness previously corrected (See Table 5-2).

Sample	m _{ReFeO3} (mg)	m _{α-Fe} (mg)	t _{ideal} (mg/cm ²)	m _{ideal} (m)
	10.8	9.9		
LaFeO ₃	6.5	5.9	17.05	21.60
	2.1	2.0		
	10.1	9.7		
PrFeO ₃	6.1	5.8	16.22	20.54
	2.2	2.1		
	9.6	9.9		
NdFeO ₃	5.7	6.0	15.15	19.19
	1.9	2.0		
	9.5	9.8		
SmFeO ₃	5.6	5.9	14.03	17.78
	2.0	2.1		

Table 5-2: Orthoferrites and α -iron masses used to prepare the different absorbers. The corresponding absorber ideal masses and thickness (Eq. (10)).

4. Results

4.1 Mössbauer spectroscopy and relative recoilless fraction (F) determination

Mössbauer spectra at room temperature were recorded and fitted using Recoil software[108] as structural and magnetic complementary characterization. All orthoferrite compounds spectra were adjusted in a sextet pattern with values of isomeric shift and quadrupole interaction which are in good agreement with the crystallographic structure and the stoichiometry of the compound, where the iron atoms are in equivalent sites with a $3d^5$ configuration, in a octahedral coordination and with an oxidation state Fe⁺³ (see Table 5-3).

Site Parameters	LaFeO ₃	PrFeO ₃	NdFeO ₃	SmFeO ₃
CS (mm/s)	0.3657	03597	0.3603	0.3596
ε (mm/s)	-0.0349	-0.0151	-0.0098	-0.0467
H(T)	52.179	51.340	51.112	50.082
A (counts·mm/s)	191200	723000	1088000	502000
W ₃ (mm /s)	0.152	0.195	0.203	0.213
A_1/A_3	2.81	2.83	2.80	2.96
A_2/A_3	1.85	1.85	1.85	1.97
W_1/w_3	1.21	1.13	1.075	1.19
W_2/w_3	1.08	1.06	1.018	1.10
X^2	0.744167	1.79733	1.6250	1.18182

Table 5-3:Hyperfine Mössbauer 57 Fe hyperfine parameters of REFeO3 orthoferrites obtained
from self-combustion method at T_{room} .

In order to calculate the relative recoilless fraction of the ReFeO₃ compounds with respect to alpha-iron , the Mössbauer spectra recorded for the prepared absorbers accorded with section 3.3 and with the masses of Table 5-2. These were fitted using the commercial software Recoil[108]. The Mössbauer Spectra were fitted using two sextet patterns associated with each one of the phases present in the absorbers. The adjusted characteristic Mössbauer spectra for these compounds are depicted in Figure 5-1 for the particular case of LaFeO₃; in the graph there are the three different masses used and in their spectra the sextet more intense corresponds to the α -iron and the other one to LaFeO₃ phase.


Figure 5-1: Adjusted Mössbauer spectra for the three absorbers of LFO-αFe

Now to the original spectra a thickness correction was performed using the Recoil software, under consideration of the fact that it was not possible to calculate the dimensionless thickness without the (f) factor and that work was only being completed with masses under the ideal mass of the compounds. The resultant spectra were fitted too and compared to the variation of the estimated areas and the calculations of the F-factors were performed with the original and corrected data to evaluate if it is really necessary to perform the thickness correction in future studies.

The areas of each one of the sextet with and without thickness correction are shown in Table 5-4. The characteristic spectra before and after thickness correction is depicted in Figure 5-2 where the spectra for the absorber 1 (M1) for $PrFeO_3$ are graphed together.

Compound	Sample	Original (%)		After Thickness Correction (%)		
Compound		REFeO ₃ Area	α-Fe Area	REFeO ₃ Area	α-Fe Area	
	M1	24.9	75.1	25.1	74.9	
LaFeO ₃	M2	24.4	75.6	24.6	75.4	
	M3	24.2	75.8	24.3	75.7	
PrFeO3	M1	20.2	79.8	19.7	80.3	
	M2	20.2	79.8	20.8	79.2	
	M3	21.3	78.7	20.8	79.2	
NdFeO3	M1	20.7	79.3	20.8	79.2	
	M2	20.2	79.8	21.1	78.9	
	M3	19.1	80.9	19.3	80.7	
SmFeO ₃	M1	19.1	80.9	19.1	80.9	
	M2	19.6	80.4	18.1	81.9	
	M3	20.9	79.1	24.1	75.9	

Table 5-4:	Sub-spectral areas for the three different masses of each one of the orthoferrite		
compounds with and without thickness correction			





With the experimental masses and the areas estimated; using Equation (5-6) the relative recoilless fraction F was calculated for the three different masses with and without thickness correction, those results are summarized in Table 5-5.

Sample –	F _{LFO}		F _{PFO}		F _{NFO}		F _{SFO}	
	*0	С	0	С	0	С	0	С
M1	1.321	1.335	1.06	1.037	1.180	1.187	1.109	1.094
M2	1.273	1.287	1.055	1.094	1.168	1.234	1.169	1.046
M3	1.322	1.329	1.132	1.098	1.089	1.103	1.263	1.180
\overline{x}	1.30	1.31	1.08	1.07	1.15	1.17	1.18	1.11
	±0.02	±0.02	±0.04	±0.04	±0.05	±0.07	±0.08	±0.07

 Table 5-5:
 Relative recoilless fraction F for the three different masses with and without thickness correction

*O(Original), C(Corrected)

With the corrected vales for the F-factors found and the literature (*f*) factor value of 0.7 for the α iron and using Eq. (3) the recoilless (*f*) factors for the orthoferrite compounds were calculated (see Table 5-6).

Table 5-6:Recoilless (f) factors for the compounds ReFeO3 (Re=La, Pr, Nd, Sm) calculated
using Eq.3.

Sample	f lfo	f _{PFO}	f _{NFO}	f _{sfo}
\overline{x}	0.92±0.02	0.75 ± 0.04	0.82 ± 0.07	0.78 ± 0.07

Now using the Debye model and the Debye temperatures reported for these compounds[102] using Recoil Software the recoilless (*f*) factors were also calculated and compared with the results shown in this experiment (see Table 5-7).

Table 5-7:Recoilless (f) factors for the compounds $REFeO_3$ (RE=La,Pr,Nd,Sm) calculated
for T_{room} using the Debye model and the Debye Temperatures reported by Eibschütz et al.[102]

DEE	θ	f
KEFEU3	[K]	Debye Model
LaFeO ₃	800±50	0.927
PrFeO ₃	780±50	0.924
NdFeO ₃	770±50	0.922

DEE	Θ_{D}	f
KEFeO3	[K]	Debye Model
SmFeO ₃	730±50	0.915

5. Discussion

The relative recoilless fraction F for the rare-earth orthoferrites ReFeO₃ with respect to α -Fe is greater than one, which implies (*f*) the probability to find recoilless events in the ReFeO₃ compounds is greater than in α -Fe. A result which can be unexpected since the intensities in the Mössbauer spectra for the α -Fe sextet are greater than the respective for the orthoferrite sextet resulting in bigger sub-spectral areas. This means that it looks logical guessing the probability to observe recoilless events should be greater for α -Fe than for NdFeO₃ but it does not, so what is happening why α -Fe area is greater than the NdFeO₃ one? The reason here is the recoil-free fraction (*f*) measured the probability of a single nucleus to absorb the gamma rays without recoil. In other words, it is an intensive and not an extensive property like the intensity or area of the sextet in the spectra, which in this case depends of the number of iron nuclei in the masses of the compounds.

According to Equation (5-1) the values of (f) should be attributed in a large extent to the crystal Debye temperature, in this sense these temperatures for the ReFeO₃ compounds should be greater than for the α -Fe; as in effect it is (the Θ_D of the α -iron is 345K). This means that the orthoferrite compounds are more stable thermally and in turn, this implies that the iron nucleus is strongly embedded avoiding the recoilless phenomena and for this reason in these compounds is easier to show the absorption of γ -rays. Now, this thermal stability may be associated with the structure type of the REFeO₃ compounds where as it was shown before in section 4.1 that the Fe atom is confined into a FeO₆ octahedral and linked by ionic bounds while in the α -Fe the atoms are linked by metallic bounds with dense plans where the heat is easily conducted.

6. Conclusions

The method of the relative recoilless factor proved to be an easy, economic and versatile way to obtain the (f) factors of compounds in order to use it for quantification of iron phases in samples with complex composition. It is recommend to apply in an adequate way this

procedure to realize the thickness corrections to the spectra since it is very difficult to work under or near the ideal thickness of the samples.

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I inform that I have made this thesis independently and with only the help of the means permitted and no others different from those mentioned in the thesis itself. All passages here taken literally or figuratively of published texts and unpublished texts have been recognized properly in the present work. No part of this work has been used in any other thesis.

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