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Characterization of Ni-Zn ferrite base materials obtained by microwave technology.

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Abstract:

The sintering of ceramic materials by microwave radiation is an emerging field in materials science and technology with an enormous potential for obtaining new materials and new microstructures. The main characteristics associated to the microwave process are summarized in: fast and uniform volumetric heating, improved production rate, improved densification and mechanical properties and inhibition of grain growth.

In this work, the sinterability of (Ni-Zn) ferrite and (Ni-Zn) ferrite/$BaTiO_3$ composites will be studied. For this purpose, two single mode microwave cavities will be used, one of them with a maximum magnetic field and a minimum electric field, and the other with a maximum electric field and a minimum magnetic field. The aims of the study are numerous. First, the sinterability of the composite with the two microwaves is tested. Then, the sinterability of the (Ni-Zn) ferrite alone is tested with electric microwave sintering. Finally, all the samples are characterised in order to observe the influence of the microwave sintering parameters on the structure, the harness and the density. Furthermore, both materials are sintered by conventional sintering to be compared with the microwave sintered samples.

Concerning the (Ni-Zn) ferrite/$BaTiO_3$ composite. After several attempts, the sintering of the composite with the magnetic microwave is a failure. Indeed, a very instable behaviour have been observed with both microwaves. In the case of the electric microwave, the use of a susceptor has enabled to sinter the material with success. Finally, the properties of the material sintered by microwave are very promising. For example, this method has enabled to increase the hardness of the material and its density.

Concerning the (Ni-Zn) ferrite, the electric microwave sintering was achieved. The characterization of the samples has shown similar properties than samples sintered by conventional sintering but at lower temperature and shorter sintering times.

Keywords: microwave sintering, (Ni-Zn) ferrite/$BaTiO_3$ composite, (Ni-Zn) ferrite, microstructure, mechanical properties.

Resumen:

La sinterización de materiales cerámicos mediante radiación de microondas es un campo emergente en la ciencia y tecnología de materiales con un enorme potencial para obtener nuevos materiales y nuevas microestructuras. Las principales características asociadas al proceso de microondas se resumen en: un calentamiento volumétrico rápido y uniforme, mejora en la densificación y las propiedades mecánicas e inhibición del crecimiento de grano.

En este trabajo se estudiará la sinterabilidad de materiales ferrita (Ni-Zn) y composites de ferrita (Ni-Zn)-$BaTiO_3$. Para ello, se van a utilizar dos cavidades de microondas monomodo, una de ellas con máximo de campo magnético y otra con presencia de máximo de campo eléctrico. Los objetivos del estudio han sido los siguientes. La sinterabilidad del composite con las dos microondas. La sinterabilidad de la ferrita (Ni-Zn) se prueba con sinterización eléctrica por microondas. Por último, se caracterizan todas las muestras para observar la influencia de los parámetros de sinterización por microondas en la microestructura, la dureza y la densidad. Además, ambos materiales se sinterizan por sinterización convencional para compararlos con las muestras sinterizadas por microondas.

En cuanto al composite de ferrita (Ni-Zn) y $BaTiO_3$. De hecho, se ha observado un comportamiento muy inestable con las dos cavidades de microondas. En el caso del microondas eléctrico, el uso de un susceptor de SiC ha permitido sinterizar el material con éxito. Por último, las propiedades del material sinterizado por microondas son muy prometedoras. Por ejemplo, este método ha permitido aumentar la dureza del material y su densidad.

En cuanto a la ferrita (Ni-Zn), se ha logrado la sinterización mediante microondas eléctricas. La caracterización de las muestras ha mostrado propiedades similares a las de las muestras sinterizadas por sinterización convencional, pero a una temperatura más baja y con tiempos de sinterización más cortos.

Palabras clave: sinterización por microondas, composite de (Ni-Zn) ferrita/BaTiO3, (Ni-Zn) ferrita, microestructura, propiedades mecánicas.

Resum:

La sinterització de materials ceràmics per mitjà de radiació de microones és un camp emergent en la ciència i tecnologia de materials amb un enorme potencial per a obtindre nous materials i noves microestructures. Les principals característiques associades al procés de microones es resumixen en: un calfament volumètric ràpid i uniforme, millora de la taxa de producció, millora en la densificació i les propietats mecàniques i inhibició del creixement de gra.

En este treball s'estudiarà la sinterabilidad de materials ferrita (Ni-Zn) i composites de ferrita (Ni-Zn) - $BaTiO_3$. Per a això, es van a utilitzar dos cavitats de microones monomodo, una d'elles amb màxim de camp magnètic, i una altra amb presència de màxim de camp elèctric. Els objectius de l'estudi són nombrosos. Primer, es prova la sinterabilidad del compost amb les dos microones. Després, la sinterabilidad de la ferrita (Ni-Zn) es prova amb sinterització elèctrica per microones. Finalment, es caracteritzen totes les mostres per a observar la influència dels paràmetres de sinterització per microones en l'estructura, la duresa i la densitat. A més, ambdós materials se sinterizan per sinterització convencional per a comparar-los amb les mostres sinterizadas per microones.

Quant al compost de ferrita (Ni-Zn) i $BaTiO_3$. De fet, s'ha observat un comportament molt inestable amb ambdós microones. En el cas del microones elèctric, l'ús d'un susceptor ha permés sinterizar el material amb èxit. Finalment, les propietats del material sinterizado per microones són molt prometedores. Per exemple, este mètode ha permés augmentar la duresa del material i la seua densitat. Quant a la ferrita (Ni-Zn) , s'ha aconseguit la sinterització per microones elèctriques. La caracterització de les mostres ha mostrat propietats semblants a les de les mostres sinterizadas per sinterització convencional, però a una temperatura més baixa i amb temps de sinterització més curts.

Paraules clau: sinterització per microones, composite de (Ni-Zn) ferrita/BaTiO3, (Ni- Zn) ferrita, microestructura, propietats mecàniques.

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CHAPTER 1: Introduction

1.1. Objectives of the project

The sintering of ceramic materials by microwave radiation is an emerging field in materials science and technology with an enormous potential for obtaining new materials and new microstructures. The main characteristics associated to the microwave process are summarized in: fast and uniform volumetric heating, improved production rate, improved densification and mechanical properties and inhibition of grain growth, which makes it especially interesting for the sintering of nanostructured ceramic powders. In microwave sintering, heat is generated internally within the sample, rather than diffusion from external sources. As a result of this internal and volumetric heating, materials can be sintered quickly and evenly.

In this work, the main objective is to study the sinterability of ferrite (Ni-Zn) and ferrite (Ni-Zn)-$BaTiO_3$ composite. For this purpose, two single mode microwave cavities will be used, one of them with a maximum magnetic field and a minimum electric field, and the other with a maximum electric field and a minimum magnetic field. Particularly, the sintering using the microwave favouring the magnetic field in a great aim of this project. Indeed, the effect of this microwave on the materials was not already tested and a success would be a first step for further research.

According to the existing literature, this sintering method has many advantages compared to conventional sintering: it allows better final properties to be obtained with lower temperatures and times. Therefore, another objective is to compare the results with those obtained by conventional sintering.

Finally, due to the dielectric and magnetic properties of these materials, controlling the temperature during sintering is very complex. Therefore, this project will also try to present the parameters that influence the interaction between the wave and the material and analyse its evolution during the heat treatment.

1.2. Workplan

In order to study the different microwaves sintering parameters (time, temperature, magnetic or electric), several samples will be elaborated, and several characterisation methods will be used. The organisation of the work will be the following:

_spherical samples of the two materials will be compacted from a powder.

_ For each material and sintering method (conventional or microwave), different parameters will be tested: the influence of the temperature, the influence of the duration.

_ Hardness test will be used. Indeed, it will enable to quickly compare the mechanical properties.

_ The density of various samples will be measured to evaluate the quality of the sintering and the porosity of the samples.

_ Then, X-Ray Diffraction will be used to determine and analyse the structure of materials after sintering.

_ Focused Emission Scanning Electron Microscopy will aim at observing the fracture section of the different samples. This way, it will be possible to compare the homogeneity, the porosity and the grain size of the samples.

CHAPTER 2: State of the art

2.1. Materials studied

The aim of the project is the microwave sintering of ceramics and above all Ni-Zn Fe2O4 based ceramics, this part will above all focus on the structure of the materials and on their magnetic and electrical properties.

2.1.1. Nickel-zinc Ferrites

Ni-Zn ferrites are very interesting materials. Known for their electromagnetic properties, they will be the base material of this project. Before describing the composite made of this material, this part will focus on the structure and properties of the ferrites in general and more especially Ni-Zn ferrites.

2.1.1.1. Structure

Ni-Zn ferrites studied in this project belongs to an important category of ceramics. It is important to clearly distinguish ferrites as a ceramic and ferrites that is a phase in ferritic alloys. In this project, the material studied is the ferrites as ceramics.

Ferrites, in ceramics, refers to ferrimagnetic oxides composed principally of Iron. Their formula is commonly $MeFe_2O_4$ in which Me is a divalent cation as Ni^{2+} or Zn^{2+} and Fe is at the third degree of oxidation (Fe^{3+}). Coming from this general formula, many varieties of ferrites exist. The simplest are ferrites involving a single divalent cation like $NiFe_2O_4$ or $CuFe_2O_4$ but other varieties involving 2 divalent cations or cations monovalent and trivalent are possible if the electroneutrality is respected.

As presented by LEBOURGEOIS R. (LEBOURGEOIS, 2014) ferrites have a spinel structure. In the material, O^- ions are in superior in number and are the biggest ions. The structure is then architected in a FCC structure of O^- ions in which the different interstitial sites are filled by the different cations. The repartition of these cations is done between the tetrahedral and octahedral sites. The primitive cell of ferrites is represented in figure 1. It is composed of 32 octahedral sites and 64 tetrahedral sites (LEBOURGEOIS, 2014).

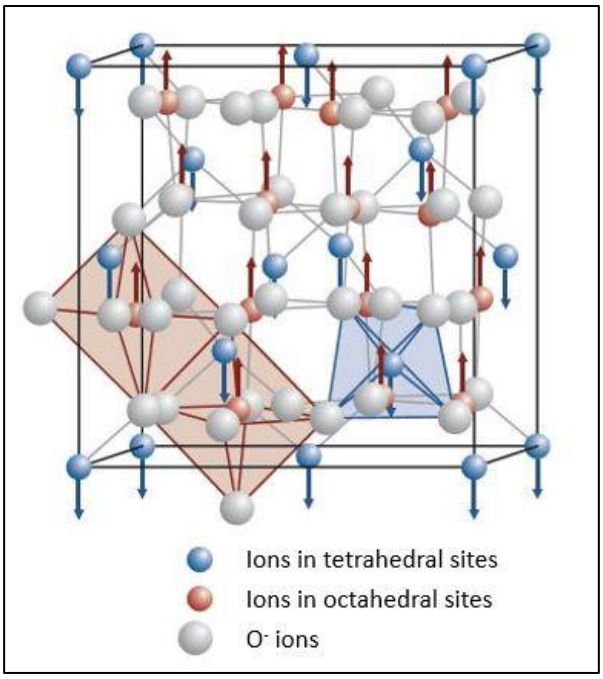

Figure 1: Elementary cell of spinel structured MeFe2O4 (LEBOURGEOIS, 2014).

Depending on the repartition of the cations, ferrites are separated into two categories: normal spinel and inversed spinel. To distinguish the repartition of the different cations, the formula can be written as following: $[Me^{2+}_{1-\delta}\ Fe^{3+}_{1+\delta}](\ Me^{2+}_{\delta}\ Fe^{3+}_{1-\delta})O_4$. In this formula, $[Me^{2+}_{1-\delta}\ Fe^{3+}_{1+\delta}]$ are cations in octahedral sites and $(Me^{2+}_{\delta}\ Fe^{3+}_{1-\delta})$ are cations in tetrahedral sites. This notation enables to quickly differentiate if the structure is normal spinel (δ=1) or inversed spinel (δ=0).

In the case of Ni-Zn ferrites, the structure is a mixed of $NiFe_2O_4$ and $ZnFe_2O_4$. Considered separately, Ni ferrite and Zn ferrites are respectively inversed and normal. The resulting structure is called mixed spinel structure and the formula of the material is written Ni_x-Zn_{1-x} Fe_2O_4. Depending on the application, different proportions can be used from x=0.3 to x=1.

2.1.1.2. Electromagnetic properties

As ferrimagnetic oxides, ferrites have good electromagnetic properties due to the magnetic spin of their metallic cations. Considering the application in microwave sintering, these properties are essential, and this part will aim at presenting the different electromagnetic properties and the influence of the structure on them.

First, it is important to explain the influence of the spinel structure on the electromagnetic properties. As explained in (LEBOURGEOIS, 2014), all metallic cations have a magnetic spin and interact in the structure. This interaction is maximal between octahedral and tetrahedral sites. To minimize the energy, the optimal alignment of spins is in antiparallel as shown in Figure 1. Resulting from this observation, Louis Néel established that the resulting magnetization is the difference of the magnetization of octahedral and tetrahedral sites. The composition of the material and the repartition of the cations is thus determinant for the magnetic properties.

In the case of Ni-Zn ferrites, the influence of the Zn proportion on the magnetic properties have been observed in (LEBOURGEOIS, 2014). As shown the Table 1, depending on the proportion of each cations,

the material can be paramagnetic or ferrimagnetic. As, a maximum of the magnetization is found for equimolar proportions of Ni and Zn which is the proportion of the material studied in this project.

Table 1: Influence of the Zinc proportion on the magnetic properties of Ni-Zn ferrites (LEBOURGEOIS, 2014).

Formula	Magnetic behaviour	Magnetization at saturation at 25°C (T)
$Ni_{0.2}$-$Zn_{0.8}Fe_2O_4$	paramagnetic	0
$Ni_{0.5}$-$Zn_{0.5}Fe_2O_4$	ferrimagnetic	0,53
$NiFe_2O_4$	ferrimagnetic	0,33

Curie temperature (Tc):

The curie temperature is the temperature in which a ferrimagnetic material turns into a paramagnetic one. This temperature is important for frequencies application because it will influence the different losses. In the case of microwave sintering, this factor needs to be taken in account.

For a Ni-Zn ferrite, the curie temperature highly depends on the proportion of Zinc and Nickel. As shown in table 1 ferrites with a high zinc content are paramagnetic and while increasing the nickel proportion, the material becomes ferrimagnetic. Following the same tendency, the curie temperature is maximal for a Nickel ferrite (around 585°C) and decreases while improving the proportion of Zn. The minimum is reach for $Ni_{0.3}$-$Zn_{0.7}Fe_2O_4$ (100°C) In this project, the Curie temperature of the Ni-Zn ferrite was 125°C ($Ni_{0.5}$-$Zn_{0.5}Fe_2O_4$).

Electric resistivity:

The electrical resistivity is the ability of the material to avoid the current propagation. In microwave sintering, this property is important because when a material resists to the propagation of the current, heat is produced by Joule's effect.

In the case of the Ni-Zn ferrite used in this project ($Ni_{0.3}$-$Zn_{0.7}Fe_2O_4$), the resistivity is $10^3\Omega$.m. Compared to the resistivity of metals that is around 10^{-7} Ω.m, this value is high. Considering now microwave sintering, this property supposes a suitability for electrical microwave sintering.

Magnetostriction:

The magnetostriction is the deformation of a magnetic material under a magnetic field or in the opposite way, the formation of a magnetic induction in the material under mechanical solicitation (LEBOURGEOIS, 2014).

Commonly, ferrites do have a negative magnetostriction: under a magnetic field, the material tends to contract. This property, in the special case of sintering is important. Even if this effect is minimal, a contraction contributes to modify the properties of the material and can increase the magnetic and dielectric losses favouring by the same time the heating.

2.1.1.3. Physical properties

Mechanical properties:

Ferrites have good mechanical properties. Like many ceramics, they are brittle and tough materials. Concerning their behaviour in traction and compression, they are resistant in compression with a failure reported between 0,2 GPa and 0,8 GPa (LEBOURGEOIS, 2014). However, as brittle materials, their resistance in traction is low (failure between 20 MPa and 70 MPa).

Finally, the young modulus of ferrites is around 170 GPa (160 GPa for $NiFe_2O_4$ and 190 GPa for $ZnFe_2O_4$)

Density:

The density of Ni-Zn ferrites depends on the proportion of Nickel and Zinc. Considering the ferrite studied ($Ni_{0.5}$-$Zn_{0.5}Fe_2O_4$) and for a full dense material, the reference density is 5,7 $g.cm^{-3}$.

2.1.2. Barium Titanate $BaTiO_3$

Baryum Titanate $BaTiO_3$ is an interesting ceramic, known for its various properties and especially its ferroelectricity. Characterised by different phase changes, it crystallises over curie temperature in a perovskite structure described there-after.

2.1.2.1. Structure and phase changes

$BaTiO_3$ is a mixed oxide belonging to the family of perovskite. Originally, the term perovskite refers to the ferroelectric mineral $CaTiO_3$. Assimilating other ferroelectric mixed oxides with the same structure, perovskite is now referring to a special phase of mixed oxides corresponding to the following formula: ABO_3. As explained by SAHRAOUI (SAHRAOUI,2008) in this formula:

_ A is a cation with an important radius like Ca or in the case of this study Ba. In the structure, this cation A is surrounded by 12 oxygen ions.

_ B is a smaller cation like Titanium (Ti) that is surrounded by 6 oxygen ions.

As represented in figure 2, the perfect primitive cell of a perovskite is FCC with A atoms in the corners (Baryum), B atoms in the centre of the cell (Titanium) and oxygen atoms in the centre of the faces.

Depending on the temperature, $BaTiO_3$ can be found on 4 different structures:

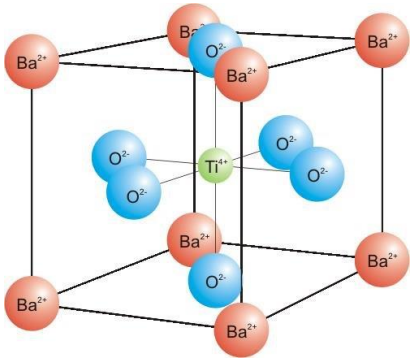

Figure 2: perovskite structure of $BaTiO_3$ (GHANIM, 2018)

_ T<-90°C: rhombohedral

_ -90°C<T<5°C: orthorhombic

_ 5°C<T<120°C: tetragonal

_120°C(Tc)<T<1625°C (Tfusion): perovskite (cubic)

2.1.2.2. Electromagnetic properties

$BaTiO_3$ is well known for its different electromagnetic properties. Above all, this material is used in electronics components such as capacitors, microphones, or transducers. In this project, the aim is to determine its contribution in the microwave sintering of the Ni-Zn ferrite/$BaTiO_3$ composite.

Ferroelectricity and Curie temperature:

As a definition, a material that has an electric polarisation without the application of an external field is told ferroelectric. If an external field is applied, the polarization of such a material can be reoriented. As for ferromagnetic materials, the reorientation of the natural polarization follows a cycle of hysteresis that is characteristic of the material and that represents the reaction delay require by the material to follow the external field.

Following this definition, $BaTiO_3$ is a ferroelectric material. Thanks to the structure of the three main phasis (rhombohedral, orthorhombic, and tetragonal) the material has a natural polarity under its Curie temperature. To go further in details, this part will focus on the transition between the tetragonal phase and the cubic phase. In fact, considering the microwave sintering of this material, only the study of the changes in the material from room temperature to the melting temperature is required.

On one hand, As presented 1.1.2.1., $BaTiO_3$ crystallises over 135°C in a perovskite cubic structure. In this cubic structure, the barycentres of negative Ions (O-) and positive cations (Ti^{4+}, Ba^{2+}) are combined. As a result, the material is thus paraelectric over this temperature.

On the other hand, between 5°C and 135°C the material crystallises in a tetragonal structure really closed to the perovskite cubic structure already presented. As shown in figure 3 in this deformed cell, the Titanium atom currently in the centre of the cubic cell is slightly deported in the tetragonal one.

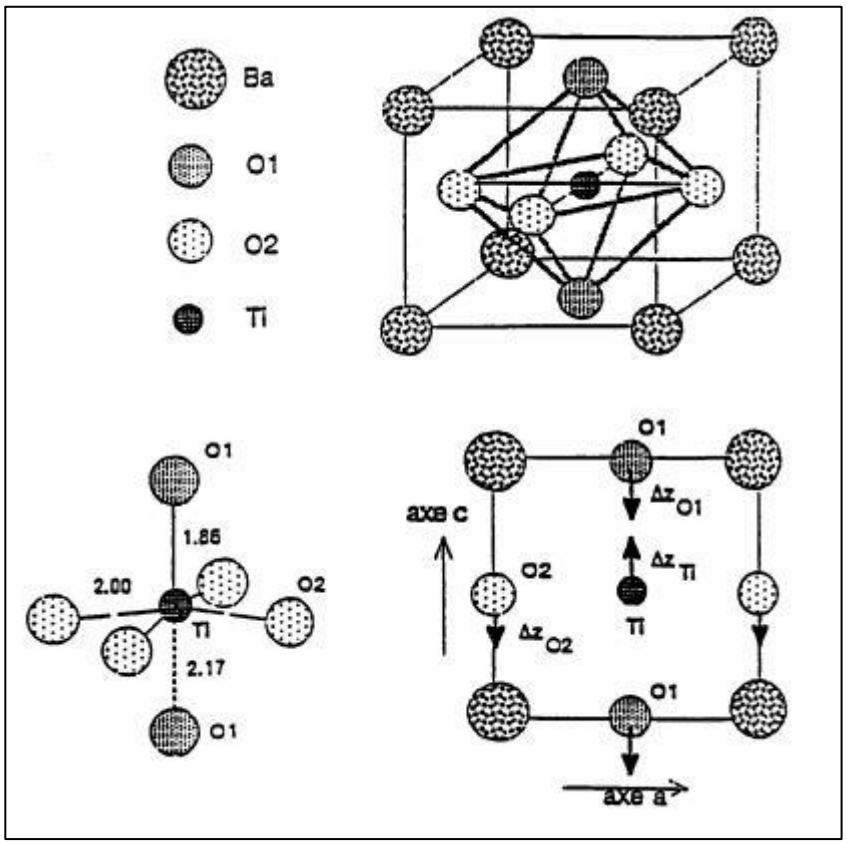

Figure 3: comparison of the cubic structure (on top) and the tetragonal structure (on the bottom) (LAABIDI,1991)

As a result, in this phase, the barycentres are distinct and the material is then ferroelectric. Finally, as reported by Khalid LAABIDI (LAABIDI,1991), different studies also shown a second contribution to this polarisation. Indeed, if the Titanium atom is slightly deported, a movement of the different oxygen atoms is noticed and contributes to the polarisation of the material.

Dielectric constant:

A dielectric material is an electrical insulator that can be polarized by an external electrical field. In fact, to conduct electricity at a macroscopic scale, a material requires free electrons. However, in dielectric materials, dipoles at the atomic scale can be polarized in an external field and confer to the material electric properties. To characterise the polarizability of a material (reaction of the material to an external field), the dielectric constant (also named relative permittivity) is defined by the equation. (1).(CHARMOND, 2009)

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = 1 + \chi_c \quad (1)$$

ε: permittivity of the material.

ε_0: permittivity of the void.

χ_c: electric susceptibility of the material.

For $BaTiO_3$, the dielectric constant (ε_r) is high and can reach, depending on the temperature, over 7000. As shown by the figure 4, the dielectric constant increases with the temperature and each phase changes and produce peak.

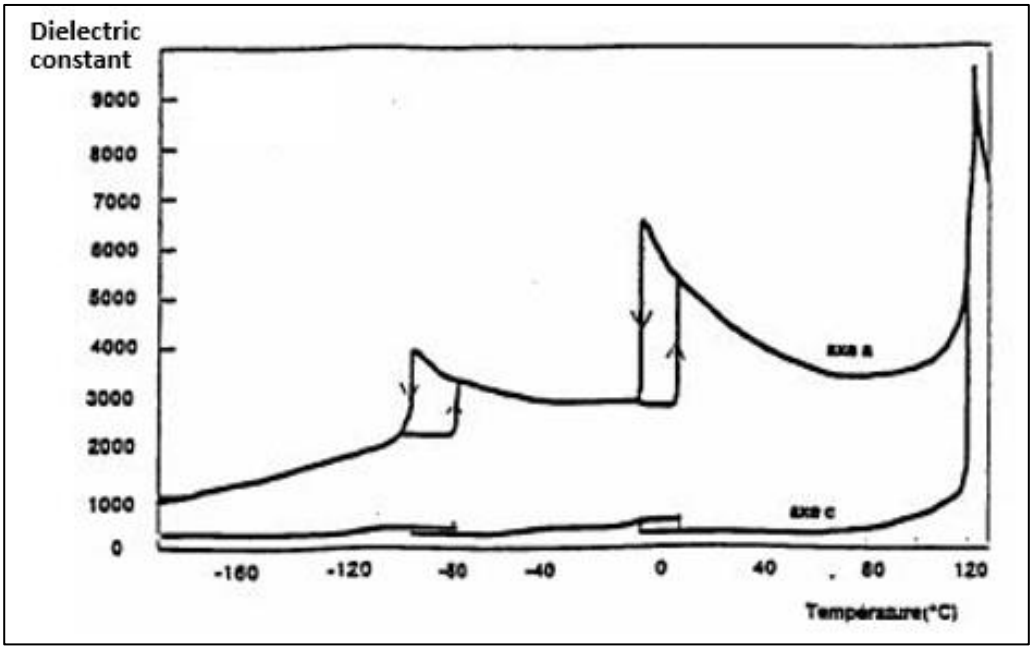

Figure 4: Evolution of the dielectric constant of $BaTiO_3$ in function of the temperature. (GHANIM, 2018)

For microwave sintering, the dielectric behaviour is one of the heating mechanisms (see part 1.2.1.4). Consequently, to control the heating rate, it is important to know the evolution of this parameter with the temperature.

2.1.2.3. Other properties

Mechanical properties:

As other ceramics, $BaTiO_3$ is a brittle material with a high young modulus. TRZEPIECINSKI and GROMADA (2018) reported the values of Young modulus and compression strength of sintered $BaTiO_3$ samples. Depending on the grain size and the porosity, they found Young modulus between 115,5 GPa

and 118 GPa. Corresponding to the common behaviour of ceramics, they highlighted that the compressive strength is higher than young modulus. The compressive strength also varies more in function of the grain size: the values are included between 486,2 GPa and 913,2 GPa.

Density:

The theorical density of a full dense $BaTiO_3$ can be calculated and is equal to 6,08 $g.cm^{-3}$. By conventional sintering and for 4h at 1250°C, TRZEPIECINSKI and GROMADA (2018) measured an average apparent density of 5,85 $g.cm^{-3}$. This value corresponds to a relative density of 96,2%.

2.2. Sintering

In this part will be explained the fundamentals of sintering. The aim of this explication is to have a better understanding of the process and above all the parameters that have an influent on the process.

2.2.1. Conventional sintering

2.2.1.1. Generalities

Conventional sintering is a very old and well-known processing method. It is during the Neolithic that the first approach of sintering was developed with the apparition of pottery. In fact, sintering processes are nowadays well developed and several kinds of sintering are now used. In this part will be described solid state conventional sintering.

Solid state conventional sintering is a thermal process that aims at improving the cohesion of a workpiece. The starting point of the process is a compacted material made of power and called green body. This material is characterised by a high porosity and dispersion. As a good model and in order to explain the evolution of the material during the process, the green boy can be represented as a sum of spherical grains closed to each other and with a certain diameter of grains. During the treatment, the green body is heated at a temperature under the fusion temperature that enables the fusing of the grains. The determination of this temperature is one of the key factors of the process as it has a great influence on the final microstructure. The determination of the parameters of the treatment requires a good understanding of the phenomenon that occurs at different scales especially at macroscopic scale.

Because the temperature is too low to enable a total fusion of the material, the main advantage of this process is to maintain the coherence of the workpiece and keep its geometry.

2.2.1.2. Thermodynamical aspects

To understand the evolution of the material structure during the treatment, the first step is to observe the thermodynamic of the system. Before the treatment, the green body is a compacted material with a high porosity and dispersion. In terms of energy, this structure is then in a metastable state. In fact, as represented in the Figure 5 a material dispersed has a superficial energy much more important than this of a full dense material. To reduce the superficial energy, the material tends to reduce the solid/air interfaces favouring solid/solid interfaces.

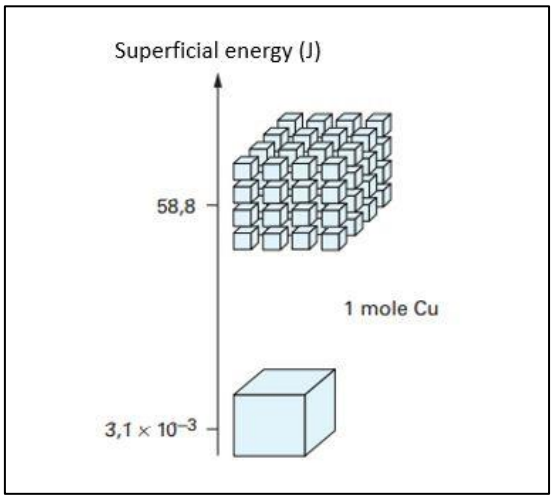

Figure 5: Superficial energy in function of the dispersion (BERNACHE-ASSOLLANT and BONNET, 2015).

Thermodynamically, the material evolution is driven by reduction of its energy, but different mechanisms occurs. When heated over a certain temperature, two phenomenon occurs: the grains' growth and the fusing of grains.

2.2.1.3. Kinetical aspects

During the sintering, the heat enables the growth of grains and the fusing of grains by enabling mass transfer. The resulting evolution of the structure is commonly divided into 3 main steps represented in Figure 6 (BERNACHE-ASSOLLANT and BONNET, 2015).

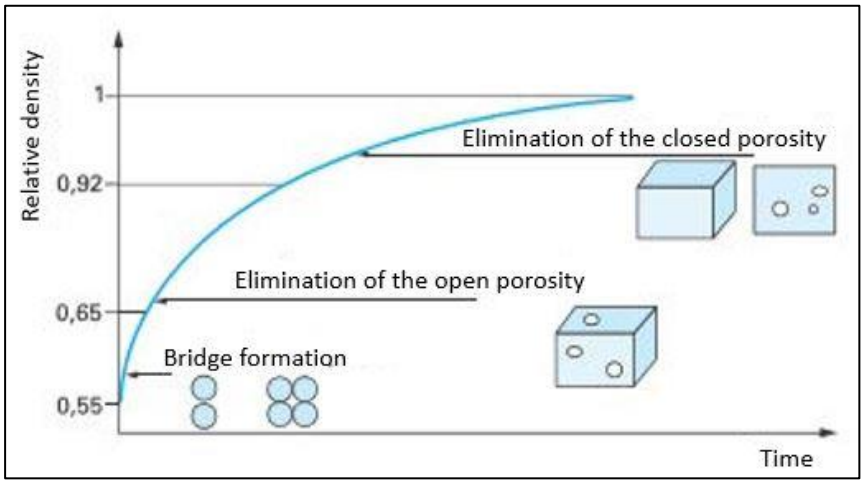

Figure 6:Relative density evolution during sintering (BERNACHE-ASSOLLANT and BONNET, 2015).

The first step is the formation of bridges between grains. This stage contributes to the consolidation of the material and the formation of grains boundaries. At this step, no important evolution of the density is observed.

The second step of the process is then the elimination of the open porosity. In fact, if bridge formation consolidates the material, it has no real impact on the density and let the material highly porous. At this stage, the material is crossed by several tunnels and cavities.

Finally, at the end of the process comes the elimination of the closed porosity. The relative density is at this point relatively high, it is considered that only closed cavities remains. This final step is the most difficult because the elimination of these cavities means the diffusion of the remaining gazes in the solid matrix.

In fact, if the Figure 6 representing an isothermal sintering gives a good representation of the three stages. However, in common sintering and especially microwave sintering, the evolution of the structure is more complex, and these three steps are not this so distinct.

As listed in Table 2 (BERNACHE-ASSOLLANT and BONNET, 2015), 6 different mechanisms are involved in the evolution of the material. As shown by Didier BERNACHE-ASSOLLANT and Jean-Pierre BONNET (2015), these mechanisms differ by the origin of the matter.

Table 2:Different matter transfer during the first step of sintering (BERNACHE-ASSOLLANT and BONNET, 2015).

Mechanism	Displacement's nature	Matter's origin
1	Vapor transport	Grain surface
2	Superficial diffusion	Grain surface
3	Volume diffusion	Grain surface
4	Volume diffusion	Grain boundaries
5	Diffusion at grain boundaries	Grains boundaries
6	Plastic deformation	Volume

Depending on the origin of the matter (grain boundaries, inside of the grain or the grain surface), the equilibrium between the growth of grains and the densification of the material is influenced. The 6 mechanisms can this way be divided into two groups:

Consolidation mechanisms:

In mechanisms involving a superficial or vapor mass transfer, the displacement of atoms does not require the modification of the distance between grains. These mechanisms conduce to the creation of bridges between grains that consolidates the structure, but no shrinkage happens meaning no densification.

Consolidation and densification mechanisms:

In mechanisms involving a volume diffusion or boundaries diffusion, the mass transfer comes from the centre of the grains or the boundary between two grains. In this special case, to maintain the coherence of the material, the mass transfer implies a reduction of the distance between grains. These mechanisms conduce thus not only to a consolidation but as well to a densification creating then shrinkage.

To control the equilibrium between these two phenomena, it is important to favour consolidation and densification mechanism. As well, more than the time of process, an early densification also contributes to limit the grain growth and thus better the mechanical properties.

To have a control on the mechanisms, two parameters are predominant: the temperature and the grain size. In fact, depending on the configuration, some mechanism can be favourited. As show the two graphs from the article (BERNACHE-ASSOLLANT and BONNET, 2015), the bridge formation rate highly depends on the temperature and the granulometry. Graph a) shows that the superficial diffusion (ds) is favourited at low grain size (r) increasing then the fusing rate. Concerning the influence of temperature, graph b) shows that superficial diffusion is favourited at low temperature. This is explained in (BERNACHE-ASSOLLANT and BONNET, 2015) the activation energy that is lower for superficial diffusion than for volume diffusion.

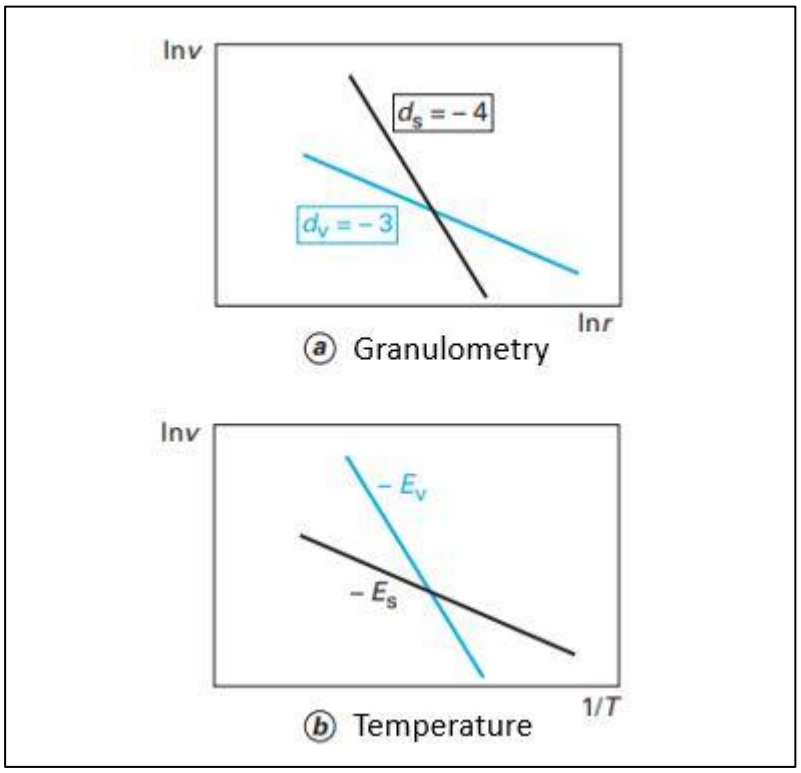

Figure 7: Influence of the Temperature and the granulometry on the bridge formation rate during sintering. (BERNACHE-ASSOLLANT and BONNET, 2015)

Because of these observations, the final microstructure will depend on the temperature rate and the granulometry. To increase the density of the material, Volume diffusion and boundary diffusion must be predominant comparing to superficial diffusion. Following Didier BERNACHE's-ASSOLLANT and Jean-Pierre BONNET's conclusions (2015), a high heating rate enables to reduce the contribution of superficial diffusion by reducing the time at low temperature. As the grain growth is thus limited until the densification temperature, the material densification is higher.

2.2.2. Microwave sintering

As a non-conventional sintering method, microwave sintering is one of the alternatives of conventional sintering. Using different kind of microwave oven, these techniques are based on the interaction between microwaves and matter and thus involves other heating mechanisms than those of conventional sintering. To enable a good comprehension of the experimental work, this part will present the theorical aspects of microwave sintering starting with some generalities and then going deeper into the propagation of microwaves and its interaction with materials.

2.2.2.1. Generalities

Microwaves are a category of electromagnetic radiations characterised by a wavelength (λ) between 1 mm and 1 m, and a frequency (f) between 0,3 GHz and 30 GHz. These radiations are commonly used in a large range of applications. Well known thanks to its utilisation for food heating in domestic microwaves, microwaves are today use in diverse applications like telecommunications, heating, or medical.

Because of the large range of applications, especially in the field of telecommunications, the use of such radiations is controlled by the Federal Communications Commission that allocate a certain frequency band for each application. As an example, one of the most common is the one of domestic microwaves (2,45 GHz).

Concerning microwave furnace, it is important to remain that two families exists: single mode microwaves and multi-mode microwaves. First, multi-mode microwaves, like for example domestic microwaves uses a microwave diffuser to redirect the radiations in all directions of the cavity. This diffuser, in addition of all the reflexions on the walls of the cavity basically to domestic ovens enables to multiply the radiations in all direction and thus contributes to the heating of the food or the sample. In opposition, mono-mode ovens as it will be described later do not use any diffuser. In these microwaves, the cavity is shorter, and the dimensions are tuned to optimise the interaction between the radiation and the matter. For sintering application, the two categories can be used but this study will focus on the development of mono-mode microwave sintering.

2.2.2.2. Microwave propagation

2.2.2.2.1. Propagation in void

As electromagnetic radiations, microwaves are described by maxwell equations. These for equations (see equations (2) to (5)) (CHARMOND, 2009), are the baseline of the electromagnetism and a key point of the development of microwave ovens.

$$Div(\vec{B}) = 0 \tag{2}$$

$$Div(\vec{E}) = \frac{\rho}{\varepsilon_0} \tag{3}$$

$$\overrightarrow{rot}(\vec{E}) = -\frac{\partial \vec{B}}{\partial t} \tag{4}$$

$$\overrightarrow{rot}(\vec{B}) = \mu_0 \vec{J} + \varepsilon_0 \mu_0 \frac{\partial \vec{E}}{\partial t} \tag{5}$$

$\vec{E}$: electrical field (V.m^{-1})

ε_0: dielectric permittivity in vacuum (F.m^{-1})

ρ: volume density of electrical charges (C.m^{-3})

$\vec{J}$: Volume density of current (A.m^{-3})

$\vec{B}$: induced magnetic field (T)

μ_0: magnetic permeability in vacuum (H.m^{-1})

As well, it is important to remain that electrical fields and magnetic fields induce electric and magnetic inductions described by equations (6) and (7) (CHARMOND, 2009)

.

$$\vec{B} = \mu_0 \vec{H} \quad (6)$$

$$\vec{D} = \varepsilon_0 \vec{E} \quad (7)$$

$\vec{D}$: electric induction (C.m^{-2})

$\vec{H}$: magnetic field (A.m^{-1})

Microwaves like all electromagnetic radiations are composed of two components. Represented in figure 8 an electromagnetic radiation is can be decomposed in two perpendicular sinusoidal waves: an electric component and a magnetic component.

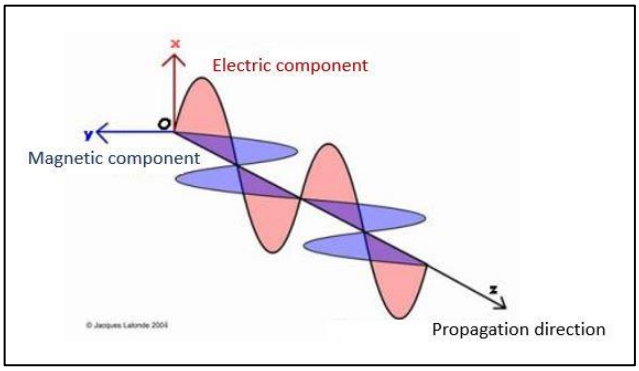

Figure 8: free propagation of a planar progressive wave (CHARMOND, 2009)

The relation between the two components of the radiation is given by the equation (8) in which the vector u is the direction of propagation and c the speed of light.

$$\vec{B} = \frac{\vec{u} \wedge \vec{E}}{c} \quad (8)$$

In case of microwave sintering, the conditions are not those of a free propagation under vacuum. As it will be developed later, the microwaves are generated and then conducted to the cavity thanks to waveguides. In both, the propagation of microwaves is not “free” but “guided”.

2.2.2.2.2. Guided propagation

In this special case of propagation, the radiation is reflected many times. To understand the propagation of the microwaves in the waveguide or the cavity, the point is in the calculation of the propagation equation. To do so, two mode of polarisation: Transversal Magnetic (TM) and Transversal Electric (TE) are commonly considered. TE mode, considering a rectangular waveguide, is the mode in

which the electrical field is perpendicular to the direction of propagation (Oz) and with its component projected on z null (Ez=0)(see figure 9).

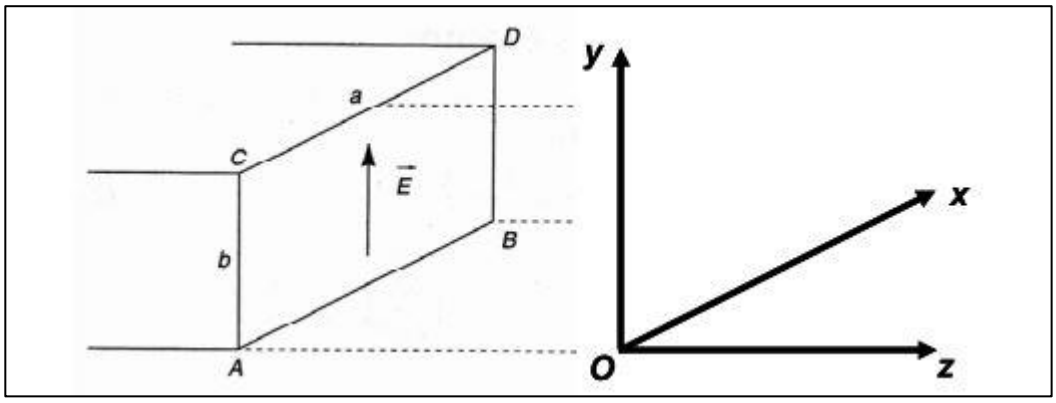

Figure 9: ABCD plan in a rectangular waveguide (CHARMOND, 2009).

Considering a rectangular waveguide, the resolution of the propagation equation is simpler. In fact, it results in determining the TM or TE modes allowed by the waveguide. The resolution and the finding of the different modes will not be developed in this report. The full demonstration is developed by CHARMOND (2009). The study of the fundamental TE mode enable the representation of the distribution of the electric field in the cavity section. (see figure 10)

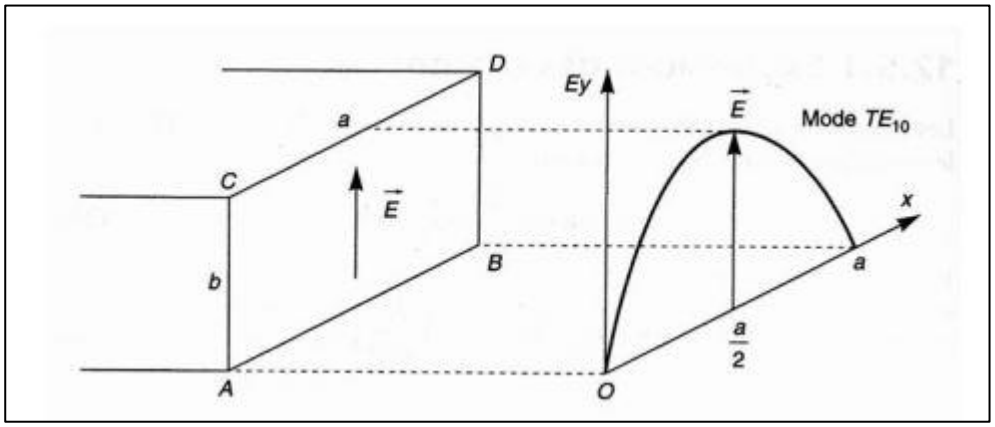

Figure 10: Electric field distribution in a rectangular waveguide for fundamental TE mode

An important remark concerning Transversal modes is that the wave (electric or magnetic) is progressive following z axis and standing along y axis. the only component of the electrical field is on the y axis. The propagation in waveguide enable to control the propagation modes. By changing the dimensions of the section for a fixed frequency of radiation, fundamental mode can be imposed. As well, this implies that the distribution of the electrical or magnetic fields in the guide can be tuned by the same time.

After the propagation in the waveguide, the microwaves are transmitted in the cavity. In order to compare, lets shortly explain the difference between multimode and single mode cavities. *(CHARMOND, 2009).*

In multimode cavities, the dimensions are way superior to the dimensions of the waveguide and of the wavelength. Thus, in multimode cavity the propagation conditions are those of free propagation. Therefore, and because of the multiple reflexions on the walls, the superposition of the different waves

implies the formation of different resonance modes. The repartition of the fields amplitudes is consequently more chaotic.

In mono-mode cavities as the dimensions remains as small as those of the waveguides, the propagation is still "guided" and the resolution leading to the modes still the same: a single mode is allowed, and the distribution is controlled. However, as described in general description of the oven, the cavity is a closed volume with a fixed section and a variable length. The length of the cavity is ended with a moving wall made of a reflective material. To achieve the understanding of the oven working, the reflexion of the radiation will now be described.

First, the reflexion on the metallic wall is considered perfect. To calculate the distribution of the fields, the superposition of the incident and reflected waves is made. Following the development made by CHARMOND (2009), the resulting propagation equation are obtained:

$$\overrightarrow{e_y}(z,t) = 2\overrightarrow{E_i}\cos\left(kz - \frac{\pi}{2}\right)e^{j\left(\omega t - \frac{\pi}{2}\right)} \quad (9)$$

$$\overrightarrow{h_y}(z,t) = 2\overrightarrow{H_i}\cos(kz)e^{j(\omega t)} \quad (10)$$

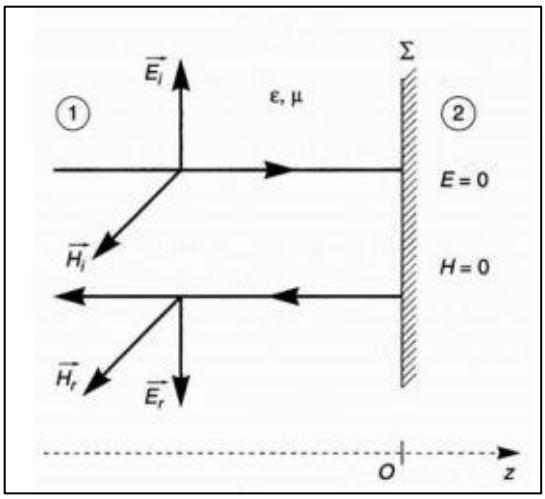

Figure 11: Reflection of the electromagnetic field with normal incidence (CHARMOND, 2009).

Thus, the electric component and the magnetic component are periodically null. According to CHARMOND (2009):

_ For z=0 and all plans parallel placed at (p.λ/2) from z=0, p ∈ N, the electric component is null, and the magnetic component is maximal.

_ For all plans parallel to z=0 and placed at (2p+1)(λ/4) from z=0, p ∈ N, the electric component is maximal and the magnetic component is null.

By simulation, the electrical field distribution can be modelized (see figure 12).

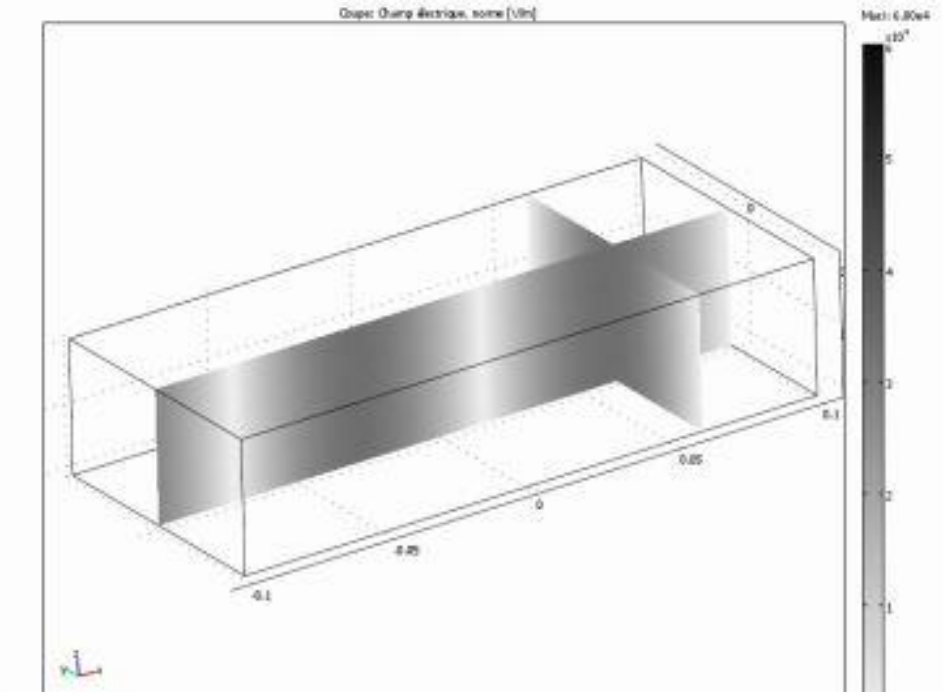

Figure 12: Modelisation of the amplitude of the Electric field (V/m) in a monomode cavity. (CHARMOND, 2009)

As a conclusion of this part, mono-mode microwave sintering is based on guided propagation. Two polarisation modes can be used to modify the distribution of the fields. As well, by modifying the length of the cavity and the dimensions, the distribution of the fields is tuned. Finally, depending on the location of the sample in the cavity, it is possible to use only the magnetic or the electric component of the radiation.

2.2.2.3. Matter/microwave interaction

Microwave heating for sintering is based on the interaction between the material and the mater. In comparison to conventional sintering, where the heat comes from heating resistance around the material, in microwave sintering, the material is heated by different mechanisms induced by the interaction with electromagnetic radiation.

Commonly, three kind of interactions exists (PRESENDA BARRERA, 2016). As represented in figure 13, a material can be opaque transparent or absorbent to microwaves.

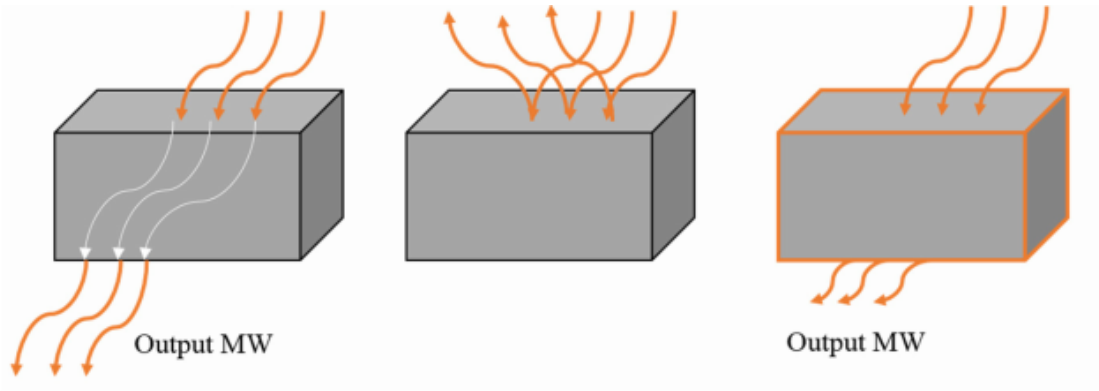

Figure 13: Matter/radiation interaction (PRESENDA BARRERA, 2016).

_ Opaque materials: do not allow the radiation to penetrate it. The radiation is then totally reflected. This is the case of conductors like metals.

_ Transparent materials let the radiation go through it. The microwave is thus transferred without any energetic loss. This is the case of material with low dielectric or magnetic losses such as ceramics at low temperature like Al_2O_3.

_ Absorbent materials are penetrated by radiations but absorb totally or partially the radiation thanks to different mechanisms. These are materials with high dielectric or magnetic losses. As examples, this is the case of many oxides and of ceramics at high temperature.

It is important to remain that the nature of the interaction between the material and the radiation depends on many parameters:

First of all, the capacity of the material to absorb the radiation intrinsically depends on the structure of the material and of its composition. Because of this, the temperature as well plays an important role. In fact, changes in temperature implies modifications in the structure and the properties of the material. As well, an increment of the temperature corresponds to an augmentation of the thermal agitation inside the material that can modify the interaction with the radiation.

Then, the comportment of the material depends as well on the characteristics of the radiation. In fact, the frequency, and the wavelength determinates the comportment of the material. A material can thus be transparent to microwaves but opaque to Infra-Red.

Microwave sintering uses the absorption of the radiation and the different mechanisms implied to raise the temperature in the material. This process is thus designed for material absorbent to microwaves.

2.2.2.4. Heating mechanisms

For absorbent materials, the interaction with the electromagnetic radiation is a source of heat. The microwave, as a superposition of two sinusoidal waves (electrical and magnetic) produces a local alternance of the magnetic and electric fields. Under the influence of these fields, a polarisation of the material is observed. In the case of a 2.45GHz microwaves, 3 main mechanisms exist divided in two categories: electric mechanisms and magnetic mechanisms (CHARMOND, 2009).

Contribution of the electric field:

Dielectric heating is the most common and known mechanism. In fact, under this name, two distinct mechanisms exist: bipolar rotation or polarization and resistive heating. These two mechanisms involve dielectric losses and are commonly observed in ceramics.

_ the dielectric polarization is the most important mechanisms in microwave sintering. Under electrical field, a polarization of the dipoles occurs. The polarization corresponds to a separation of the charges' barycentre. Depending on the material, this polarization can be induced if it requires the application of an external field or permanent if the material is intrinsically polarised like the quadratic phase of $BaTiO_3$ for example. When submitted to an alternative electrical field, the bipolar molecules in the material are reorientated and follows the amplitude of the signal.

_ the resistive heating is well known for conductors. Under electrical field, the free electrons displacement is opposed to the resistivity of the material. Resulting from this opposition to the displacement of free charges, heated is produced by joule's effect. In conductors, the resistivity is low, and this effect is minimized. In the case of semiconductors or valence oxides as ferrites or BaTiO3, the high resistivity of the material improves this effect.

Contribution of the magnetic field:

In most materials, magnetic losses are almost nulls comparing to dielectric losses. For this reason, microwave sintering using mono-mode magnetic microwaves is not suitable for many ceramics. In the case of ferrites like Ni-Zn Ferrites, magnetic losses are not negligible. The mechanisms involved by the magnetic component of the radiation are complex and not this so study by the literature.

The most important mechanism involved by the magnetic part of the radiation is the process of magnetization and remagnetisation of the material. Similarly, to the mechanism of polarization under electric field, the application of the magnetic field H resulting from the radiation causes an inducted magnetic field B this relation is given for a magnetic material by the equation (11)

$$\vec{B} = \mu\vec{H} \tag{11}$$

In the cavity, the oscillating magnetic field implies the cycles of magnetization and remagnetisation to the material. Furthermore, the induction is not instant, a hysteresis effect occurs. As a result, depending on the magnetic properties of the material, magnetic losses are involved and contribute to heat the material. As for the polarizability of the material under electric field, the magnetizability of the material is linked to the relative permeability of the material (see equation (12)).

$$\mu_r = \frac{\mu}{\mu_0} = 1 + \chi_M \tag{12}$$

2.2.2.5. General description of the microwave

Singles mode micro-wave oven are composed of three main parts. First, the most important part is the source which generates the microwave. Then comes the transmission part composed of different kinds of transmission lines and finally, the resonant cavity that can be tuned and in which the sample is placed.

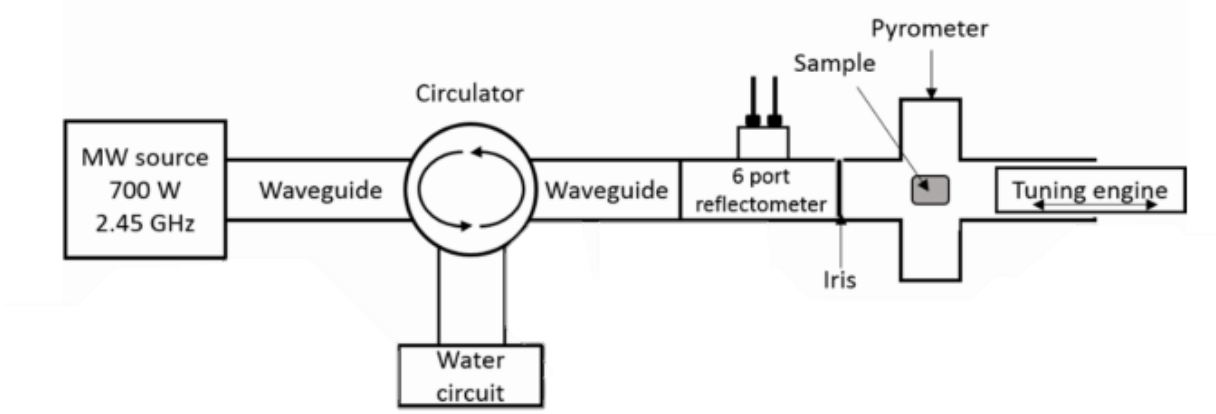

Figure 14: Schematic of a microwave system with a rectangular cavity. (PRESENDA BARRERA, 2016)

For each part of the oven, various components and technologies can be used. The different possibilities are listed below.

Microwave source:

Three different microwave sources exist the choice depends on the budget and frequency required.

_ Gyrotrons generates frequencies between 30GHz and 300 GHz. This kind of source can be highly powerful and reach 1 MW of power. They are used for example in nuclear fusion to generate plasmas.

_ Magnetrons are the most commons generators for microwave sintering because of their frequencies between 1 GHz and 30 GHz and their cost (between 3500 $ and 50000 $).

_ Klystrons are powerful generators that can reach several thousand of KW. This kind of generators can produce frequencies between 0,3 GHz and 100 GHz but their used is limited because of their price.

Waveguides:

Waveguides aim at transmitting the radiations from the generator to the cavity. Depending on the frequency, and the application, different possibilities exist.

_ Coaxial cables are suitable for low frequencies applications. Their use for microwave sintering is not optimum because of their important losses at high frequency.

_ Rectangular or circular waveguides are made of a conductor material that totally reflects the radiations contained in the waveguide. For high frequencies application like microwave sintering, they are the most suitable option.

Circulator:

In order to protect the generator from reflected radiations, this security component redirects the reflected radiations to a water circuit that will absorb it.

Reflectometer:

This instrument measures the absorbed power by comparing the input power of the radiation to the output power of the reflected radiation.

Iris:

The Iris aims at coupling the radiation coming out from the waveguide to the cavity.

Pyrometer:

The pyrometer is placed on top of the oven in order to measure the temperature of the sample. In case of microwave sintering, it is the only possibility. In fact, thermocouples used in conventional sintering cannot be used because they are metallic.

Tuning engine:

The tuning engine is a moving extremity of the cavity that aims at modifying the length of it to tune the distribution of the electric and magnetic field. By the same time, it changes the resonance conditions.

CHAPTER 3: Equipment and method

Following the state of the art, the chapter will focus on the presentation of the equipment used during the project and the way that the samples were prepared. First, the microwave equipment will be detailed, presenting the difficulties of this method as well. Then, the conventional sintering equipment will quickly be presented, and finally a last part will be dedicated to the sample preparation.

3.1. Microwave sintering

The microwave sintering of the samples was carried out in two different ovens. As explained in part 1.2.1., by changing the configuration of the oven, it is possible to favour the electric component of the field or the magnetic component. Depending on the properties of the material, the sintering can be possible or not with one or the two microwaves. By using the two different microwaves, it is possible to highlight the differences of sinterability and to increase the chances to succeed in the sintering.

3.1.1. Electrical microwave

As represented in figure 15 the electrical single-mode microwave that was used in this project has a common design for this application. Developed by ITACA-UPV (Instituto de Aplicaciones de las Tecnologías de la Información y de las Comunicaciones Avanzadas de la Universitat Politécnica de Valencia), this microwave is composed of:

_ a magnetron of 2,45 GHz with a power between 300 W and 800 W

_ rectangular waveguides

_ a rectangular cavity

_ a circulator

_ a reflectometer

_ an Iris

_ a refrigeration system

_ a tuning engine

Figure 15: Annotated picture of the electrical single mode microwave.

3.1.2. Magnetic microwave

As shown on figure 16 magnetic microwave is very similar to the electric one. There are no changes in the composition of this microwaves except the dimensions of the cavity and of the waveguides. As presented in the state of the art, to favour one component of the field, it is only a question of radiation orientation and geometry of cavities.

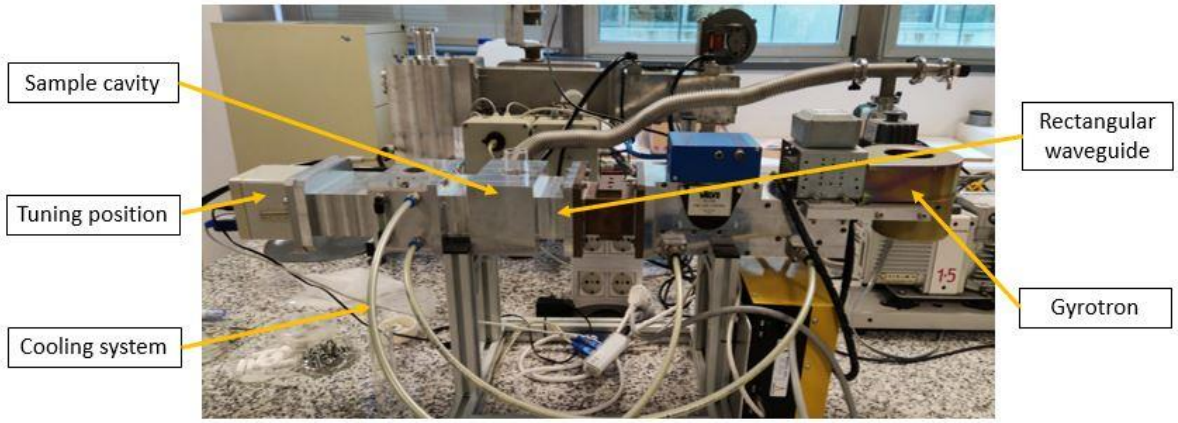

Figure 16: Annotated picture of the magnetic single mode microwave

3.1.3. Pyrometer

To control the temperature in the microwave, it is impossible to use a thermocouple. Indeed, the use of metals in the cavity is impossible in order to avoid perturbations of the radiations. In general, it is important limit the quantity of materials in the microwave in order to control the process. If the objective of the process is the controlled absorption of radiation by the sample, all other materials can as, as well absorb the radiation or be a perturbation. Therefore, the measured power absorbed would be falsified and the heating rate uncontrolled.

The chosen solution for temperature measurement is the use of a pyrometer on top of the cavity. As shown on figure 15, it is positioned over a small hole in the cavity so that it has no great influence on the process.

Before using the pyrometer, it is important to calibre the pyrometer. To measure the temperature of the material, it is important to determine first its emissivity and transmissivity. These data will then be set in the pyrometer for every sample sintering. Obviously, as these properties highly depend on the temperature, it is important to determine the emissivity for different temperatures. To do so, a piece of the material is placed in conventional oven with on top the pyrometer fixing the material. When the desired temperature is reached (information given by the oven) the emissivity is changed on the pyrometer to make the temperature of the pyrometer correspond to the real temperature. By doing this for several temperatures, it is possible to obtain the emissivity and transmittivity of the material for a range of temperatures. Of course, for precision, this demarche must be done for each pyrometer.

Once the emissivity of the material is set, the last step before using the pyrometer is to position it right. Indeed, the pyrometer must be at the right distance from the sample to be focus on it. To do so, two lasers on both sides of the pyrometer head enables to set the right position.

3.1.4. Process control

In order to pilot and control the process, the whole system is connected on a computer. From the software, it is then possible to pilot the power furnished by the generator, the dimensions of the cavity and to measure the temperature. The figure 17 shows the interface that is used during sintering. On the top right-hand corner is an instant curve representing the evolution of the temperature in function of time. On the left is a Smith chart and the power selector. Finally, on the right can be find the temperature, the heating rate (slope), the absorbed power the tuning position and other parameters.

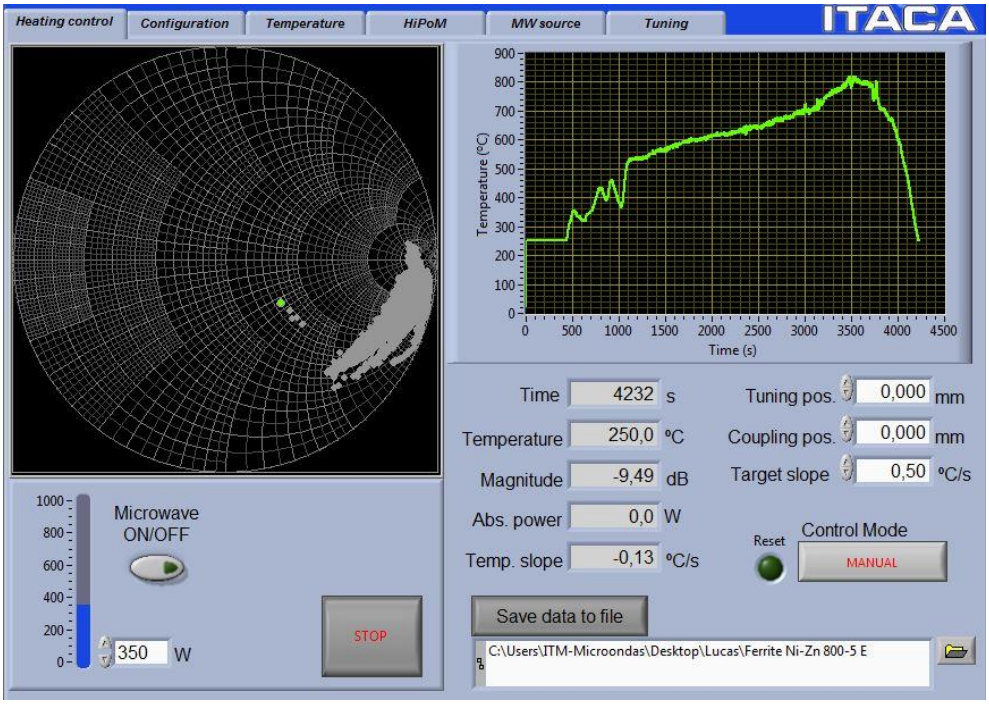

Figure 17:monitoring interface of the electrical microwave.

The control of microwave sintering can, depending on the material be difficult. By now, this method is still not suitable for series because it requires the constant control of an operator. As presented before, the heating of the material reposes on the interaction between the material and the radiations. As well, it is presented that the distribution of the field in the cavity is tuned by changing the dimensions. Based on this, the method is the following:

_ First, the power of the generator is set and the tuning position (that pilots the dimensions of the cavity is set at the minimum or the maximum.

_ Then, after launching the generator, the operator changes little by little the tuning position on order to increase the interaction between the sample and the field. Theoretically, it is possible to represent this evolution with a gaussian curve with on x-axis the tuning position and on y-axis the absorbed power. For each material exists a maximum of power absorbed in which the heating rate would be maximum.

_ Finally, all the process success results in controlling the interaction between the sample and the radiation to keep the heating rate constant.

3.1.5. Sample support

As presented in figure 18, the sample is placed in the centre of the cavity using a quartz tube and a support. The quartz tube does not perturb the radiation because quartz is transparent in this range of wavelength, nevertheless, it is important to ensure that it is cleaned before every sintering.

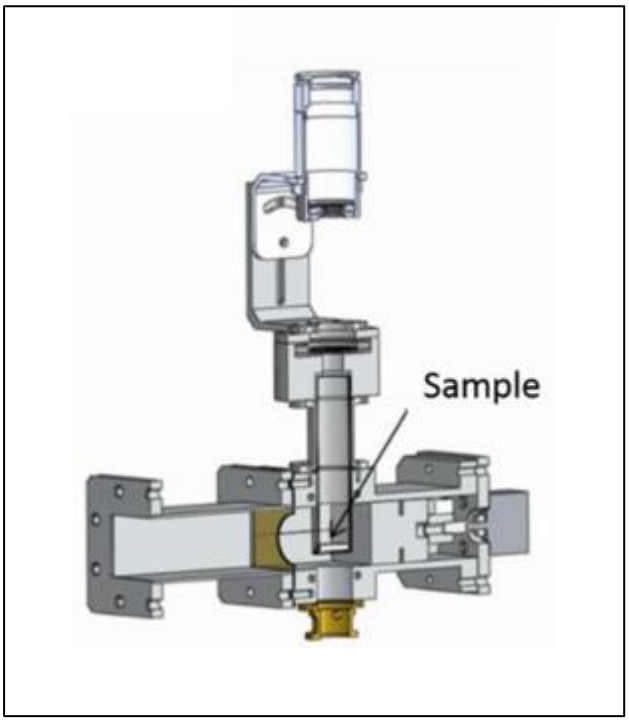

Figure 18: cross section of a microwave oven with recatangular waveguides and cavity. (PRESENDA BARRERA, 2016)

As well, more than the tube, a support is needed to mut the sample at the right height. The choice of this support is delicate. First, the introduction of another material will have an influence on the absorbed power and the control of the temperature. Then, as this support is in contact with the sample, it is required to ensure that no reaction will occur at high temperature between the two materials.

Figure 19 shows the disposition of the sample and its support in the tube. For this study, the support used is an alumina cylinder.

Figure 19: Disposition of a sample and it support in a quartz tube.

3.1.6. Hybrid sintering

Principle and applications:

For some materials, the microwave sintering is difficult or impossible for various reasons. First of all, in some cases, it appears impossible to heat the material. In fact, depending on the properties of the material and as they vary with temperature, some heating mechanisms cannot be activated at low temperature.

As a solution, it is possible to use another material called susceptor close to the sample in order to help the heating of the material. In this method, the susceptor is chosen in a manner that it absorbs well the radiations and can be heated with the technique. Consequently, during the beginning of the sintering, the sample is partially heated by the susceptor until that its properties enables him to sufficiently absorb the radiation and heat.

In the opposite direction, the microwave sintering of some materials appears impossible or difficult because the heating rate cannot be controlled. As an example, the case of the composite (Ni-Zn) ferrite/$BaTiO_3$ is presented in part 4.1.2.. In the case of the tuning of the sintering parameters is not sufficient to control the heating, the use of a susceptor can be a solution.

In this second case, the susceptor role is to absorb a part of the radiation in order to reduce the radiation absorbed by the sample. Also, it is important to use a susceptor that is stable during microwave sintering. Consequently, during the process, the sample absorbs less radiation, and the heating rate is then lower. As well, the because of its stability, the susceptor induces a certain inertia to the system that can avoid sudden increases in the heating rate.

As a conclusion, In the two previous cases, the use of a susceptor is required. Such sintering is then called Hybrid sintering because a part of the heating is done by thermal transfers as radiation of convection.

Material and disposition:

In the study, the material use was Silicon Carbide SiC. Indeed, this material is a semiconductor with good electromagnetic properties. Concerning the disposition of the susceptor in the quartz tube, various possibilities exist. As an example, the disposition used in this study is presented in figure 20.

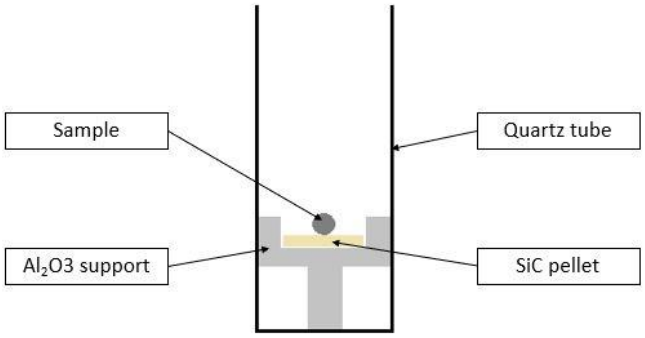

Figure 20: Schema representing the disposition of the susceptor in the quartz tube.

3.2. Conventional sintering

To compare with the samples made by microwave sintering, conventional sintering was also used. All samples have been sintered in an electrical furnace (Garbolite-gero HTF 1800) that is shown in figure 21, This oven enables to heat materials at a maximum temperature of 1800°C for hours.

Concerning the temperature, the desired heating rate is set before the treatment and the temperature is then automatically controlled and measured by a thermocouple. Following the constructor references, the maximum power of this kind of oven can reach more than 4500 W.

Concerning the sintering parameters, different temperature and times have been used. Samples were maintained during one or two hours at temperatures between 1100°C and 1250°C. For all samples, the heating rate was 10°C/min and the cooling was progressive in the furnace.

Figure 21: Conventional electric furnace

3.3. Sample preparation

3.3.1. Compaction

The compaction is the very first step of this process. In sample preparation, the starting point is the powder. The aims of the compaction are multiple. First of all, the objective is to elaborate the green body by giving to the workpiece its shape. To do so, the baseline is to put the powder in a mould and to apply pressure on it. Then, depending on the desired geometry various method exists. To create a

Figure 22: Compaction cylindrical mould

cylindrical geometry for example, the common method is to put the desired quantity of powder into a cylindrical mould as presented in figure 22. The mould is then pressed in a uniaxial traction/pression machine.

In this project, a spherical geometry has been chosen. To do so, the powder was first put into balloons and then pressed by isostatic pressure. This method uses a hermetic cylinder filled with a water and lubricant in which the powder in balloons is placed. To apply the pressure, the system is then placed in an isostatic press as presented in figure 23. By applying the pressure on the extremity of the cylinder, the pressure is transmitted to the liquid and the samples.

Figure 23: Isostatic press

Finally, it is important to remain that the compaction have a direct influence on the sintering process. Indeed, by applying the pressure, the density of the sample is already decreased. Depending on this pressure, the distance between the grains is changed and the process is influenced. In this study, the influence of the compacting has not been tested. All samples have been compacted with the same force of 5 tons.

3.3.2. Cutting

After sintering, the spherical samples were cut in order to obtain a planar section of the material for the characterization. By separating the sample in its middle, the objective is to observe the section of the workpiece and to determine the homogeneity of the sintering. As well, by dividing all samples in two, it was possible to use one half for hardness tests and the other half for FESEM and DRX.

To cut the workpiece, a WELL wire cutting saw has been used. This machine enables a very precise cutting thanks to wires between 0,13mm and 0,30mm. As shown on the figure 2, The saw is composed of a wire covered with diamonds, a cleaning tray filled with water to cool the wire down, a drum and a tension pulley.

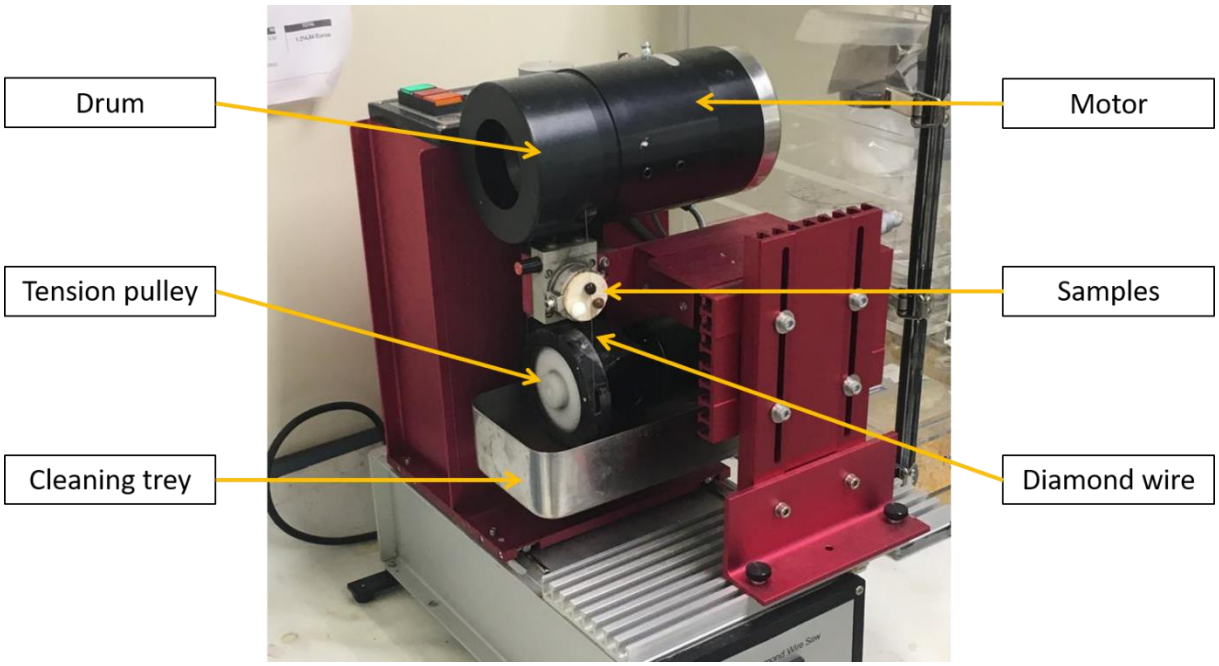

Figure 24: wire cutting saw

3.3.3. Coating and Polishing

After the cutting step, the samples are put into a resin in order to polish them. The same polishing has been used for both the Ni-Zn ferrites and the Composite Ni-Zn Ferrite/$BaTiO_3$. As presented in table 3 the polishing was carried out in 7 steps. For each step all the parameters are detailed.

Table 3: Polishing parameters

Disc	Lubricant	Force	Velocity	Time
Lapping 75 µm	Agua	10 N	100 rpm	1 min
Lapping 40 µm	Agua	10 N	100 rpm	1 min
Lapping 20 µm	Agua	10 N	100 rpm	1 min
Lapping 10 µm	Agua	10 N	100 rpm	1 min
MD Largo	6 µm	20 N	150 rpm	10 min
MD Plus	3 µm	20 N	150 rpm	8 min
MD Nap	1 µm + lubricant	10 N	150 rpm	8 min

3.4. Characterization methods

3.4.1. XRD

X-Ray Diffraction (XRD) is an essential characterisation method in material science. The theory of this method is based on the diffraction of the X-rays by crystalline structure. In fact, in contact with a crystalline structure, the incident X-rays are diffracted in specific directions. By analysing the intensities

and the angles between the incident and the diffracted rays, it is possible to determinate the structure of the material, especially the lattice parameter, and the phasis present in the structure.

This method is a common characterisation method used for metals, ceramics, or all crystalline materials. In this project, the aim of this method is to verify the different phases composing the material and to observe the evolution of these phases proportion for different sintering parameters and methods.

3.4.2. Micro-hardness

Material hardness is the mechanical resistance of a material against penetration. Different tests and scales exist (Brinnel, Vickers, Rockwell, etc…). In this project, the hardness of the materials has been determined using micro-hardness with the Vickers test. In this test, a footprint is made on the material by a penetrator with a pyramidal shape. By measuring the section of the footprint and knowing the pressure applied, it is possible to calculate the Hardness of the material. As well, in order to have reliable, 10 measurements have been done on each material. From these 10 values, the 2 extremes are delated to avoid aberrant values. Finally, the hardness is calculated as the mean of the 8 remaining measurements.

For the characterisation of ceramics, hardness is a simple test that enable to compare quickly different processes. As this property also depends on the density of the material, its porosity and the sintering process, this test was a baseline to compare the efficiency of microwave sintering comparing to conventional sintering.

3.4.3. Density

The density of the material ratio of its mass divided by its volume. For full dense material, the density is fixed and can be calculated knowing the element that composes the material and its structure. Concerning a porous material, the density is more complex and vary. In the case of powder sintering, the process starts from a powder. By thermal treatment, it creates links between the powder grains and make the system evolve until the elimination of the porosity. The ideal product would then be a full dense material.

To determinate the quality of the sintering, the measurement of the real density of the material is an important indicator. By comparing it to the theorical density of a full dense material, it is possible to calculate the relative density of the material and its porosity.

In this project a simple measurement of the density of the samples was impossible. Indeed, the complex geometry of the samples make impossible a simple calculation of the volume followed by a mass measurement. As well as the samples are porous, the measurement must present the apparent density. To obtain a great precision, the measurement was done following Archimedes' method.

Archimedes' method:

Based on Archimedes' principle, the Archimedes' method consists in measuring the mass of a sample two times. The first measurement is done for the dry sample m_A. The second measurement is done on the same sample immerged in a liquid and is noted m_B. The density of the liquid is known and is noted ρ_{liquid}. With the two masses and knowing the density of the liquid it is possible to calculate the density of the material thanks to equation 13.

$$\rho = \frac{m_A}{m_A - m_B} . \rho_{liquid} \tag{13}$$

3.4.4. Field Emission Scanning Electron Microscopy (FESEM)

FESEM as an improvement of Scanning Electron Microscopy (SEM) is an electronic microscopy method. To sum up, the principle of SEM is the following. An electron beam is produced and directed on the sample. By the interaction between the matter at the surface of the sample and the electrons, secondary electrons are emitted. Thanks to a system of sensors, all these electrons are received and turn into an electric signal that is treated by a software in order to recreate a topography of the surface. As presented in figure 25 and commented by PRESENDA BARRERA (2016), both microscopes are composed of:

_ an electron source called electron gun.

_ a column in which various lens and coils are disposed in order to control the electron beam.

_ sensors that receive the secondary electrons.

_ a computer that treat the data and recreates an image.

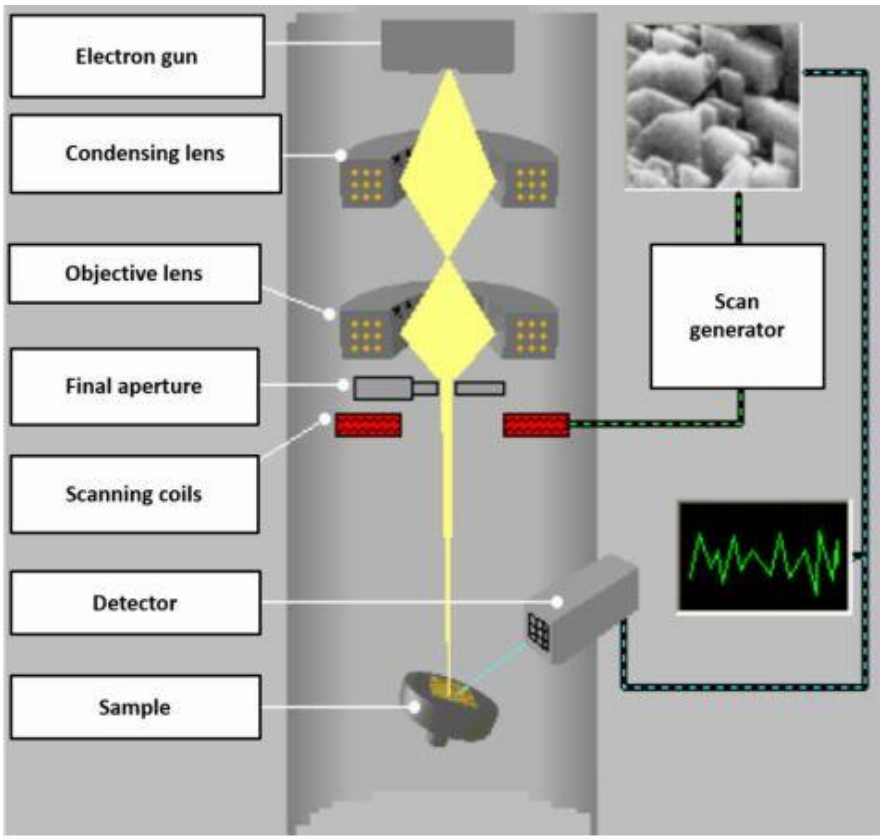

Figure 25: Schematic of SEM system (PRESENDA BARRERA, 2016).

The great difference between FESEM and SEM is the source of electrons. In FESEM, a field emission electron gun is used. As a consequence, this technique has several advantages: it enables clearer images, a better resolution and especially scales down to 1,4 nm (PRESENDA BARRERA, 2016).

Commonly, SEM and FESEM are well used in material science. Principally, they enable to have a direct look on the structure of the material. As examples, it is possible to measure the grainsize, to observe the porosity or to highlight precipitates of different phasis.

In the study, the samples have been fractured in order to observe the fracture zone. By this method, it is possible to observe the cohesion of the grains and the fracture profile. In addition to the fracture, the samples have been lightly polished, and a thermal attack have been done to reveal the shape of the grains. Concerning the parameters of this attack, each sample was put for 30 minutes at a temperature 100°C under the sintering temperature.

CHAPTER 4: Characterization and results

This part will focus on the characterization of the sample. To do so, an overview of the different samples and the test made on each of them will be done. In this recap, all the treatments parameters will be detailed in order to facilitate the analysis. Then, the different characterization method used in this project and their results will be discussed.

4.1. Samples Overview

4.1.1. Produced samples

As presented in the workplan, (1.2.), numerous samples have been produced. All the parameters used are resumed in table 4 for (Ni-Zn) ferrite and in table 5 for (Ni-Zn) ferrite + $BaTiO_3$ composite. In these tables, CS refers to Conventional Sintering and MW(E) refers to Electrical Microwave.

Table 4: List of the (Ni-Zn) ferrite samples and presentation of the sintering temperatures and times.

Sintering method	Temperature	Time
CS	1150°C	2h
	1200°C	2h
	1250°C	2h
MW(E)	800°C	5 min
	800°C	10 min
	900°C	10 min
	1100°C	10 min

Table 5: List of the (Ni-Zn) ferrite/$BaTiO_3$ samples and presentation of the sintering temperatures and times.

Sintering method	Temperature	Time
CS	1100°C	1h
	1200°C	1h
	1200°C	2h
MW(E) sin susceptor	1000°C	10 min
MW(E) with susceptor	1000°C	10 min

To design the sintering, all temperatures have been chosen below fusion temperature and by comparing with other studies. For example, the conventional sintering of (Ni-Zn) ferrite has been designed based on the study of HUA Su and al. (2006) presenting the effect of the sintering temperature in (Ni-Zn) ferrite. In fact, as presented in figure 26, by comparing the density of the samples for different sintering temperature they highlighted that for (Ni-Zn) ferrite, the optimal sintering temperature (in conventional sintering) is around 1250°C.

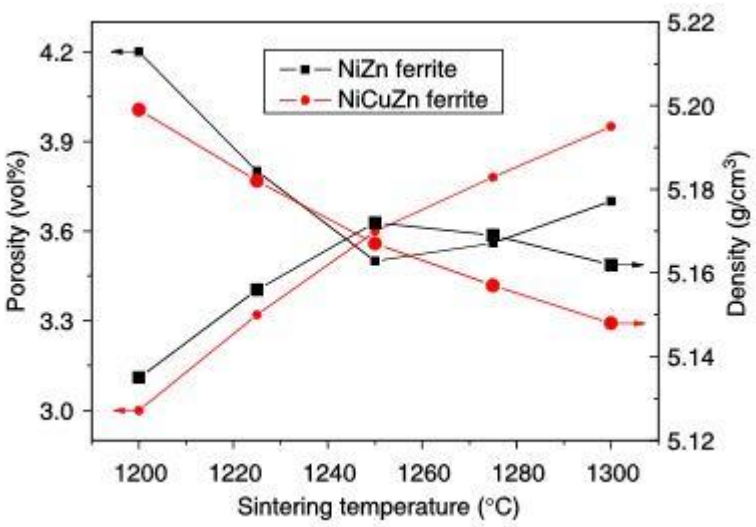

Figure 26: effect of sintering temperature on porosity and density of Ni-Zn ferrite and Ni-Cu-Zn ferrite (HUA and al., 2006)

In the same study (HUA and al., 2006) the samples were sintered in an electric furnace for 3h and let cooled inside the oven. As the aim of the project was to compare the samples from different technique, it has been decided that a duration of two hours was enough and more economic.

Concerning the decisions taken for (Ni-Zn) ferrite + $BaTiO_3$ composite samples, it has been decided to use almost the same sintering temperatures than for Ni-Zn ferrite. In fact, as 50%wt of the composite is of Ni-Zn ferrite, such temperatures were coherent and more convenient it was possible to sinter some samples together. Furthermore, no great study has been found dealing with the sintering of this composite. As a comparison, in their study, P.K. Roy and J. Bera (2012), sintered a MgCuZn ferrite/$BaTiO_3$ composite at 950°C for 2h. Consequently, if a downer temperature could be possible, sintering conditions presented in table 5 are still coherent.

About the microwave sintering temperature, first, at least one sample of each material has been sintered at the same temperature than in conventional sintering in order to compare. Then, as it is supposed that lower sintering temperatures are sufficient in microwave sintering, different temperatures below conventional sintering temperatures have been tested.

4.1.2. Failures

As a part inherent of every research job, failures as well as results are important. Microwave sintering, especially using single mode magnetic microwaves are at the beginning of their development. Also, according to the state of the art, the magnetic heating mechanisms are still partially unknown and the reaction of the different materials during microwave sintering are difficult to predict. For all these reasons, this part will focus on presenting the various failures in order to be a baseline for further research.

In this project, one of the most difficult part have been to succeed in the microwave sintering process. First of all, as one of the main challenges was to sinter the (Ni-Zn) ferrite/$BaTiO_3$ composite by magnetic microwave sintering, all the tests were focused on this. After several attempts, with and without susceptor the magnetic microwave sintering of the composite appears to be ineffective or uncontrollable. Indeed, by following the temperature evolution, it is observed in all attempts that a sudden acceleration of the heating occurs around 450°C. Consequently, a plasma generally occurs and causes the fusion of the sample.

To explain this sudden increase of the heating rate, an evidence is that a changing of the material properties occurs. The first possibility is that a phase change occurs at this temperature. Comparing separately the phase transitions of the two materials, no transitions occurs at this temperature. Another explanation is that, as previously presented, the different electromagnetic properties of the materials evolve in function of the temperature. To confirm this hypothesis, a monitoring of these properties (magnetic permeability, etc…) is required. Unfortunately, the microwave used is not adapted for such monitoring.

Faced to a lack of powder and a total impossibility to use this method for this material it has been decided to go on and to focus on the electric microwave sintering of material. In order to preserve the little quantity of powder of the composite, it has been decided to start by sintering only the (Ni-Zn) ferrite. The aim of this procedure was to firstly determinate if one of the two material that composes the composite is suitable for electric microwave sintering.

After the success in the microwave sintering of (Ni-Zn) ferrite, the microwave sintering of the composite has been tested. Observing the evolution of the temperature, the material has a very instable behaviour. In fact, during the various samples heating, it has been observed that the composite is much more sensible to the variations of the cavity size than the (Ni-Zn) ferrite alone. Consequently, it is very difficult to control the intensity of the interaction between the electrical field coming from the radiation and the material. As a result, it is hard to stabilise the heating rate.

Finally, the last observation concerning the electric microwave sintering of the composite is that the heating over 1000°C was impossible. Indeed, all attempts were concluded by a stagnation of the temperature or a rupture of the sample.

4.2. XRD

4.2.1. (Ni-Zn) ferrite

Figure 27 shows the XRD patterns of (Ni-Zn) ferrite sintered by conventional sintering (blue, red and black curves) and by electrical microwave sintering. Regarding the patterns, it clearly appears that the material is composed of a unique phase of cubic (Ni-Zn) ferrite. Comparing now the position of the peaks and their intensity, no impact of the method and temperature is observed.

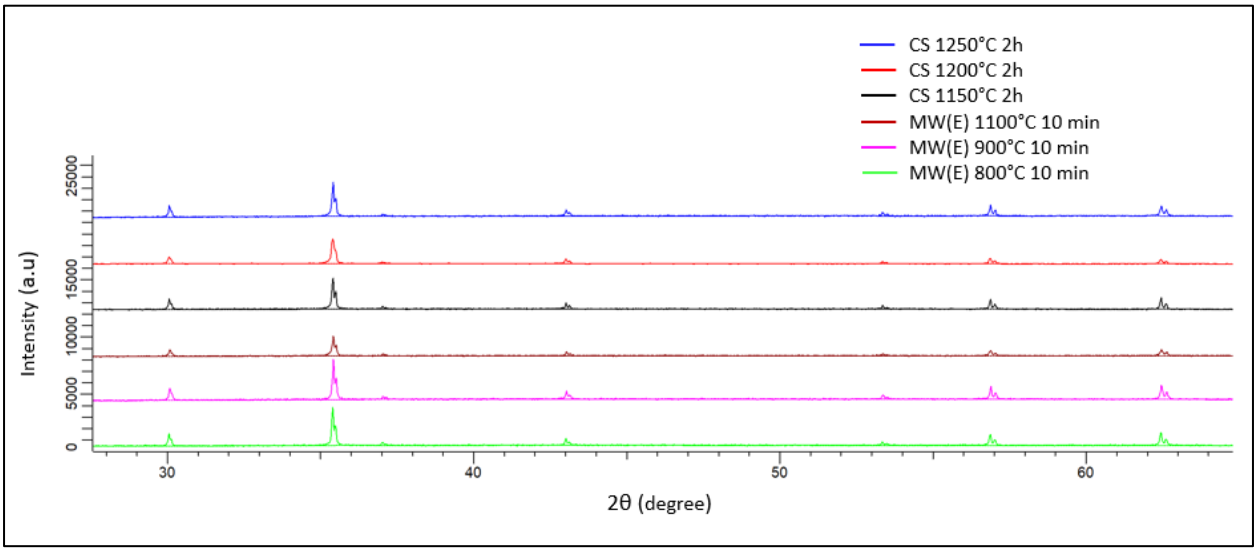

Figure 27: XRD patterns of the (Ni-Zn) ferrite for different sintering methods

4.2.2. (Ni-Zn) ferrite/$BaTiO_3$ composite

Figure 28 shows the XRD patterns of the (Ni-Zn) ferrite/$BaTiO_3$ composite. On top of the graph, the (Ni-Zn) ferrite pattern is as well presented to clearly spot the different peaks.

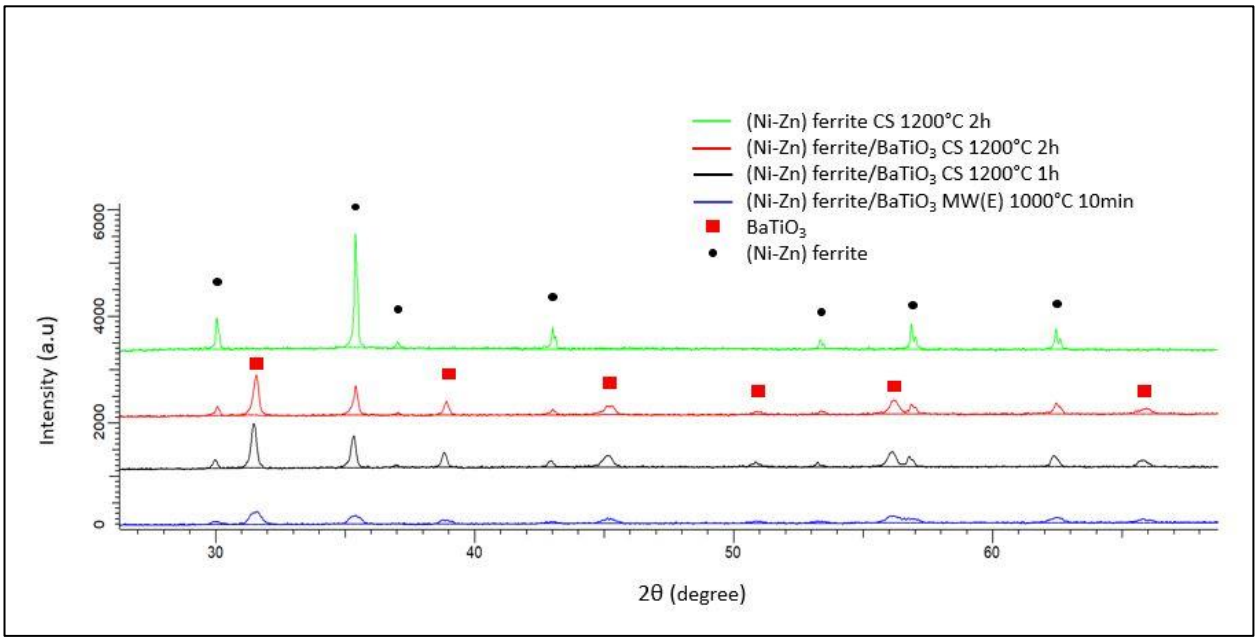

Figure 28:XRD patterns of (Ni-Zn) ferrite/$BaTiO_3$ composite for different sintering temperatures, times, and methods.

Regarding the patterns of the composite sintered by conventional sintering, the formation of the two phasis is clearly demonstrated. As well, comparing the intensity of the two phasis, no influence of the temperature on the phasis repartition is noticed.

Finally, concerning the sample sintered by microwave sintering, the intensity of both (Ni-Zn) ferrite phase and $BaTiO_3$ phase are way lower than for another sample. However as shown on figure 29, by increasing the scale, it appears that the relative intensity of both phases peaks is similar to the one of other patterns. Thus, the proportion of each phase seems to be conserved.

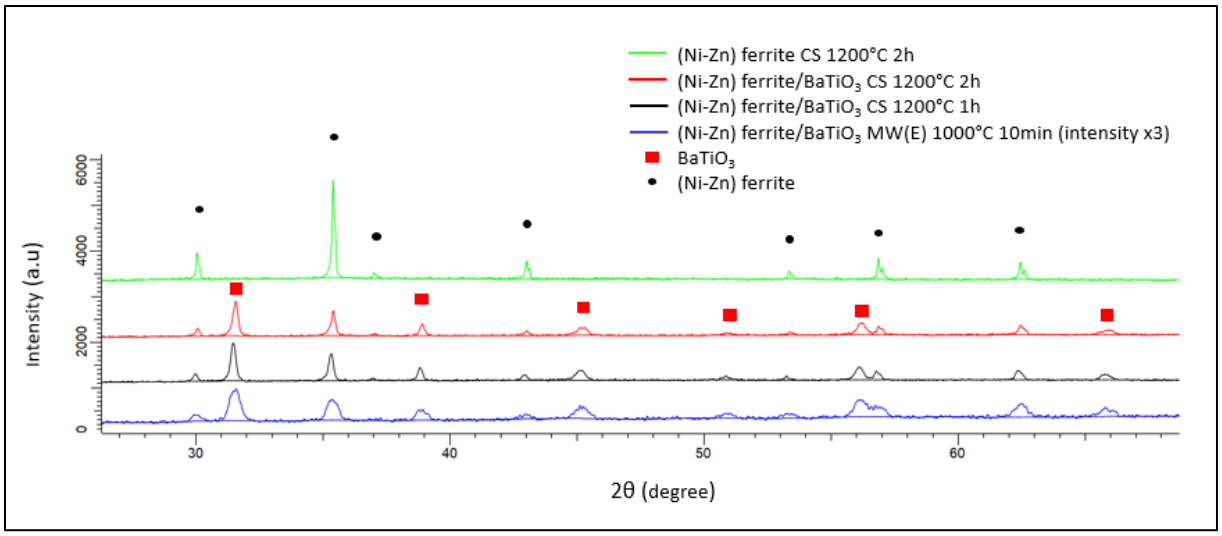

Figure 29:XRD patterns of (Ni-Zn) ferrite/BaTiO3 composite for different sintering temperatures, times, and methods. (scales modified)

4.3. Micro-hardness

As explained, in this project, the aim of measuring the hardness of the material was to have an easy indicator of the sintering quality. In the following tables (table 6 and 7) will be presented the hardness measured by micro-hardness for the different samples. Both materials will be analysed separately.

4.3.1. (Ni-Zn) ferrite

In table 6 are presented the results obtained for the Ni-Zn ferrite. Sorted by increasing hardness, the maximum hardness is obtained for the samples sintered by conventional sintering at 1200°C during 2h and at 1250°C during 2h. This observation confirms the expectations and will thus be taken as a reference for the comparison with MW sintering.

Table 6: Hardness results for (Ni-Zn) ferrite

Sample	Method	Time (min)	Temperature (°C)	Hv (GPa)
(Ni-Zn) ferrite	MW(E)	5	800	0,5
	MW(E)	10	800	1,6
	MW(E)	10	900	2,0
	MW(E)	10	1100	4,9
	HC	120	1250	5,6
	HC	120	1200	6,1

According to the results, various observations are made:

_ By comparing the hardness of the sample sintered at 1100°C during 10 min by microwave sintering (4,9 GPa) and the hardness of the two references (5,6 GPa and 6,1 GPa), it appears that the mechanical properties obtained by microwave sintering can easily approach those obtained by conventional sintering. This confirms that microwave sintering can consequently reduce the sintering times and the temperature.

_ Considering only the samples sintered in the electrical microwave, the measured hardness let supposed that samples sintered at 800°C and 900°C are not properly sintered. To confirm this expectation, FESEM will be carried out.

_ In complement to the first observation, it appears that, as expected, the different parameters tested have a great influence on the mechanical properties. Indeed, even if the samples are not properly sintered, at 800°C 5 minutes more have multiplied by 3 times the hardness of the material. Similarly, for a 10 minutes treatment, increasing the temperature by 200°C enables to multiply the hardness by 2,5.

4.3.2. (Ni-Zn) ferrite/$BaTiO_3$ composite

In table 7 are presented the results obtained for the (Ni-Zn) ferrite/$BaTiO_3$ composite. Similarly, to table 6 the samples are sorted by increasing hardness. In this case, the hardest sample obtained Is the one sintered by microwave sintering. Furthermore, the hardness is 1 GPa higher than the hardest sample obtained by conventional sintering.

Table 7: Hardness results of the (Ni-Zn) ferrite/$BaTiO_3$ composite.

Sample	Method	Time (min)	Temperature (°C)	Hv (GPa)
(Ni-Zn) ferrite+BaTiO3	HC	60	1100	5,1
	HC	60	1200	6,7
	HC	120	1200	7,0
	MW(E)	10	1000	8,0

Regarding these results, various observations can be made:

_ (Ni-Zn) ferrite/$BaTiO_3$ composite despite its difficulty to be sintered appears to be a suitable material for electric microwave sintering. Indeed, at lower temperature and for a duration six times shorter, the material hardness overpasses the hardness of the samples obtained by conventional sintering.

_ Answering the doubt in the choice of the sintering temperature for conventional sintering, a temperature of 1200°C seems to be the most adequate. Indeed, observing the samples sintered during an hour, the hardness of the sample sintered at 1200°C overpasses the 1100°C. Consequently, a sintering temperature of 950°C would have been too low.

_ In complement to the previous observation, only a small increase in the hardness is observed for the sample at 1200°C for 2 hours comparing to the one at 1200°C for 1h. The duration does not have this an influence on the material hardness between 1 hour and 2 hours. Consequently, a sintering time of 2 hours is not worth it for this material with this method. To confirm this observation and statement it will be interesting to observe FESEM images.

4.4. Density

Similarly to the presentation of Hardness test results, all the density measured by the Archimedes method are presented in table 8 for (Ni-Zn) ferrite and in table 9 for the composite. Before analysing these results, it is important to remain that the porosity is calculated using the density measured and that, consequently, does not take into account close porosity that can only be observe on FESEM images.

4.4.1. (Ni-Zn) ferrite

In order to facilitate the analysis of the table, all results have been sorted by increasing density. As presented in table 8 the density of four (Ni-Zn) ferrite have been measured: the two references sintered by conventional sintering and presented in part 4.3 and two samples made by electrical microwave sintering.

Table 8: Density measurements for (Ni-Zn) ferrite samples.

Material	Method	Time (min)	Temperature (°C)	ρ (g/cm^3)	Porosity (%)	Density (%)
(Ni-Zn) ferrite	HC	120	1250	5,0125	12	87,9
	HC	120	1200	5,0887	11	89,3
	MW(E)	10	1100	5,1269	10	89,9
	MW(E)	5	800	5,2115	9	91,4

Analysing the density values and the porosity of each sample, numerous observations can be made.

_ The highest density is obtained for the sample sintered by microwave sintering at 800°C for 5 minutes. Comparing to the other samples, this value seems to be aberrant. In fact, this high density does not correspond to the very low hardness presented in the previous part. As well, as such a value can indicate that the sample is well sintered, before taking conclusions, the FESEM images will be analysed.

_Confirming the conclusions made after hardness test, the sample sintered at 1100°C for 10 minutes present a density similar to those of samples sintered by conventional sintering. At this stage, and before observation of the sample fracture by FESEM, it can be concluded that the microwave sintering at 1100°C for 10 minutes produces a similar sintering quality than conventional sintering processes.

_ Finally, it is confirmed that the conventional treatment at 1200°C is optimal. Indeed, this sample has a higher hardness and a higher density than the one sintered at 1250°C.

4.4.1. (Ni-Zn) ferrite + $BaTiO_3$

Similarly to the table presenting the densities of (Ni-Zn) ferrite, all the densities measured for the samples of the composite are sorted by increasing densities and presented in table 9. In this table, the sample sintered with the help of a susceptor can be compared to the samples sintered by conventional sintering.

Considering the values presented in the table 9, several observations can be made:

_ The sample sintered by microwave sintering present the approximately the same density than the sample sintered for an hour at 1200°C. As a reminder, the harness of this sample was the highest considering conventional sintering.

_ Comparing the density of the two samples sintered at 1200°C, it appears that a duration of two hours implies a reduction of the density. An increase of the sintering time is then useless and nefarious for the mechanical properties.

Table 9: Density measurements for (Ni-Zn) ferrite/$BaTiO_3$ composite samples.

Sample	Method	Time (min)	Temperature (°C)	ρ (g/cm^3)	Porosity (%)	Density (%)
(Ni-Zn) ferrite + $BaTiO_3$	HC	60	1100	4,0774	31	71,5
	HC	120	1200	5,1729	12	90,8
	HC	60	1200	5,2747	10	92,5
	MW(E) with susceptor	15	1000	5,2830	10	92,7

4.5. Field Emission Scanning Electron Microscopy (FESEM)

In order to avoid surcharging this part with images, all FESEM images have been placed in annexes. First of all, figure 30 is composed of the (Ni-Zn) ferrite images organised by method and sorted by increasing temperature. Then, images representing the (Ni-Zn) ferrite/$BaTiO_3$ composite are presented in figure 31. In the following points will be analysed separately each material. In both cases, the influence of the temperature, the influence of the duration will be analysed. Finally, answering the previous statement, the comparison between the two sintering method will be made.

4.5.1. (Ni-Zn) ferrite

Observing images from figure 30, various observations can be made. First of all, considering the samples sintered by microwave sintering at 800°C and 900°C and the sample sintered by conventional sintering at 1150°C, it is confirmed that the sintering of theses samples was not sufficient. Indeed, the fracture analyse shows the loosening of entire grains instead of a fracture of these grains. This behaviour is a direct consequence of a poor grain cohesion. Finally, by comparing the grains size of the different samples, it appears that the sintering process of these three samples is still at an early stage. Indeed, the size of the grains is way smaller in their case.

Concerning the samples sintered by conventional sintering at 1200°C and 1250°C, and the sample sintered by microwave sintering at 1100°C, all three sample are confirmed to be well sintered. First, the fracture of the grains is clearly visible, and no loosening is observed consequently, the cohesion of the grains is ensured. Then, observing the porosity, the open porosity is low and appears to be similar in the three cases. However, the presence of closed porosity is confirmed for the three samples and particularly for the sample sintered by microwave sintering. In this case, the density measured is lower than the real density and the sintering is not achieved.

Finally, a comparison of the grain size of the well sintered samples (MW(E)-1100°C; CS-1200°C; CS-1250°C) indicates even at an advanced sintering stage, the grain size is smaller for samples sintered by microwave sintering.

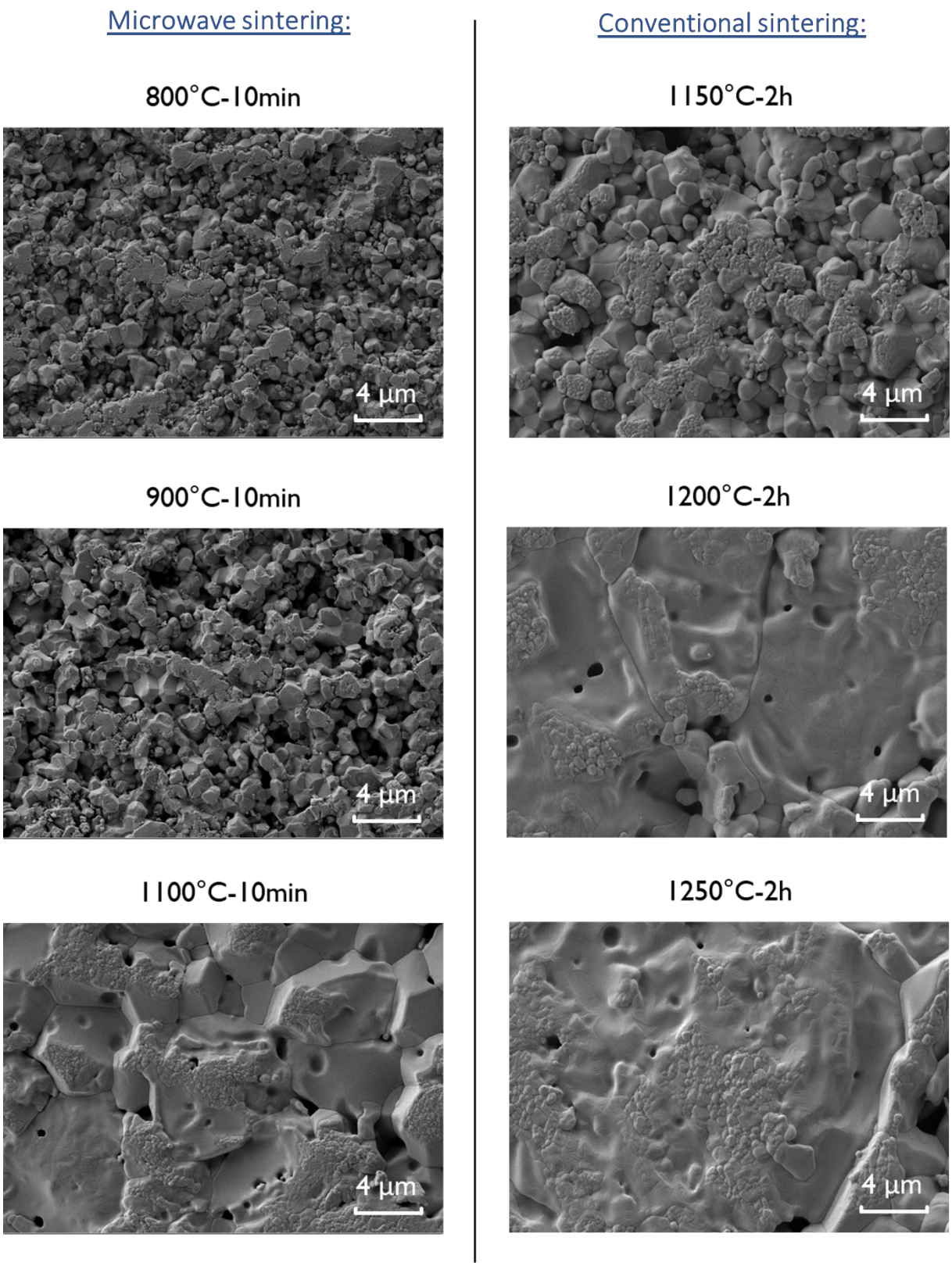

Figure 30: Influence of the temperature on (Ni-Zn) ferrite samples.

4.5.2. (Ni-Zn) ferrite/$BaTiO_3$

In figure 31, similarly to the previous analysis, the sample sintered at 1100°C for 1h appears to be not enough sintered. As the samples of (Ni-Zn) ferrite sintered at 800°C and 900°C, the loosening of grains is visible and is a witness of the poor cohesion between the grains. Observing now the sample sintered a 1200°C for an hour, the grains coalescence is visible. A remaining porosity is visible but very few loosening is observed. Consequently, the observation of the FESEM images is coherent with the hardness measured. Finally, on the images from the sample sintered for two hours at 1200°C, it is possible to observe the orientation of the grains and confirms the sintering of the sample. Nevertheless, the important loosening present in this image confirms the statements made on the hardness analysis and density analysis: the increase of sintering time reduces the quality of the sintering.

Finally, the observation of the sample sintered by microwave sintering indicates that the parameters enable to obtain a structure similar to the one obtained by conventional sintering (grain size and porosity).

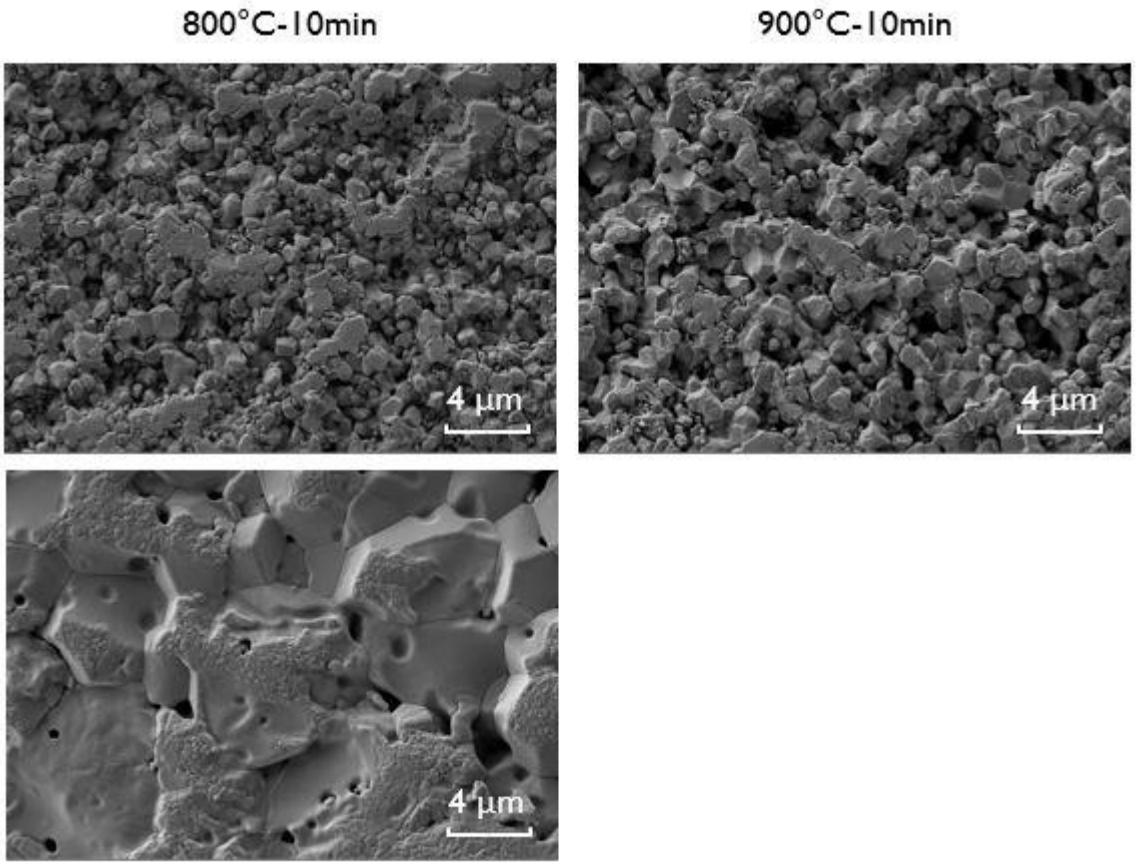

Figure 31:Influence of the temperature on (Ni-Zn) ferrite/$BaTiO_3$ samples.

CHAPTER 5: Conclusion

The objectives of this project where numerous. First, the main objective was the sintering of the (Ni-Zn) ferrite/$BaTiO_3$ composite using single mode electric and magnetic microwaves. Concerning the use of the magnetic microwave, this study was also the opportunity to determinate if such a microwave can be suitable for this application. Considering now the global objective of this project, the point was to highlight the possibilities of this method and to determinate the sintering parameters adequate for the microwave sintering of the two materials. Also, faced to a difficulty to sinter the composite material, a part of the study was focused on the microwave sintering of the (Ni-Zn) ferrite that composes the composite. Thus, several samples where produced for different sintering parameters by microwave sintering. In parallel conventional sintering have been used for to compare the sintering quality obtained by the two methods. Finally, as a necessary step in the microwave sintering of these complex materials, the last objective was the understanding of the mechanisms involved in both electric and magnetic microwave sintering.

As an important point, this study was also the opportunity to determinate if a magnetic microwave can be suitable for this application. Belonging to this first objective, an important part of this study has been focused on the microwave sintering of the (Ni-Zn) ferrite that composes the composite. Indeed, in this part, the key point was to observe the possibilities of the microwave method. To do so, the samples produced were characterised and compared to samples sintered by conventional sintering with different time and temperature parameters.

Concerning the sinter ability of the composite, the use of the magnetic microwave was a total failure. Indeed, the analyse of the different attempts revealed a brutal change in the material behaviour around 400°C. Consequently, the control of the heating rate was impossible and, in all cases, the result was a break or a fusion of the sample. To solve this problem, the use of a susceptor was tested. Unfortunately, this method appeared ineffective with this microwave.

If the use of the magnetic microwave was a failure, the electric microwave sintering of the composite confirmed the very instable behaviour of the material. Several attempts have been necessary to sinter the material but finally the characterization of the samples obtained was encouraging. Indeed, the different characterization methods used confirmed that microwave sintering enables to obtain similar densities and hardness than conventional sintering at lower temperatures and for durations four times shorter. In order to stabilize the heating rate, the use of a SiC susceptor was effective.

Considering now the microwave sintering of the (Ni-Zn) ferrite, the influence of the temperature has been tested. After a characterization of the samples and a comparison with samples obtained by conventional sintering, it is concluded that the microwave sintering enables to sinter at lower temperatures and for sintering more than 10 times shorter. Finally, if the sintering temperatures can be decreased, the characterization has shown that a minimum of 1000°C (instead of 1200°C by conventional sintering) is still required.

To sum up, this study confirms the potential of microwave sintering. In the case of the electric microwaves, the two materials were successfully sintered, and the characterization confirmed the quality of the sintering and the advantages of microwave sintering. Concerning now the magnetic microwave, the failures have highlighted the need of further studies.

In the continuation of this project, several development or improvements are possible. First of all, the finding of adequate susceptors for magnetic microwave sintering is a key step in the development of

this method. As well, the improvement of the equipment would enable a better control. For example, a possibility to follow the evolution of the magnetic properties of the material during the process would give precious information.

CHAPTER 6: Budget

6.1. Laboratory equipment investment

In table 10 is presented the different prices of the laboratory equipments. In a laboratory, such equipments are used and amortize during several years. Thus, it is possible to consider that a part of these equipments is already amortized. Consequently, the total cost of these equipment is a necessary investment made by the laboratory.

Table 10:Price laboratory equipments

	Quantity	Unit price (€)
Wire cutting saw **Stamping machine** **Polishing machine with discs**	1	63000
Micro hardness equipment	1	22900
Conventional oven	1	28000
Microwave	2	50000
Precision scale	1	400
Magnetic hotplate	1	325
Total		214625 €

6.2. Estimation of costs

6.2.1. Energy

Table 11: Energy consummed

	Power (W)	Hours of utilization (h)	Quantity (Wh)
Wire cutting saw	750	8	6000
Stamping machine	1000	2	2000
Polishing machine	570	10	5700
Micro hardness equipment	150	10	1500
Conventional oven	4500	10	45000
Microwave	800	30	24000
Precision scale	15,5	2	31
Magnetic hotplate	1020	1	1020
Total			85251 Wh

Table 12: Energetic costs

	Quantity	Price per unit	Cost (€)
kWh	85,251	0,21	17,90

6.2.1. Equipment

Table 13:Consummable costs

	quantity	Price per unit	Price (€)
Polishing discs	7	200	1400
latex gloves box	1	4,39	4,39
spatula	1	2,89	2,89
Quartz tube	2	30	60
metallic pliers	1	2,55	2,55
Total			1469,83 €

6.2.2. Characterization costs

Table 14:characterization costs

	Number of hours (h)	Price per hour (€/h)	Cost
FESEM	10	20	200
XRD	10	8	80
Total			280 €

6.2.3. Material costs

Table 15: Material costs

	Quantity (kg)	Price per kg (€/kg)	Cost
BaTiO3/(Ni-Zn) ferrite	1	99,84	99,84
(Ni-Zn) ferrite	1	120,90	120,9
Total			220,74 €

6.2.4. Labor costs

Table 16: Labor costs

	Number of hours (h)	Price per hour (€/h)	Price (€)
Project director	50	24	1200
Total			1200€

6.3. Total of the costs

Table 17: Costs' total

	Cost (€)
Energy consummed	19,17
Labor	1200
Material	220,74
Characterization	280
Small equipment	1469,83
Total	**3183,74 €**

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