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MICROWAVE SINTERING OF MgO-TiO₂ COMPOSITE: CHARACTERIZATION AND COMPARATION WITH CONVENTIONAL PROCESSING

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ABSTRACT, RESUMEN, RESUM

Abstract:

Microwave sintering has emerged as a potentially promising low-energy technique for materials science research. Based on the interaction of microwaves with matter, it offers unlimited possibilities for rapid synthesis and sintering of micro- and nanostructured ceramics. There are two main reasons why microwave consolidation of materials can improve their final properties, especially in the case of ceramic nanopowders; being a fast-heating technique - it controls the growth of grain size and homogeneity of the microstructure - which significantly differs from other types of sintering. Therefore, this technique opens up the possibility of achieving advanced ceramic materials with a combination of exceptional structural and functional properties adapted at all times to an increasingly sophisticated technological market.

In this work, the different sintering processes, conventional and non-conventional, of MgO-TiO₂ composite materials will be compared. Regarding the microwave method, the influence of the electric field and the heating parameters will be studied: such as heating/cooling rate, final temperature, dwell time, applied power and dielectric properties vs. temperature. Once the densified materials have been obtained, their final properties will be studied in order to determine their technological application.

For this purpose, the density will be determined by the Archimedes method, (studying the internal and external porosity), the mechanical properties such as hardness and fracture toughness and, finally, a phase study will be carried out by X-ray technique and a microstructural study by scanning electrical microscopy. Finally, the results will be discussed and correlated with each other and the final conclusions of the work will be drawn.

Keywords : Microwave sintering, nanoindentation, dielectric properties, MgO-TiO₂

Resumen:

La sinterización por microondas se ha convertido en una técnica potencialmente prometedora de bajo consumo energético para la investigación en ciencia de los materiales. Basada en la interacción de las microondas con la materia, ofrece posibilidades ilimitadas para una rápida síntesis y sinterización de cerámicas micro y nanoestructuradas. Hay dos razones principales por las que la consolidación de materiales por microondas permite mejorar las propiedades finales de estos, especialmente en el caso de los nanopulvos cerámicos; al tratarse de una técnica de calentamiento rápido - controla el crecimiento del tamaño de grano y la homogeneidad de la microestructura - lo cual difiere mucho de otros tipos de sinterizado. Por lo tanto, esta técnica abre la posibilidad de conseguir materiales cerámicos avanzados con una combinación de propiedades estructurales y funcionales excepcionales adaptadas en todo momento a un mercado tecnológico cada vez más sofisticado.

En este trabajo se compararán los diferentes procesos de sinterización, convencional y no-convencional, de materiales compuesto de MgO-TiO₂. En cuanto al método de microondas, se estudiará la influencia del campo eléctrico y los parámetros de calentamiento: como es la rampa de calentamiento/enfriamiento, temperatura final, tiempo de permanencia, potencia aplicada y propiedades dieléctricas vs. temperatura. Una vez obtenidos los materiales densificados, se procederá a estudiar sus propiedades finales para poder determinar su aplicación tecnológica.

Para ello, se determinará la densidad mediante el método de Arquímedes, (estudiando la porosidad interna y externa), las propiedades mecánicas como la dureza y tenacidad y, por último, se hará un estudio de fases mediante la técnica de rayos X y un estudio microestructural mediante microscopía eléctrica de barrido. Finalmente se discutirán los resultados y se correlacionaran entre ellos extrayendo las conclusiones finales del trabajo.

Palabras clave : Sinterización por microondas, nanoindentación, propiedad dieléctricas, MgO-TiO₂

Resum:

La sinterització per microones s'ha convertit en una tècnica potencialment prometedora de baix consum energètic per a la investigació en ciència dels materials. Basada en la interacció de les microones amb la matèria, ofereix possibilitats il·limitades per a una ràpida síntesi i sinterització de ceràmiques micro i nanoestructurades. Hi ha dues raons principals per les quals la consolidació de materials per microones permet millorar les propietats finals d'aquests, especialment en el cas dels nanopolvos ceràmics; en tractar-se d'una tècnica de calfament ràpid - controla el creixement de la grandària de gra i l'homogeneïtat de la microestructura - la qual cosa difereix molt d'altres tipus de sinterització. Per tant, aquesta tècnica obri la possibilitat d'aconseguir materials ceràmics avançats amb una combinació de propietats estructurals i funcionals excepcionals adaptades en tot moment a un mercat tecnològic cada vegada més sofisticat.

En aquest treball es compararan els diferents processos de sinterització, convencional i no-convencional, de materials compost de MgO-TiO_2 . Quant al mètode de microones, s'estudiarà la influència del camp elèctric i els paràmetres de calfament: com és la rampa de calfament/refredament, temperatura final, temps de permanència, potència aplicada i propietats dielèctriques vs. temperatura. Una vegada obtinguts els materials densificats, es procedirà a estudiar les seues propietats finals per a poder determinar la seua aplicació tecnològica.

Per a això, es determinarà la densitat mitjançant el mètode d'Arquimedes, (estudiant la porositat interna i externa), les propietats mecàniques com la duresa i tenacitat i, finalment, es farà un estudi de fases mitjançant la tècnica de raigs X i un estudi microestructural mitjançant microscòpia elèctrica d'escombratge. Finalment es discutiran els resultats i es correlacionaren entre ells extraient les conclusions finals del treball.

Paraules clau : Sinterització per microones, nanoindentació, propietats dielèctriques, MgO-TiO_2

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INTRODUCTION

A. OBJECTIVES OF THE PROJECT

Through the recent years, microwave sintering has been developed as a new way to sinter materials like ceramic to obtain significant advantages compared to conventional sintering. The volumetric heating provided by this method gives enormous potential to fasten the operation and improve the production rate as well as the material quality. This innovative mechanism is a great hope to save energy and time to reduce environmental impact of technical materials processing.

In this work will be compared the different sintering processes of MgO-TiO₂. Regarding the microwave method, the influence of magnetic rather than electric field will be studied. For this purpose, repercussions of different parameters such as density/porosity on mechanical and electrical properties will be examined. As well, the relation between microstructures and those properties need to be discussed.

Powders characterization regarding size and compaction methods need to be taken into account. About the sintering parameters, time and heating rates will be the two major focuses of study. Finally the biggest part of the project would be to determine microstructures, mechanical and electrical properties by X-Ray Diffraction and Electronic Microscope (FESEM).

B. WORKPLAN

To obtain results for this subject, different microwaves sintering parameters will be studied. By sintering several samples with different sintering times, temperatures, in an electric or magnetic field, it is possible to study effect of each parameters on materials properties. To acquire sintered pieces, it requires to perform those following steps :

- Characteristics of powders need to be determined. Size of powders and its distribution are linked to a homogenous compaction so on properties. Uniaxial
- As well, density after sintering is measured to estimate the quality of the process and porosity of the samples.
- Regarding the sintering process itself, the main objective is to achieve the sintering of this material with different parameters. Thus it is possible to differ temperature and heating rates to obtain the wanted microstructures.

Multiple characterization processes will be put through on samples once they are sintered. Mechanical and microstructure characterization will be done on every sample.

- Hardness and micro-indentation tests will be provided in order to determinate mechanical properties such as elastic modulus and toughness.
- As said before, density and porosity by Archimedes method
- To determine microstructure formed through the process, X-Ray Diffraction will be used at different temperatures to observe apparition of phases.
- FESEM will be used to determine grain sizes and porosity.

2. STATE OF THE ART

A. SINTERING

Sintering is a process of densification of raw material in powder form into a solid product in the desired shape and structure. In the case of forming ceramics, the melting temperature is far too high to expect to form materials only by melting and cooling raw material. In a sintering process, densification is carried out at a temperature below the melting temperature. Therefore, it is not necessary to go through a liquid phase to bind the components, where the growth of grains and bridges between them is mainly done by diffusion. This process allows to obtain the desired compositions, phases and microstructures. However, there are several densification methods that allow the parts to be heated by different mechanisms: Spark Plasma, Furnace and Microwaves sintering. In this paper, the two last methods will be studied.

The sintering of powders in solid phase is carried out using several mechanisms [1, 2] from different parts of the grains:

- Material at the grain surface (b) or grain boundaries (c) moves along the surface by diffusion to reach the neck of the chemical bridge that is about to form. For material at the surface, it can also move by evaporation (a) before condensing at the neck.
- Intragranular lattice diffusion (d, e, f) is possible with several defect origins: vacancies, grain boundaries and dislocations.

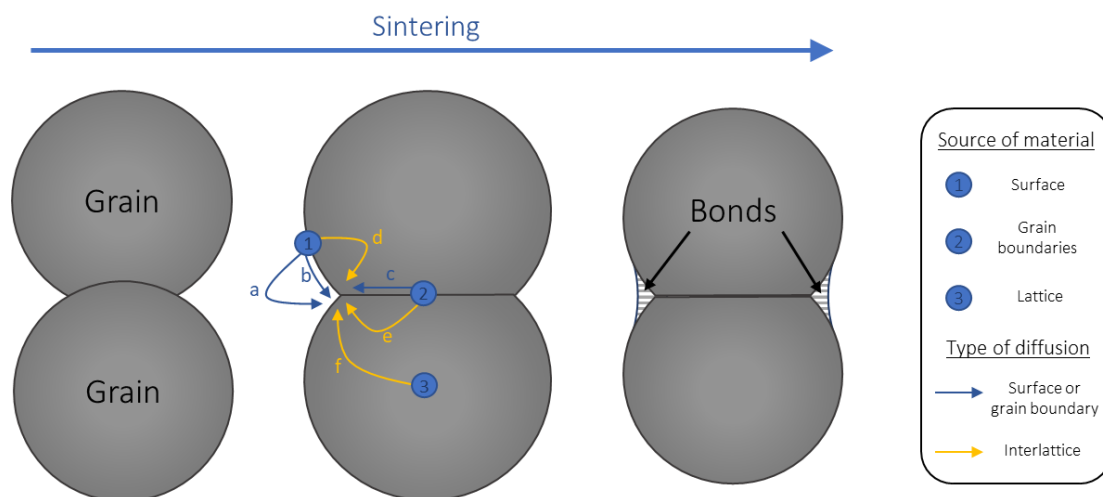


Figure 1 - Formation of bonds between grains during sintering with different mechanisms.

All these mechanisms participate in the formation of chemical bridges and the modification of the pore shape, but not all of them are involved in the densification of the material. The mechanisms that contribute most to the densification are the mechanisms of material diffusion from the grain boundaries (c) [1].

I. CONVENTIONAL SINTERING

Because of the high melting point of its components, the conventional approach to form ceramic materials is delicate and expensive. Forming parts by fusion and casting isn't adapted; plastic deformation at low temperature is impossible and still complex at high temperature. Thus, it is necessary to elaborate ceramic materials from powders. There is a wide variety of kilns for firing ceramics. Smaller furnaces, such as laboratory ovens, are powered electrically. Induction furnaces are also sometimes used in laboratories and industry, but they remain marginal because of the difficulties of controlling thermal cycles. In industry field, furnaces are most often gas-fired and do not rise above 1600 °C.

1. GENERALITIES

Once raw material is crushed and grounded, and when composition and granulometry are controlled, a certain amount of powder is pressed to reduce porosity and form the wanted shape. Powder pressing revolutionized the production of plates in the 1980s, using so-called isostatic pressing machines. The ceramic raw material must have no moisture, only small amounts of binders and plasticizers, and is usually in powder form, which is injected into a mold. High-pressure pressing is also used on a small scale, in the laboratory or for the manufacture of small series and simple geometries, using steel molds in which the powders, free of moisture and additives, are subjected to pressures of over 100 bar by hydraulic cylinders. This is sufficient to give a certain coherence to the raw parts, knowing that demolding is not always easy. The technique for pressing can be chosen regarding the production rate or the porosity quality wanted. It is very important to prepare a dense green part to obtain a ceramic part with good properties; a variation of the density within the part induces a difference of shrinkage and then a deformation of the part. Some additives can be incorporated in the green part to improve cohesion and agglomeration during the sintering process. The management of raw materials is not simple, as the natural products used are often very sensitive to humidity [2].

The two main objectives of a sintering process are to reduce porosity and consolidate bonds between particles. It is a densification process without going through fusion, even if a reactive liquid phase can exist during the heating. Sintering processes eliminates all or part of the interstices initially present between the grains of the raw -not yet cooked and simply shaped- product. The part is said to be densified; the densification can be as high as 100% if all the porosity contained in the in the raw product is eliminated. The final properties of the ceramic part depend on atomic structure of component (ionocovalent bonds) and on the crystalline microstructure; size grain and its shape, porosity, intergranular phases.

The need for grinding stems from the fact that, at the time of curing, the grains of powder "weld" together and the ceramic parts become denser all the more easily as the grains of the starting powders are smaller. At the same time as the grains weld together in this way they grow by displacement of the grain boundaries: the larger grains tend to absorb the smaller ones and become larger and larger. The larger the grains, the more mechanically brittle the parts, as cracks propagate along the grain boundaries, which are more brittle, and rarely through the grains. In addition, the exaggerated coarsening of polygonal grains causes the reappearance of intergranular porosity, which is often unwanted. Reducing the size of the grains is one of the main ways to limit the temperature of

the firing stage or its duration, and/or to reduce the porosity of the parts obtained. It is also sometimes interesting to mix together large and small grains: when shaping, the small grains can be lodged in the interstices of the large ones, which reduces the gap between the grains and limits the shrinkage during sintering. This use of a "staggered grain size" is practiced in particular in the preparation of certain refractors like those used in this study. In fact, the problem is very complex because, depending on the morphology of the grains and the nature of the raw materials, the firing behavior is different.

Particles will minimize their total surface energy by creating bonds with the other particles and ignite densification of the part. The higher specific surface the higher is its reactivity, and the temperature is the parameter that activates diffusion processes.

2. THERMODYNAMICAL ASPECTS AND KINETIC PARAMETERS

The single grain has a lower specific surface area (surface area per unit mass) than the dispersed system. This decrease in surface area corresponds to a decrease in energy. This surface tension is the amount of energy that the system gives back to the outside when its surface area decreases. A massive system is more stable than a dispersed system. To lower its surface energy, a dispersed system can move in two directions:

- Decrease in the overall area of the solid-gas interfaces by decrease in the number of grains, which corresponds to an average grain size called Ostwald ripening.
- Decrease in the area of the solid-gas interfaces (highly energetic) in favor of the solid-solid interfaces (less energetic) by the welding of the grains. This welding leads to an increase in the cohesion of the material, which is called sintering.

The grain boundaries formed still represent an excess of energy that the system can eliminate by making the grains grow larger by moving the grain boundaries. To reach the theoretical density, two paths can be considered: one in which the grains weld together and then densify and grow, and another in which the grains grow and then weld and densify. This second path is unlikely doable from a kinetic point of view because the rate of densification decreases very quickly as the size of the grains increases. Although they have the same origin, densification and grain size increase appear to be two competing processes from the point of view of part development. Wherever possible, the former should be favored over the latter.

The pressure difference between the internal pressure of the solid and the pressure at the surface of the grain engages the diffusion of material to create a physical bond between the grains. This positive difference for the internal pressure reflects the existence of compression forces acting at the surface, and has the temperature increase as origin. This force is called vapor pressure due to the method of material diffusion to the bonds. By regulating temperature, heating rate and time, the densification of the material can continue until reaching the full density.

II. MICROWAVES SINTERING

Since the beginning of the 80s, numerous papers have shown that most of ceramic powders could be heated and sintered by microwave energy providing thinner microstructures. This uniform way to heat raw powder of ceramic materials can facilitate sintering processes by providing energy within the piece.

1. WAVE PROPAGATION AND INTERACTION WITH MATTER

Microwaves are electromagnetic waves with frequencies ranging between 300MHz and 300GHz corresponding to wavelengths between 1m to 1mm. In this portion of electromagnetic spectrum, some frequencies are used in modern technology such as radio astronomy, spectroscopy, communication relays and wireless networks, but also in other non-communication uses such as medical applications for cancer treatment. For heating applications such as food cooking and materials curing, dielectric absorption mechanisms are used to provide thermal energy in matter, mostly at 2.45 GHz for its high electric conversion rate and its penetration depth which is sufficient to have multiple heating applications. Guided propagation of electromagnetic waves used in microwaves ovens is described by Maxwell formulas [3].

When a material is exposed to microwave radiation, it occurs with 3 types of interaction:

- If the material is a metal, free charges will distribute themselves within the solid and particularly at its surface so that the incident wave is reflected. In this situation, penetration depth is very low ($< \mu\text{m}$) so heating matter is very complicated if not impossible.
- For glasses materials, they are relatively transparent to microwave energy, wavelengths being too large to interact with their microstructures.
- Such as ceramic powders, some dielectric materials absorb microwaves radiation and dissipate it in heat thanks to their dielectric properties. Polarization concerning ions and dipoles induce heating through. Those heating mechanisms will be explained in the next part.

All materials share a part of each those 3 behaviors regarding microwaves interaction. The frequency of the wave has a major role in the heating mechanisms.

2. HEATING MECHANISMS AND THEORETICAL ASPECTS

The microwave heating mechanism is linked to an electric polarization phenomenon in an alternative field. Dielectric constants of the material make the most pertinent property to anticipate its aptitude to be heated by microwaves. The heating is volumetric and the penetration depth is about centimeters. This property comes with high heating rates thanks to high and privileged interaction between wave and matter, leading to a reduction of sintering temperatures, times and energy consumption as well as an augmentation of density.

The constant ϵ^* is the complex dielectric permittivity of the medium which is expressed as a function of its real ϵ' and imaginary parts ϵ'' . Respectively dielectric constant and loss factor, these properties are used to calculate the loss tangent (Equation 1), which is a term that rely the ability of a material to polarize and heat by its own. The dielectric constant is the amount of electric energy that can be stored within the heated material. The loss factor describes the ability of the material to dissipate microwave energy into heat [1].

$$\frac{\epsilon'}{\epsilon''} = \tan \delta \quad (1)$$

These two parameters depends on temperature, and with the frequency of the electric field that plays a major role in the polarization mechanism [1], the absorbed power (Equation 2) of the sintered material can be calculated [4].

$$P = \sigma |E|^2 = 2\pi f \epsilon_0 \epsilon_r' \tan \delta |E|^2 \quad (2)$$

For dielectrics, the depth of wave penetration (Equation 3) is inversely proportional to the frequency and the loss factor $\tan(\delta)$. It is then understood that the electric field will easily penetrate within an electrical insulator while it will be more quickly attenuated by a semiconductor material [5]. To put the orders of magnitude into perspective at 2.45 GHz at room temperature, this depth is of the order of a few tens of centimeters to few millimeters depending on the materials. These remarks are to be put in perspective with the strong temperature dependence of the loss factor. It generally increases significantly with temperature, which means that a material that is transparent at room temperature can become absorbent above a critical temperature. These elements are all the more important to consider as the sintering of ceramics is performed at high temperature.

$$D = \frac{3\pi_0}{8.686\pi \tan \theta \left(\frac{\epsilon'}{\epsilon_0}\right)^{1/2}} = \frac{c}{2\pi f \sqrt{2\epsilon'}(1 + \tan^2 \theta - 1)^{1/4}} \quad (3)$$

Knowing that the heating mechanism results from the movement of electrically charged species in solids, it appears important to understand these microwave/material interactions by evaluating the dielectric properties of solids subjected to microwave frequencies, and this, if possible, as a function of temperature. The microwave heating mechanism is linked to an electrical polarization phenomenon in the alternating regime; the complex dielectric constant of the material is therefore the most relevant physical property to anticipate its suitability for microwave heating. The transfer of energy within the part is generally done in its volume, at least in the case of electrical insulators: the depth of penetration of the wave is then of the order of a few centimeters. This process is therefore frequently referred to as “volume heating”. The challenge of sintering materials by microwaves radiation is to heat uniformly the part in all its volume [6, 7, 8]. Compared to conventional sintering process, the core and the surface will not share the same profile (Figure 2) of temperature during sintering and produce different shrinkage in the part leading to its rupture. In order to prevent this problem, some susceptors sensible to microwaves radiation can help to heat the surface of the part [4, 9]. Some hybrid routes [6, 10] that use conventional and microwave sintering allow the part to heat uniformly but this way will not be investigated in this study.

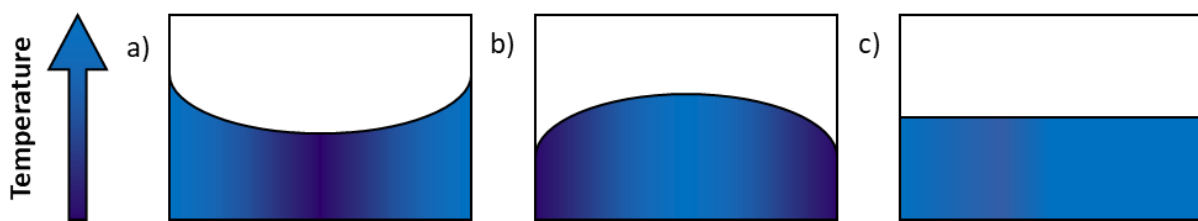


Figure 2 – Temperature profile within the sample in: (a) conventional heating, (b) microwave heating and (c) microwave hybrid.

This property is also accompanied by high heating rates (> 200 °C/min), which result from a privileged interaction between the material and the microwave radiation. Only the part and its immediate environment are heated, which results in a significant gain in terms of energy consumption. Microwave heating would also allow to decrease sintering temperatures and/or to increase densification and thus diffusion rates of materials.

3. DESCRIPTION OF THE MICROWAVE

The description of the global microwave heating system is detailed in the literature of the previous studies in UPV laboratories [3, 11, 12, 13, 14]. All components that are part of a microwave system is given with details and their function. The oven used for this study will be described later in this paper (3.c.iii).

B. MATERIALS STUDIED

Magnesium oxide MgO also called magnesia is a ionic crystal with a density of 3.5 g/cm^3 and a temperature of fusion of 2800°C . It is obtained by decarbonation of magnesium titanate and can be used as pigments or refractors depending on the temperature of the process. Its high melting point and its chemical stability deliver good properties for industrial applications as insulators [15].

Titanium dioxide TiO_2 is also used as pigment in paintings, for production of electrodes, capacitors, solar cells and for photocatalyst [16, 17]. This semiconductor powder offers UV-active catalyst and can be sintered with different nanometric shapes such as tubes and rods. It can then be used to dope metal and non-metal material for photocatalyst activities.

The mix of these two powders lead to the sintering of multiple phases depending on the molar ratio of MgO- TiO_2 . Magnesium Titanate MgTiO_3 carries excellent dielectric properties which allow microwaves to perform heating with its high permittivity and low loss tangent; however, some reductions of quality factor have been found for this material [18, 19, 20, 21] compared to other materials used for these same applications. The sintering of this materials can lead to several electric applications such as capacitors, but pure magnesium titanate without any additional phases such as MgTi_2O_5 or Mg_2TiO_4 seems highly difficult to obtain by solid state reaction [20]. These unwanted phases promote shrinkage processes within the part and induce changes in the final dielectric properties.

Multiple additions in MgTiO_3 -based ceramics have been tested in several papers [20, 22] to engage cation substitution to help diffusion in the material. Inclusion of Zn, Sn and/or Al are possible but few reports are available [16].

Thanks to its environmentally friendly and economically low cost, pure MgO- TiO_2 mix has been sintered by different method to obtain magnesium titanate : sol-gel reaction [20], calcination by solid suspensions [20], post-sintering with HIP [23], flame synthesis [16]. Although, no paper about sintering of pure MgO- TiO_2 ceramic parts by microwave heating have been found.

Once the MgO- TiO_2 mix is sintered, this ceramic material is used as microwave filters [21] and oscillators [24], insulating material [23], water treatment [24] but more importantly in electric capacitors thanks to its dielectric properties.

3. METHOD AND EQUIPMENT

A. MATERIALS

I. AT AND UT POWDERS

The materials used in this study were commercial MgO (Wenzhou JingCheng chemical Co. Ltd, Japan) powders with the purity over 99% and two different grain size $<1\ \mu\text{m}$ and $\geq 5\ \mu\text{m}$. These prepared compositions with 50 wt% MgO and 50 wt% TiO₂ are labelled as *at* and *ut*, respectively. The powder mixtures were prepared by high-energy attrition milling (Union Process, USA) using alumina media of 2 mm diameter was done at 400 rpm and milling times of 1 hour. The starting powders were dispersed in ethanol (Panreac Quimica). The ball-to-powder ratio was 4/1. After milling, the resultant slurry was dried at 60 °C and the dried powder was sieved under 63 μm .

II. DOPAJE POWDER

Commercial MgO (Wenzhou JingCheng chemical Co. Ltd, Japan) powder with the purity over 99% and grain size $<1\ \mu\text{m}$ a nanosized anatase-TiO₂ synthesized following by colloidal sol-gel route were used as starting powders. The synthesis of TiO₂ was performed by dropwise addition of Ti (IV)-isopropoxide (97%, Sigma-Aldrich, Germany) on deionized water (18.2 M Ω -cm⁻¹, ultrapure Milli-Q) with a water/alkoxide molar ratio of 50/1. HNO₃ (65%, PANREAC, Spain) was utilized as a catalyst in a molar ratio of $\text{H}^+/\text{Ti}_4^+ = 0.2$. The synthesis was performed under constant stirring at a temperature of 50 °C in closed flask to prevent evaporation and maintained at these conditions for 24 h. At these conditions it was assured that peptization process was complete and the average particle size of the resulting suspension was 20-30 nm, as measured by dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern S, Worcestershire, U.K). This nanoparticulate suspension was frozen using a rotary evaporator (RV10 basic, IKA, Germany) immersed in a liquid-N₂ bath, and subsequently freeze-dried (Cryodos-50, Telstar, Spain) at -50 °C and 0.3 mPa for 24 h. Suspension was dispersed using an ammonium salt of poly(acrylic acid) (Duramax D-3005, Rohm & Haas, Dow Chemicals, USA) as a deflocculant in a concentration of 1.5 wt% (on a dry solids basis). The preparation of the suspension involved the addition of freeze dried TiO₂ nanopowder on deionized water containing the deflocculant in a first step, and the subsequent addition of MgO powder maintaining mechanical stirring. Afterwards, the mixture was sonicated for 1 min using an external ice bath to prevent overheating. The solids content was maintained at 50 wt%. The final suspension was frozen and subsequently freeze dried using the same equipment and conditions as for titania solutions. The final mixture of powders was sieved using a 63- μm mesh nylon sieve before sintering.

B. SAMPLE PREPARATION

I. COMPACTION OF SAMPLES

In order to use powders in sintering processes, it is necessary to compact them in the wanted shape to fit in the different furnaces. Depending on the shape wanted, it is possible to use different methods to compact the workpiece. For microwave and conventional sintering uses, the samples need to be the more compact it can be to avoid porosity after sintering. However, some microwaves ovens can only work with given dimensions and shapes. Some characterization methods on green body just need the powder to stay compact during the process.

To do so, Cold Isostatic Pressure is used on the samples to create a spherical shape. A small inflatable balloon is poured with 0.5g of ceramic powders and closed with a knot. The bag is put in a cylinder press (Figure 3) larger than dimensions of the bag and filled with lubricant. When the pressure is applied by a uniaxial press, it is transmitted by the fluid and all around the sample. The pressure of 5kN is kept on during 2 minutes, then the bag is taken out and opened to take the compacted sample. This procedure can be used with two bags at the same time in the cylinder. Just before the sintering process, it is used to smooth the corners of the samples with sandpaper to remove all the sharpen prominences which do not work very well with microwaves because of the peak effect.



To create cylindrical shape, a mold with an uniaxial pressure machine is used. Ceramic powder is poured in a cylindrical mold press is subjected to 10 kN for 2 minutes. Two cylindrical shapes with two different dimensions are used. For the microwave oven from the other laboratory, dimensions of the green body need to be 10 mm diameter and about 5 mm height. For the measure of emissivity, dimensions are and about 2-3 mm height.

Figure 3 – CIP piston.

II. CUTTING

Once the samples are sintered, it is necessary to access to the sample's core to process some characterization. The cores of the samples are the part where the temperature is the higher during the sintering process (1.a.i.2) so this is where the most useful information will be found : quality of the sintering, phases and microstructures of the sintered material. By cutting the part, two halves with a planar section are ready for characterization. The best choice to make is to use one for destructive methods such as hardness and the other one for non-destructive ones like FESEM and DRX.



Figure 4 – Diamond disc saw cutter.

Because of the high hardness of the material, it is necessary to use diamond discs. The saw used (Figure 4) is a STRUERS Secotom-15 with 3000 rotations per minute at advance speed of 0.05 mm/s. Water is used as lubricant on the disc to avoid heating and preserve the disc and the sample integrity.

III. RESIN COATING

The samples once they are cut are very thin and complicated to manipulate to polish since they are about 4 mm wide. The resin coating is carried out by STRUERS CitoPress-1 with about 20 g of a transparent phenolic resin BUEHLER TransOptic. This quantity corresponds to the yellow spoon given with the powder and will synthesize a 2 cm height sample to fit in the polishing machine. The sample is placed at the bottom of the mold and recovered with about 15 g of phenolic powder.

A description of the sample is written on a small paper and placed on the upper part of the sample, then recovered with the rest of the powder. The mold is closed with a piston lubricated with a ZnO powder. The system is poured with powder and the sample is heated at 180°C during 7 minutes under a pressure of 15 kN and then cooled down during 7 minutes.

IV. POLISHING

After resin coating, the samples are ready to be polished. The dimensions of the resin coating machine correspond to the needed ones for STRUERS LaboPol-5 (Figure 5). Many polishing discs with different grain sizes are used, with different rotation speeds, forces, lubricants and times. In a first time, disc with lapping between 75 μm and 10 μm with distilled water as lubricant, 10 N force, 100 rpm during 1 minute each. In a second time, textile discs are used with grain size of 6, 3 and 1 μm with a STRUERS DP-Suspension M diamond suspensions as lubricant corresponding to the grain size, with a force of 20 N at 150 rpm during about 10 minutes each.



Figure 5 – Polishing disc.

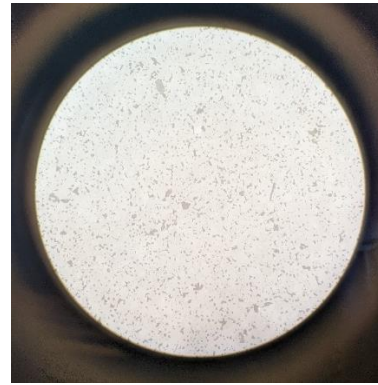


Figure 6 – Microscopic observation of a polished sample.

The polished samples are verified with an optic microscope (Figure 6) and then placed in a box padded with cotton to avoid scratching the sample surfaces.

C. FURNACES AND MICROWAVE OVENS

I. CONVENTIONAL FURNACES

In order to compare with samples sintered with microwaves ovens, multiple samples must be sintered in conventional furnaces; the principal furnace used (Figure 7) is the CARBOLITE Gero HTF 1800. All samples are put in an alumina box with a FERRO MTH Process Temperature Control Ring to determine the real temperature within the system. Multiples process temperature have been carried out during 2h with a heating rate of 10 °C/min.



Figure 7 – Conventional furnace used in this study

For the measure of the emissivity (3.d.i), the High Temperature Furnace used is a SYBRON Thermolyne Type 46100 (Figure 8).



Figure 8 – Furnace used for measuring emissivity with the pyrometer on top.

II. PYROMETER

As temperature being one of the most important parameters for sintering processes, its control during all the process by non-perturbing methods in the microwave cavity represents a priority for this study. Thus, pyrometers are chosen to measure temperature without any absorption of radiation and any contact with samples. They are placed above the furnace cavity through a hole (Figure 8), at the right distance from the sample to be focused on.

For the range of temperature between 250-1650 °C, the pyrometer Optris G5H CF2 with a spectral range of 5.0 μm is used. For situations with temperatures below 250 °C, the Optris CB3 CF3 pyrometer is used.

III. MICROWAVE OVENS

Microwave sintering have been carried out by an experimental microwave system composed of a rectangular cavity designed, optimized and build by ITACA, UPV [3, 11]. All the component of a microwave and their function are described (Table 1) and shown in a schematic view in the Figure 9.

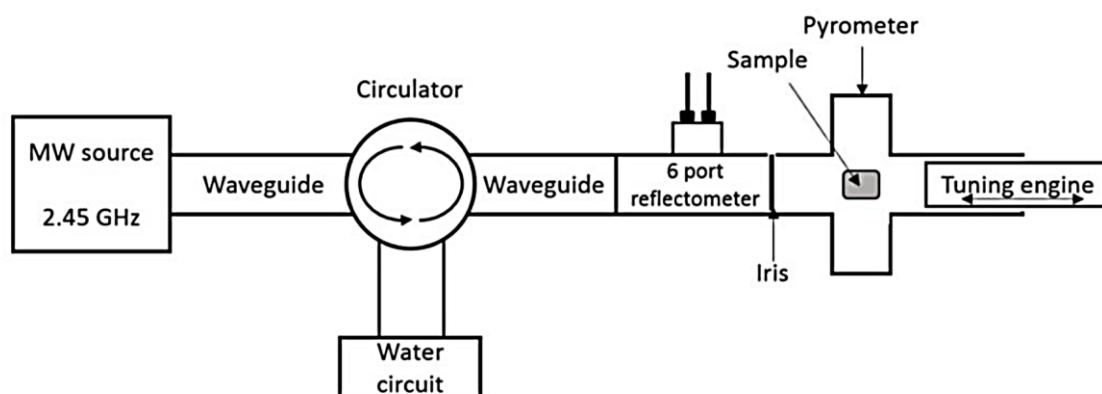


Figure 9 – Schematic view of rectangular cavity microwave oven.

The pyrometer is placed on top of the rectangular cavity (Figure 10) to get in front of the heated sample.

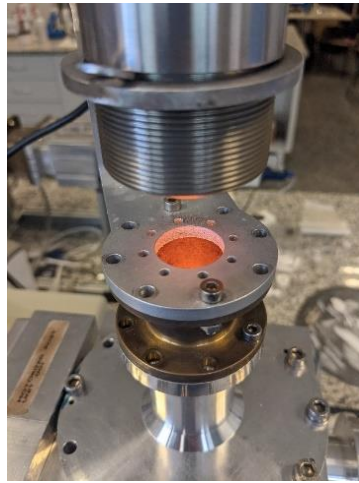


Figure 10 – Picture of the pyrometer support of the microwave oven.

Table 1 - Description of element name with their function

<i>Element name</i>	<i>Function</i>	<i>Remarks</i>
<i>Source</i>	Remotely controlled source of microwaves power	Power at 700 W and frequency at 2.45 GHz
<i>Circulator</i>	Redirection and protection of waves from the source to the cavity	Capture the non-consumed energy by heating water to prevent power source damage
<i>Reflectometer</i>	Measure the incident and reflected power in the cavity	Connected to the sintering software
<i>Iris</i>	Coupling microwave radiation entering the cavity	
<i>Cavity</i>	Rectangular-shaped box to optimize resonance of waves and prevent leakages of energy. Has multiple orifices to let the sample, the pyrometer and the tuning engine in.	86.36mm x 43.18mm with variable length of tuning engine. Has multiple orifices to let the sample, the pyrometer and the tuning engine in.
<i>Sample</i>	Placed in a microwave transparent quartz tube	Located at the top of the cavity with the pyrometer
<i>Pyrometer</i>	Measure temperature within the cavity	
<i>Tuning engine</i>	Modify the height of the sample to optimize power consumption	

D. CHARACTERIZATION EQUIPMENT

I. EMISSIVITY

Pyrometer need to be calibrated to correctly work during sintering processes. For that, the emissivity of the magnesia titanate powder need to be measured. One thing to note is that emissivity is a temperature dependent property, so it is necessary to measure this characteristic for several temperatures. A green body sample with emissivity dimensions explain in compaction methods (3.b.i) is placed in an alumina box within the oven; it is then densified from 1000°C to 1600°C with Optris G5H CF2 and from 650°C to 950°C with Optris CB3 CF3 by steps of 100°C with a heating rate of 10°C/min. At each step, the temperature stage is stabilized during 5 minutes where the emissivity is measured. Emissivity is obtained by changing parameter in the controlling box of the pyrometer until the temperature indicated fits with the temperature given by the oven.

II. DENSITY

One of the most useful properties to evaluate the quality of sintering is the density of the material from which it is possible to calculate the porosity of the sample. Starting from a powder, sintering creates physical bonds between the grains of the powder filling the pores until they disappear, the ideal situation being a fully dense material. Measuring the density in a conventional way by measuring the mass and volume is complicated because the irregular porous geometry does not allow to calculate its volume. To determine the apparent density of a porous material, must be used the Archimedes method: first measuring the wet and dry mass of the material, and then it is possible to calculate the volume of fluid contained in the sample, and thus to calculate the open porosity of the sintered part. The samples are placed in a heated beaker filled with water for 4-5 hours so that the water penetrates the pores. After letting the sample rest in the water for 24 hours, the sample is then weighed in a tared water bath SARTORIUS YDK01. Indeed, the mass of water included in the porosity of the sample realizes a buoyancy which changes the mass measured by the balance compared to the real mass, it is for this reason that the soaked mass is lower than the dry mass. Once this measurement is made, the sample is placed in an drying furnace to evacuate the water from the pores during 2 hours at 110°C, then the dry sample is weighed. The density of the material ρ is given by the formula (Equation 4).

$$\rho = \frac{m_d}{m_d - m_w} \rho_{water} \quad (4)$$

with m_d the mass of the dry sample, m_w the mass of the wet sample and ρ_{water} the density of the fluid, here water.

III. POWDER SIZE

Distribution of powder size is a material property important for a good sintering; the grains of powder must be distributed in such a way as to have two different sizes to allow the small grains to fit between the larger ones, to fill the pores. As a general rule, the powder grains should be small in size to increase the specific surface area of a given amount of material. Powder size distribution is obtained by using MALVERN Hydro 2000SM as a sample dispersion unit. After calibrating the, a very small quantity of powder is put in the disperser filled with water and the mix is agitated by an axis at 2000 rpm. For each sample, 3 measures are done.

IV. MICRO-HARDNESS, TOUGHNESS AND NANO-INDENTATION

Hardness processes are carried out on polished samples with SHIMADZU HMV-2. Ten consecutive loadings are applied on each sample with a P force of 980.7 μN and the size of each impression d left by the micro-indenter is measured. Toughness is measured with Model HD9-45 Superficial Rockwell & Vickers Optical Hardness Tester CENTAUR. For both methods, the length of the diagonals is measured with the software and the Vickers hardness is then calculated with the Evans formula (Equation 5).

$$Hv = 1.8 \left(\frac{P}{d^2} \right) \quad (5)$$

To obtain other mechanical properties of the material, Berkovich nano-indentation tests are carried out with Keysight Technology G200. Following Oliver and Pharr method discovered in 1992 [25], this characterization method allows to obtain hardness and elastic modulus by carrying a nanometric elastic-plastic deformation of the sample and coupling loading and depth of insertion [14]. The coating resin of the sample must not measure more than 1 cm to fit in the cavity. Those characterization methods have been carried out on samples from 1400 °C, twice on 1500 °C and on sample from microwave sintering that could have been coated (Table 4, Table 5). Regarding the samples sintered by microwaves, mechanical properties of both phases have been measured.

V. X-RAY DIFFRACTION

X-Rays Diffraction is a characterization method used to analyze atomic structure of solid materials by interaction of waves on atoms. When the X-Ray beam interacts with a part, the phenomenon of diffraction appears when atoms are arranged in specific microstructures. By measuring the beam's incidence angle, the microstructure of the solid, its lattice parameters and properties of phases can be calculated with Bragg's Law [3].

Samples' DRX patterns have been measured with a BRUKER AXS D5005 diffractometer on the 2θ angle range [20°;70°] for phase identification purpose. Multiple measures have been made on conventional samples through different temperatures, and on conventional and microwaves samples at final sintered state.

VI. FESEM

Field Emission Scanning Electron Microscopy will be used to observe topography of microstructure of the material within the part. Mechanisms of interaction and detection are well explained in the literature [3, 11]. Samples have to be polished, coated with Pt film and thermally attacked to unveil its grain structure and porous profile. Working with a field emission electron gun, this method allows better resolution than SEM until a spatial resolution of 1.4 nm. Once optic captures are made, it is possible to measure grains size and observe the porosity of the material.

VII. DIELECTRIC PROPERTIES

Dielectric properties were measured on a powder sample during microwave sintering in heating and cooling process steps. Measuring temperature, absorbed power, frequency of the electric field and dielectric properties, it is possible to calculate the depth penetration as function of temperature, which can be linked with the apparition of phases observed by DRX [1, 5, 26].

To sinter the powder sample, it is compacted in a cylindrical shape and is introduced in a quartz holder in a single-mode microwave cavity semblable to the one used in laboratory. In addition, the system to measure all these values must be composed of a pyrometer, a cross coupling filter and two microwave emitter/receiver. The resonant frequency and the quality factor are measure by cavity perturbation method and the contribution of magnetic field heating is not considered for two reasons explained in the literature [1].

4. RESULTS AND DISCUSSION

A. EXPERIMENTAL RESULTS

I. EMISSIVITY

The two ranges of emissivity are shown in the . A decrease is first observed until 1000 °C then an increase is observed until 1500 °C. This allows to correctly calibrate the pyrometer during the microwaves sintering processes.

Table 2 - Emissivity of MgO-TiO₂ at powder at different temperatures.

G5H CF2		CB3 CF3	
TEMPERATURE (°C)	Emissivity	TEMPERATURE (°C)	Emissivity
660	0.923	1000	0.825
700	0.935	1100	0.855
800	0.920	1200	0.877
900	0.912	1300	0.914
950	0.909	1400	0.950
		1500	0.965

A quick reminder that these emissivity measures do not represent the real emissivity of the material and can only be used for measuring the temperature in furnaces with the pyrometer that has been used for measurement.

II. POWDER SIZE

The powder size distributions of the 3 types of powders are shown in volume percent.

Table 3 - Quartiles, median and specific surface for *dopaje*, *at* and *ut* powders.

Powder	d _{0,1}	d _{0,5} (µm)	d _{0,9}	Specific surface (m ² /g)
<i>dopaje</i>	11.0	60.5	149.9	0.2
<i>at</i>	1.5	11.2	107.1	1.5
<i>ut</i>	1.7	30.5	127.8	1.2

The *dopaje* powder shows a single peak of powder size concentration around 80 µm and a median at 60.5 µm (Figure 11 a.). Having a single powder size concentration drastically reduces the specific surface area (Table 3) of this powder type, which reduces the sintering dynamic of the material. The compaction of the powders then leaves many closed pores within the green part and the total densification of the material is more complicated to achieve, leading to a loss of mechanical and dielectric properties.

The *ut* powder has a better powder size distribution, the graph (Figure 11 b.) shows two peaks at 3 and 100 µm. According to the measure carried out on the 3 tests, the distribution between the

two peaks has a slight tendency of the majority for the higher value, the median being at $30.5 \mu\text{m}$ (Table 3).

The *at* powder shows an excellent powder size distribution with a similar distribution between small and large powder grains. Indeed, the two peaks at 3 and $90 \mu\text{m}$ (Figure 11 c.) as well as the median, equal to $11.1 \mu\text{m}$ (Table 3) and located between the two orders of magnitude of the peaks, reflect a possibility of the small grains to infiltrate the interstices of the large powder grains. This property demonstrates optimal pore reduction capabilities to maximize the densification of the material during compaction and sintering.

In the case of *at* and *ut* powders, the specific surface area is much higher than that of the *dopaje* powder which has only a majority powder size (Table 3).

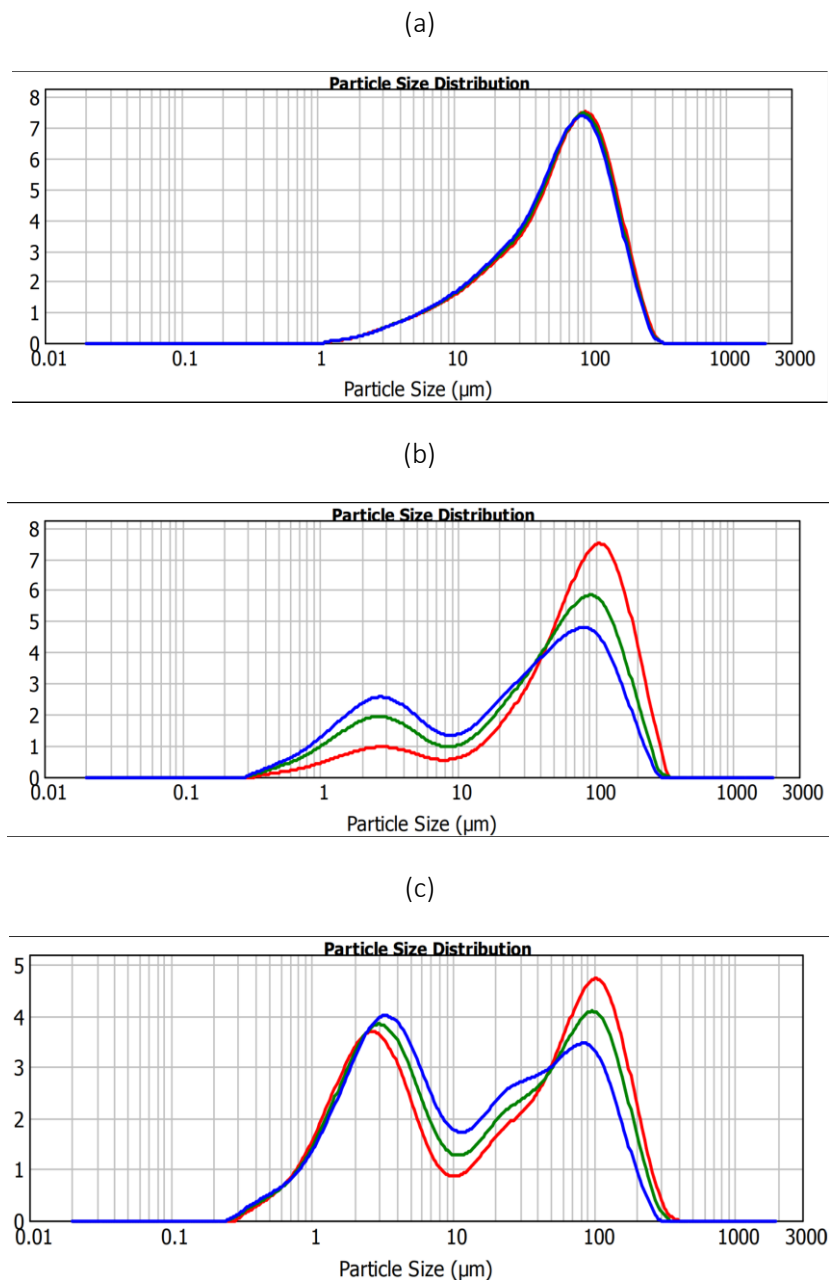


Figure 11 - Distribution of powder size for (a) *dopaje*, (b) *ut* and (c) *at*.

III. LIST OF SAMPLES

Many samples were sintered by conventional sintering and by microwave sintering. The list of samples (Table 4, Table 5) is sorted by sintering date, then the type of powder used and the measured temperatures are indicated for each sample. For conventional sintering, the temperature indicated by the PTCR is given. For microwave sintering, the presence of susceptors is indicated.

Table 4 - List of samples sintered by conventional method.

Method	Time	Powder	Oven Temp.	PTCR Temp.
CS	2h	at	1400°C	1430°C
		dopaje		
		ut	1500°C	1520°C
		dopaje		
ut				

Table 5 - List of samples sintered by microwave heating.

Method	Time	Powder	Pyrometer Temp.	Susceptor
MW	10'	at	750°C	-
		at	800°C	-
		at	850°C	SiC
		at	1000°C	-
		at	1200°C	-
		dopaje	300°C	-
		ut	1200°C	-
		ut	1000°C	-
		ut	1000°C	-
		ut	1050°C	SiC

For every sample from conventional sintering, the sample is cut in two parts that can be used for characterization since. On the other hand, samples from microwaves sintering does not offer two parts to analyze because they break themselves during the process. These problems will be discussed in the next part of this study. The samples from microwaves sintering that can be characterized are put in grey in the Table 5.

IV. SINTERING AND FAILURES

The sintering temperature of magnesia titanate powders by conventional means are taken from the literature [15, 19, 22]. The 50/50 powder mixture must sinter between 1350°C and 1450°C to allow the bonding of the powder grains. The first batch of conventional sintering is performed at 1400°C for 2 hours with a heating rate of 10°C/min. Once the heating is achieved, the samples are left to cool down to room temperature. The first output of the ceramics reveals spherical shapes identical to the green part which seem to have uniformly reduced in volume. The very whitish color of the raw powder has given way to a slightly more golden hue. Results are similar for the second batch at 1500 °C during 2 hours.

The problem of this study is to determine if microwave sintering is compatible for the mixture of Magnesium and Titanium oxide powders. No study explains microwave sintering for this material, it is then necessary to determine the ideal temperature to allow the total cohesion of the powder. As a reminder, microwave sintering is a volumetric heating method that mainly heats the core of the part, which then diffuses the heat to its surfaces. It is then necessary to control the heating rates of the samples to avoid a too important temperature gradient between the two regions of a part, causing uneven thermal expansion in the sample and breakage of the ceramic material.

Among the samples sintered by microwaves during this study, the majority failed to maintain their integrity: the temperature gradient between the surface and the core that is induced in the sample causes the material to break up as the core densifies and reduces in volume compared to the outer layer. The sample is then sintered, but is not applicable for use due to the size of the pieces.

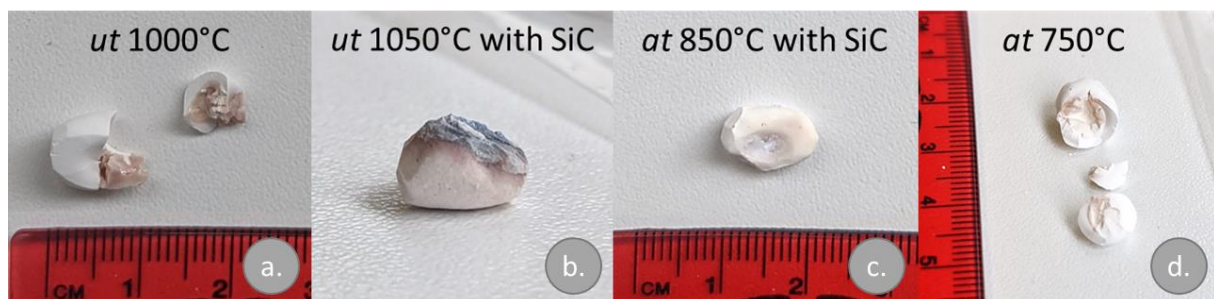


Figure 12 - Samples sintered by microwaves with and without susceptors.

The first sample sintered by microwave at 1000 °C (Figure 12 a.) breaks up and shows a burnished phase in its core. After heating very quickly, the temperature gradient seems to have caused the sample to break up. For the next sample, the addition of SiC susceptor around the part could mitigate this temperature gradient by heating the surface. This is indeed the case, but the contact with SiC causes a blackening of the part at 1050 °C on the touching part (Figure 12 b.), with a gradient going to the other side of the part with the brown phase in the middle. In spite of the integrity of the sample, no characterization will be carried out on this part because of this black stain, but could be done for an in-depth study. To overcome this problem of chemical contamination, the next sample (Figure 12 c.) is sintered at 850 °C but with a SiC susceptor which is not in direct contact with the part. The sample

kept its integrity, but a crack is present in the middle of the part. As for the previous sample, no characterization was performed.

For the *dopaje* powders, several failures occurred: first, a sample does not heat up and the initial power of 500W is only slightly absorbed. Secondly, heating by magnetic heating was tried, without any effect; after many tries the use of magnetic field to heat ceramic powder samples is renounced. Subsequently, another sample is heated to 300°C (Figure 13 g.) but does not reach a densified state.



Figure 13 - Samples sintered by microwaves at high temperature and with magnetic field.

For the samples *ut*-750 °C (Figure 12 d.), the two *ut*-1200 °C (Figure 13 e. f.) and the second *ut*-1000 °C (Figure 14 j.) samples, they all broke into several pieces and only the last one could give good quality parts to be put in resin and carry characterization.

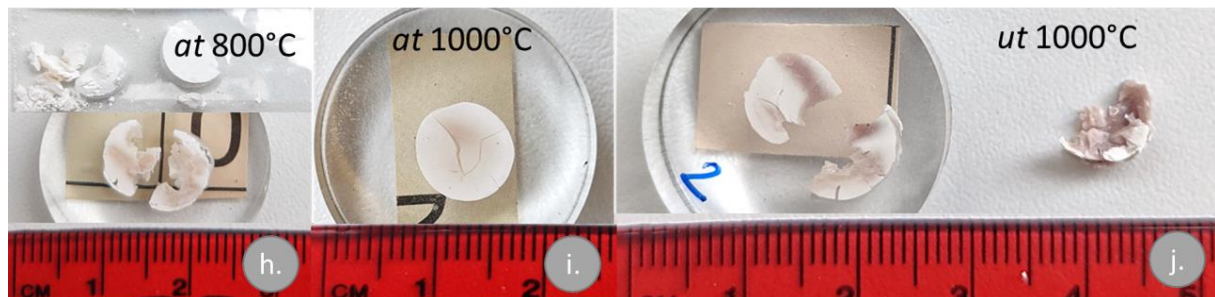


Figure 14 - Samples sintered by microwaves used for characterization measures.

Finally, the *at* powder samples are the ones that are sintered in greater numbers: the tests at 800°C (Figure 14 h.) and 1000°C (Figure 14 i.) were successful. For the 1200°C test (Figure 13 f.), the power of the generator is reduced to 350W to have a better control of the heating, but the high temperature causes the sample to break.

As a general remark, all samples show a difficulty to heat at low temperature. It is often several minutes that it is necessary to reach 250°C which is the minimal temperature detected by the pyrometer. For the continuation of the study, another pyrometer is used to measure the heating at low temperatures. The origin of this phenomenon is explained in the following section on dielectric properties. Then, the difficulty to control the heating of the ceramic powder from a certain

temperature makes the complete and progressive sintering of the parts complex. The core of the part is often heated too quickly at the expense of the solid surface, which causes the part to break and become unusable. The presence of susceptors to help the heating seems to work since the part concerned keeps its initial shape. As expected, *dopaje* powder with a poor powder size distribution is the most problematic to sinter. Finally, the use of the magnetic field heating mode does not seem to be effective but this hypothesis must be verified.

V. DIELECTRIC PROPERTIES AND PENETRATION DEPTH

One of the problems of this study is to succeed in sintering a sample in all its volume. It was explained that microwave sintering is a method that allows volumetric heating by penetrating to the core of a sample. The penetration depth is a property that evolves during the sintering process and depends on the dielectric properties of the material, which in turn depend on the temperature of the material. Measurements of these properties were carried out on a sample of *at* powder; their evolutions are represented on the graphs below (Figure 15).

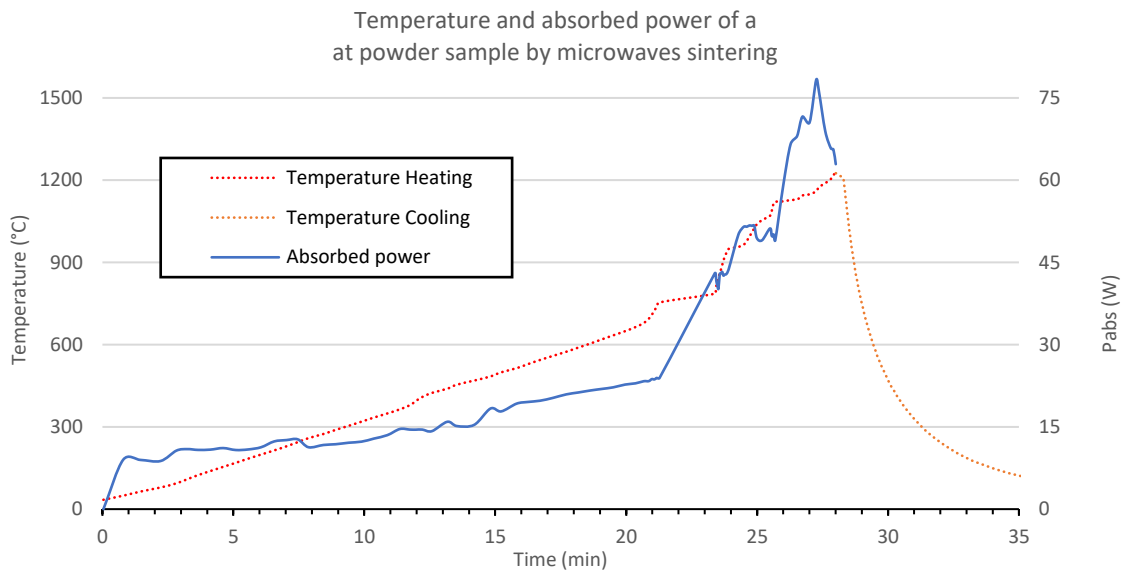


Figure 15 - Temperature of a *at* powder sample during its microwave sintering.

A second problem is the nature of the powder regarding microwave heating at low temperatures. Indeed, at the beginning of the microwave heating, the magnesia titanate powder is mostly transparent to microwaves up to 400 °C with a loss factor close to 0. This explains the difficulty encountered to launch the sintering in laboratory. The use of a hybrid heating can be studied, by heating the sample in an oven up to 500 °C, to then continue the sintering by microwaves.

The temperature increase (Figure 15) is constant up to 700°C with a heating rate of 30°C/min. This temperature and heating rate causes a change in the dielectric properties from 400°C onwards. From this point up to 700°C, the dielectric constant and the loss factor fluctuate greatly and reach a maximum at 600°C. This rapid fluctuation of the dielectric properties makes it difficult to control the sintering process with manual control methods such as the one used in the laboratory with the elevation of the sample (3.c.iii), since the power absorbed depends directly on these properties and the magnitude of the field (0). Moreover, at this point in the process, the dielectric properties allow the microwaves to penetrate up to 2 cm deep (Figure 16). For the case of laboratory samples, this depth is sufficient to allow the entire volume to absorb microwaves and perform the complete sintering of the part. However, for thicker ceramic parts, low temperature sintering is complicated for the MgO-TiO₂ mixture.

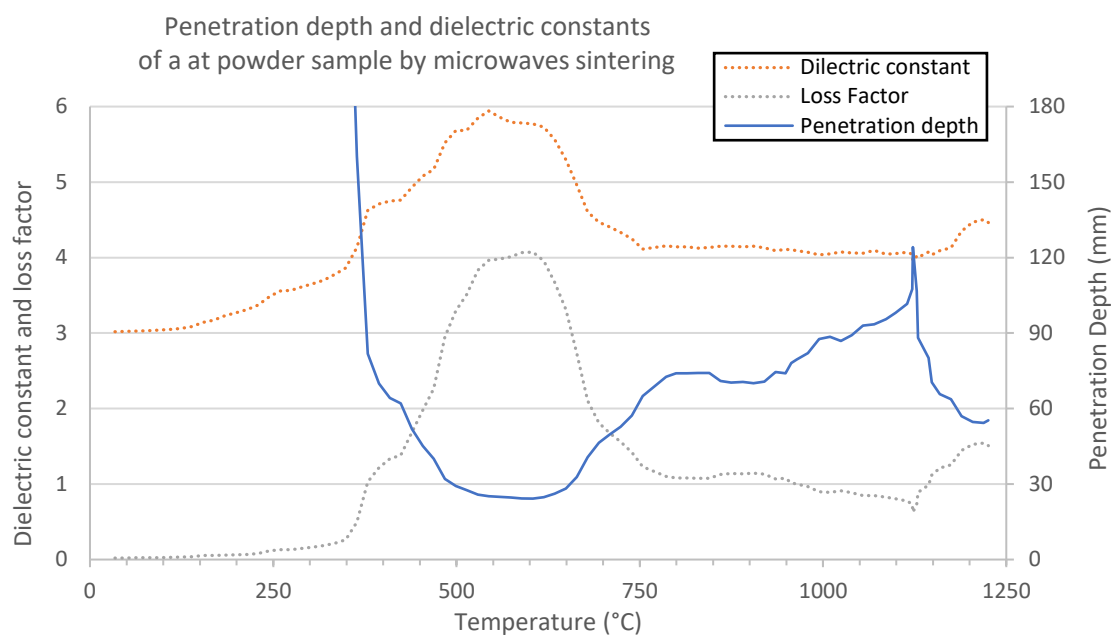


Figure 16 - Penetration depth, and dielectric properties of a *at* powder sample during microwave sintering.

Fortunately for a larger scale application, the dielectric properties increase after reaching 700 °C, stabilize from 800 °C to 1000 °C for a depth of 7 cm and increase again from 1100 °C to reach a maximum of 10 cm of penetration depth. In exchange for this gain in depth, a reduction in the loss factor is measured and reflects a difficulty in heating the sample beyond 1200 °C.

VI. DENSITY

Measurement of density (Table 6) have been carried out only on conventional sintering samples; The microwave samples had such a complex geometry that they were trapped in the resin and could not be put out of it. Relative density would have been a constitutive value by knowing density of the complete sintered ceramic material. Theoretical density of 4.05 g/cm³ from a 50/50 mix rule of MgO and TiO₂ is used.

Table 6 - Density of conventional sintered samples

Sample		Density	%	
Conventional sintering	dopaje	3,84	0,95	
	1400°C/2h	at	3,67	0,91
		ut	3,68	0,91
	1500°C/2h	dopaje	3,90	0,96
		at	3,97	0,98
		ut	4,04	0,99

A systematic increase is observed for sintered samples at higher temperatures. For a difference of 100°C, a small increase of 2% in density is observed for the *dopaje* powder, and an increase of 8% and 10% respectively for the *at* and *ut* powders. This increase difference between the powders can be explained by the unequal size distribution of the powders. Indeed, as explained in the previous section

(4.a.ii), the *dopaje* powder does not have small grains that fit between the larger grains. The construction of bonds between the grains is strongly increased for the case of *at* and *ut* powders with the increase of temperature but this improvement in density must be contrasted with the increase of grain size observed by FESEM. The lack of data for densities of microwave sintering samples does not allow to determine the success of sintering. It should be determined by mechanical studies (4.a.vii) or by methods of characterization of the microstructure in DRX (4.a.viii) or FESEM (4.a.ix).

VII. ELASTIC MODULUS, HARDNESS AND TOUGHNESS

Toughness measures could not be carried neither on CS and MW samples. For every load available on the testing machine, every test lead to a local rupture of the surface and size of the indenter could not be measured. The elastic modulus and Vickers hardness measures for CS and MW samples are obtained from nanoindentation tests [5].

Table 7 - Modulus and Hardness of samples.

Sample		Modulus (GPa)	Hardness (GPa)	
Conventional sintering	dopaje	135,6 ± 66,8	7,56 ± 5,43	
	1400°C/2h	at	180,4 ± 34,2	
		ut	192,8 ± 38,3	
	1500°C/2h	dopaje	159,0 ± 36,2	11,40 ± 3,80
		at	200,5 ± 38,4	10,70 ± 3,20
		ut	207,5 ± 24,5	12,40 ± 3,00
Microwave sintering	800°C/10'	at	207,2 ± 18,3	
		(brown part)	100,2 ± 27,5	
	1000°C/10'	at	190,5 ± 40,8	9,58 ± 3,44
		(brown part)	106,0 ± 20,5	5,03 ± 1,93
		ut	185,3 ± 19,5	10,33 ± 2,28
		(brown part)	106,6 ± 34,0	5,25 ± 2,88

Results confirm what was previously stated: for conventional sintering, the *dopaje* powder has an elastic modulus and hardness 25% to 30% lower than the values of *at* and *ut* powders sintered at the same temperature (Table 7). However, the difference is reduced to 20-23% for conventional sintering at higher temperatures.

Between the two conventional sintering batches, an increase of 10% is noticed on the elastic modulus of the samples. The temperature increase seems to have a direct impact on the elastic modulus of the material. However, for the hardness, an increase of 20% and 30% respectively is observed for the *ut*

and *dopaje* samples, but a slight reduction for the *at* powder (Figure 17). These increases in mechanical properties are going in the same way than the increase in density (4.a.vi). This indicates that the densification of the material has an important influence on the hardness. The effect of grain growth must be confirmed by the study of the microstructure by FESEM.

Between the *at* powder samples sintered by microwaves ovens, the increase in temperature shows a decrease of 8% for elastic modulus and 24% for hardness by changing temperature from 800°C to 1000°C. This decrease reveals unexpected effect of too high temperature on sintering ceramic parts by microwaves.

To compare the two sintering methods, the *at* powder sample sintered by microwave during 10 minutes at 800°C reaches higher mechanical characteristics than the samples sintered by conventional method in a furnace during 2 hours at 1400°C and 1500°C. This result shows that the magnesia titanate material can be sintered by microwave and reach good mechanical properties despite the higher temperatures and longer heating times employed in conventional sintering processes. It has to be noted that these properties can be reached only when the powder is well prepared and has a powder size distribution that allows high densities to be achieved. However, it should be noted that the samples sintered by microwaves did not keep their integrity as explained in the failure section (4.a.iv).

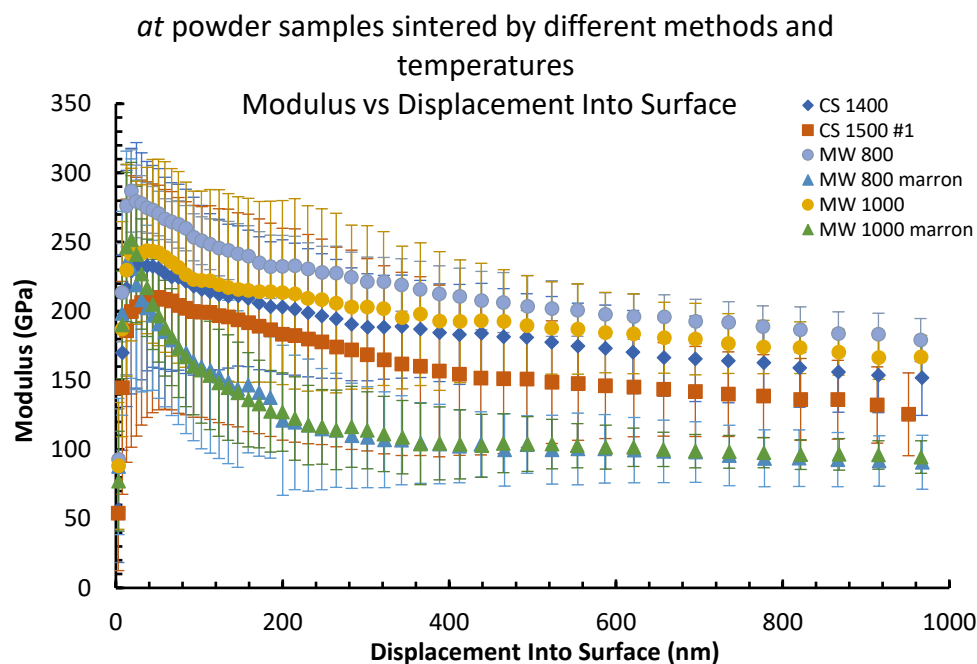


Figure 17 – Elastic modulus Vs. displacement for a *at* powder sample at different temperatures and sintering methods.

Hardness and elastic modulus measurements were made on the brown phase that forms in the core of the sample. As explained earlier (1.a.i.1), sintering a sample's core faster than its outer layer can cause the material to break. However, it is worth considering whether the resulting phase has good mechanical properties to determine how much it affects the overall properties of the material. The brown phase has an elastic modulus and hardness values half those of the white sintered phase (Figure 17).

VIII.DRX

For the study of the microstructure of the samples, the graphs (Figure 18, Figure 19) of the X-ray diffraction patterns show the evolution of the presence of phases in the sample during a sintering process.

First, each type of powder is presented with several measurements at different temperatures. For the *at* and *ut* powders, the sample is composed of TiO_2 and MgO at low temperature. As the temperature goes up, TiO_2 begins to diffuse into MgO to form phases. From 700°C and 800°C respectively, the MgTiO_3 phase appears with a quantitative reduction of the original MgO and TiO_2 components. This change can be correlated with the fluctuation of dielectric properties at these temperatures. The growth of this phase will continue until the end of the sintering until the disappearance of the two others as the temperature increases. During sintering, the MgTi_2O_5 phase appears at 1000°C but seems to disappear mainly at the final temperature, as well correlated with changes in dielectric properties.

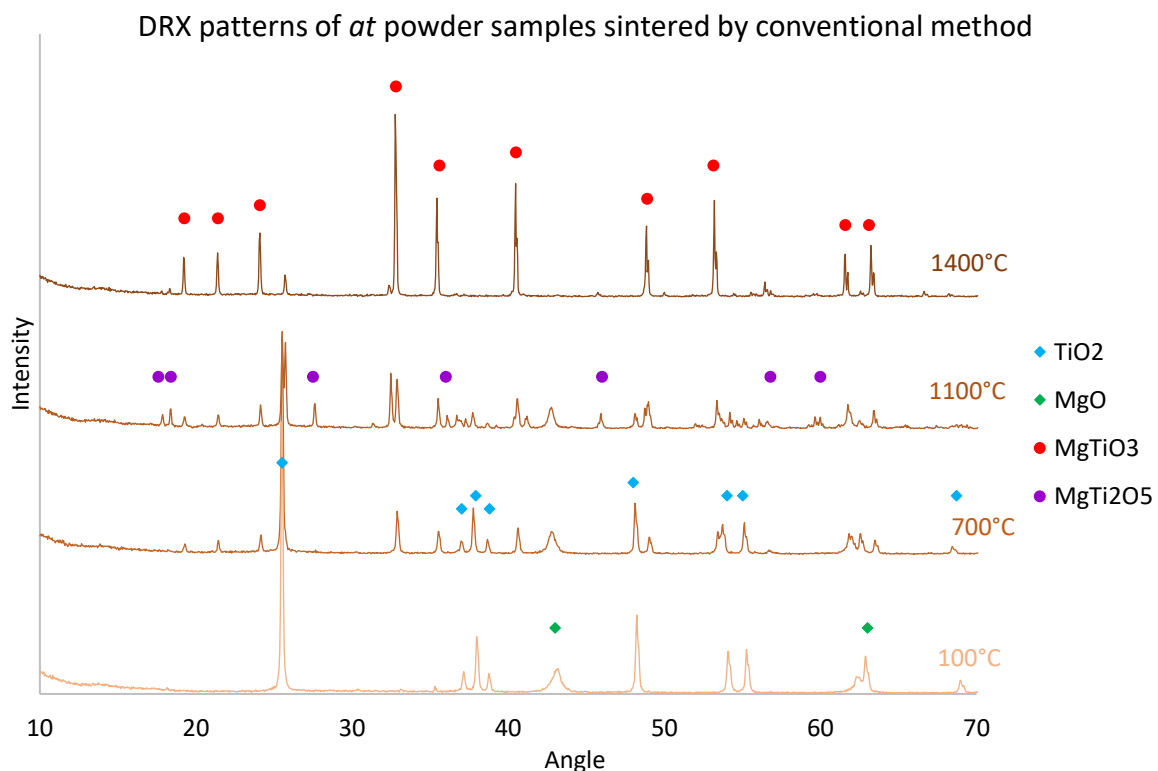


Figure 18 - DRX patterns of *at* powder samples sintered by conventional method.

The first phase obtained during sintering is MgTiO_3 . White in color, it has very good dielectric properties and is used for the manufacture of electrical capacitors. Of rhombohedral structure $R\bar{3}(\#148)$ with a density around $4\text{g}/\text{cm}^3$, this phase seems to appear from 700°C for some samples to a late appearance at 900°C for others. On the other hand, the MgTi_2O_5 phase is a secondary parasitic phase which tends to decrease the mechanical and dielectric properties of the final material. Of orthorhombic structure with a density of $3.6\text{g}/\text{cm}^3$, it is recognizable to the naked eye with its brown color and it seems to cause the rupture of the samples at high temperature. Another secondary phase Mg_2TiO_4 may exist within the specimen and has already been observed in other works; however, it was not observed in this study.

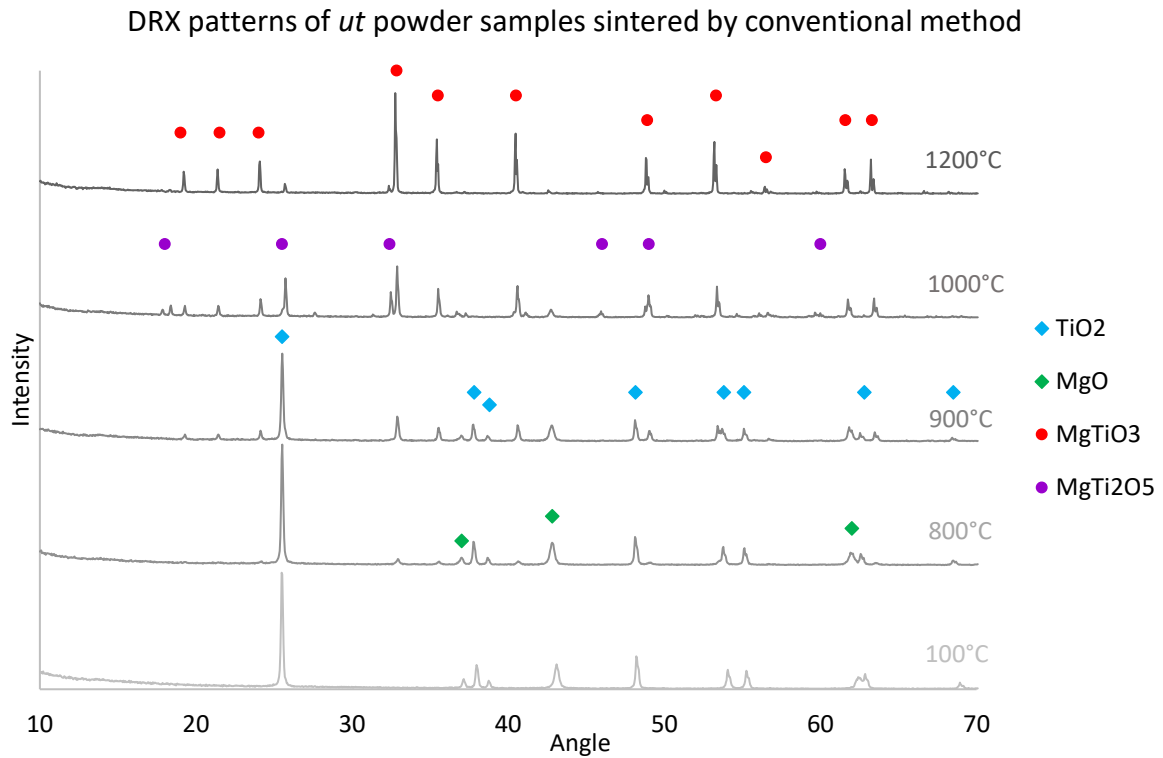


Figure 19 - DRX patterns of *ut* powder samples sintered by conventional method.

In a second step, the 3 samples sintered conventionally at 1400°C are compared (Figure 20) to determine if the final state of the samples contains the same phases. At first sight, from a qualitative point of view, the intensity peaks seem to be at the same positions for the 3 samples, reflecting the presence of the same phases for all samples.

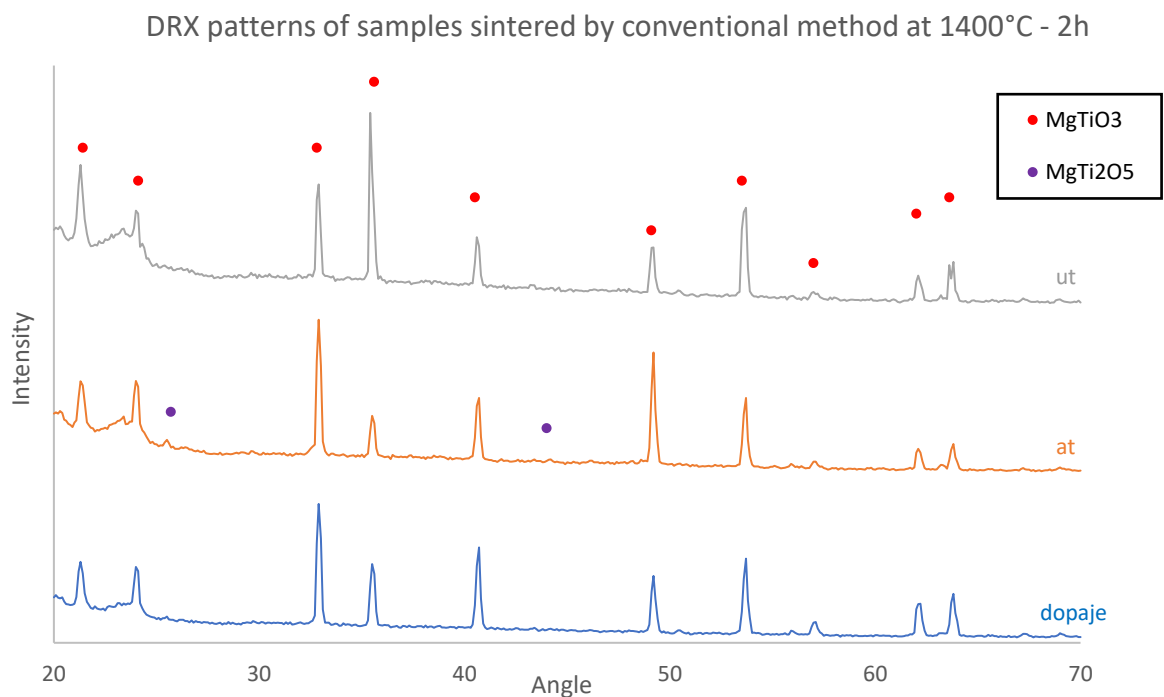


Figure 20 - DRX patterns of samples sintered by conventional method.

From a quantitative point of view however, and since the peaks appear to be of equal thickness, the phase concentration is related to the height of the peaks. There is a large difference in height between the peaks at 33° and 36° and between the two peaks at 49° and 54°.

For the further study of the XRD characterization results, the microwave sintered samples are compared (Figure 21). In contrast to the conventional samples, the microwave-formed parts show the same diffraction peaks and the same peak intensities. However, two remarks should be noted:

- First, the presence of the parasitic phase MgTi_2O_5 is more prominent in the sample *at* sintered at 1000°C. Despite this observation, no explanation is found for any relationship between the presence of this phase and the type of powder, the temperature and the sintering method. The randomness of the microwave sintering and the final state of the samples may explain this anomaly. It is however possible that this phase disappears at higher temperatures as for the samples sintered by conventional way.
- Secondly, the presence of MgO even on a sample sintered at high temperatures, as well as the profile of the DRX pattern which presents a lot of noise up to 50° shows that the sintering of the whole powder is not complete; there remain raw powders reflecting a global semi-crystalline structure of the samples which is not observed in the conventionally sintered samples

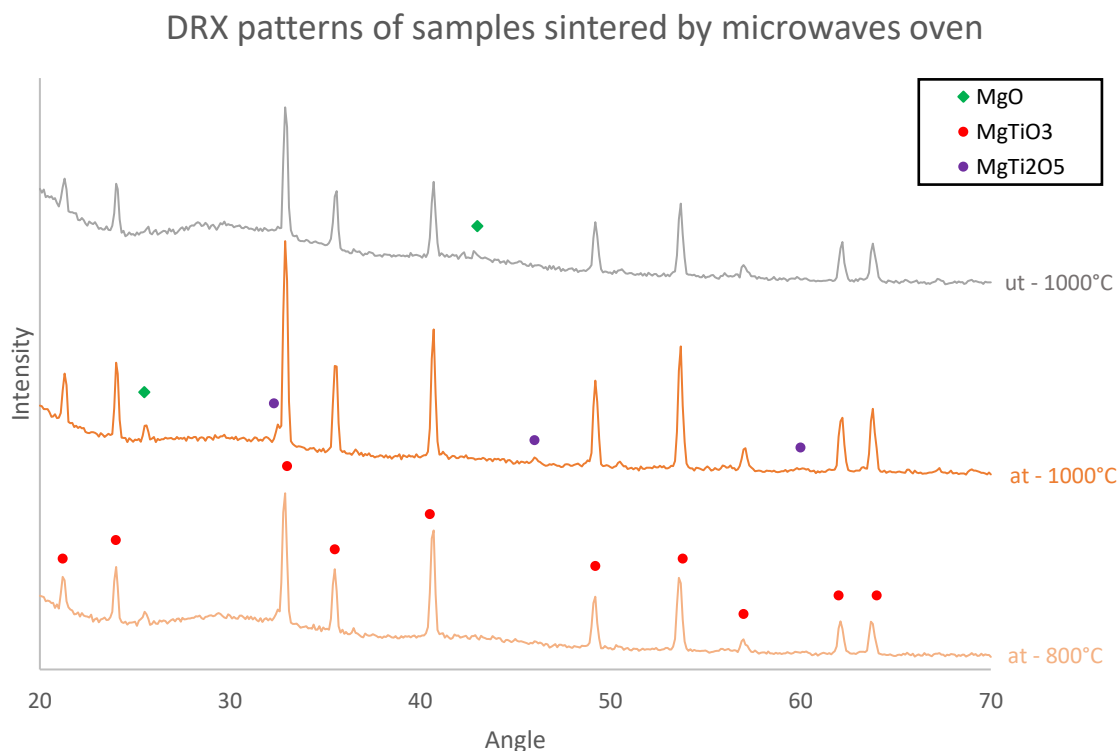


Figure 21 - DRX patterns of samples sintered by microwaves oven.

Finally, to compare the two conventional and non-conventional sintering methods, several DRX patterns of different samples are compared (Figure 22). Samples from the same type of powder are plotted.

DRX patterns of at and ut powder samples sintered by conventional and non-conventional methods.

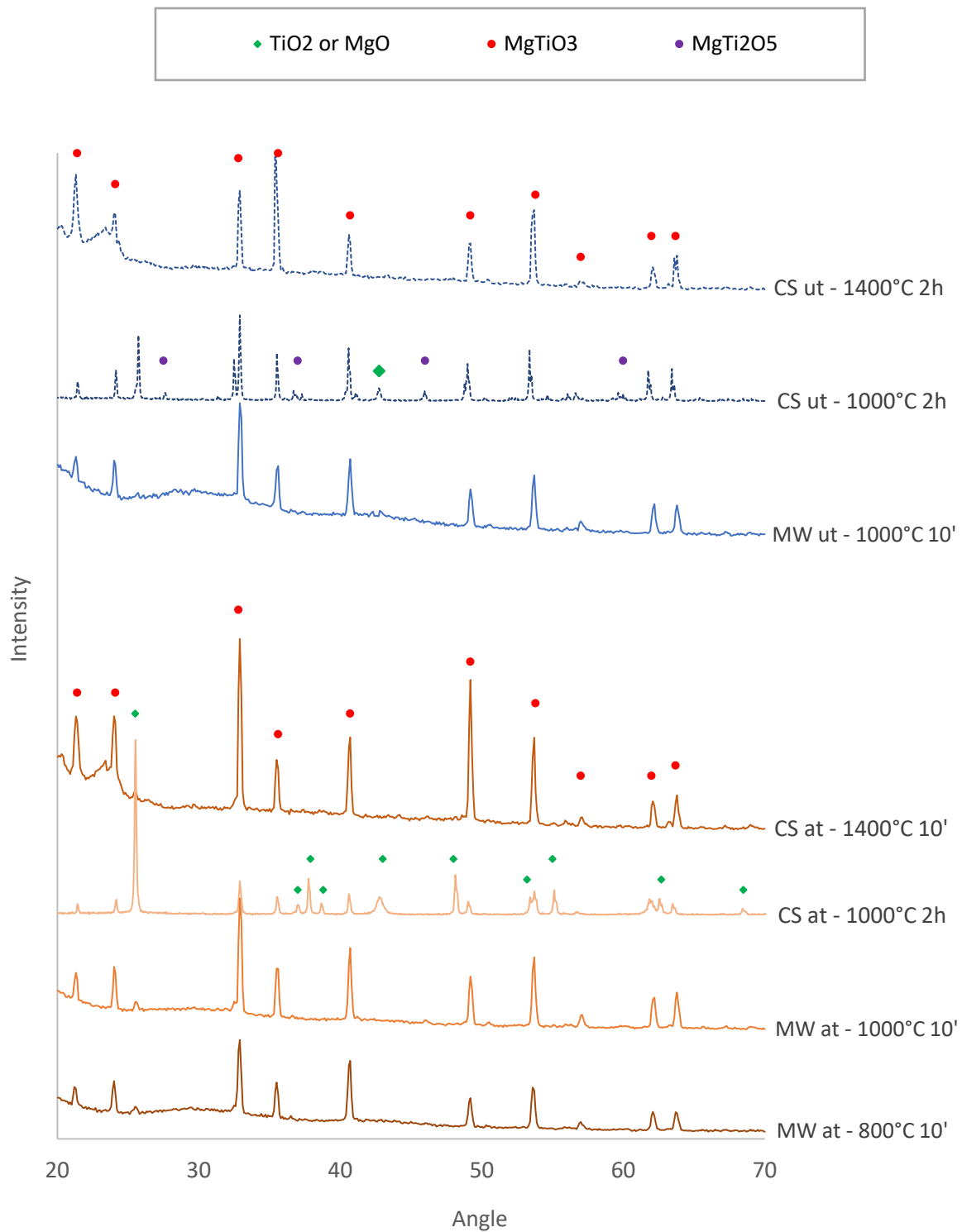


Figure 22 - DRX patterns of samples by different sintering methods.

The *at* and *ut* samples sintered by microwave at 1000°C reach the same microstructures as the samples sintered at 1400°C by conventional way, with a twelve times less production time. This saving in time and energy is qualified by the residuals of raw products found in the previously microwave sintered samples (Figure 21). It is also noted that the noise profile at low angles reflects the difference in crystallinity rate between the CS and MW samples, being lower in the latter.

IX. FESEM

FESEM observations reveal the nanoscopic structures of conventionally sintered materials. By comparing the different types of powders used for sintering, the hypothesis of poor densification for the *dopaje* powder is confirmed by the images: huge porous cavities are present in the sintered material at 1400°C (Figure 23 a.), and just as much at 1500°C (Figure 23 b.). The growth of the grains, even at high temperature, is not sufficient to fill the void between the powder grains. In the case of *at* and *ut* powders, the densification is already complete at 1400°C (Figure 23 c. e.) and the temperature increase (Figure 23 d. f.) seems to have an effect on the overall densification of the material: the number of porous cavities has decreased, even if the volume of the remaining cavities is higher, showing a reduced pore volume between the samples. Indeed, densities calculated for these samples confirm this hypothesis showing a reduction of porosity for the samples sintered at highest temperature.

The increase of the sintering temperature has however an effect on the grain growth. For all powders, the number of grains at 1400°C is much higher than in the material sintered at 1500°C, where the smaller grains were absorbed by the larger ones during growth. Another effect of temperature is the grain diameter, which is totally different from sample to sample. At low temperature, the diameter of the grains varies from 5µm for the small grains in large numbers to 25µm for the largest grains. In the case of high temperature samples, the grains can reach radius of several tens of µm or even exceed a hundred µm for the largest ones. As a general remark, no sample presents a uniform distribution of grains on their size or their number. Although this grain growth, the intergranular cohesion of the materials seems to be positively affected: the *at* sample 1500°C shows cracks in the core of the grains and not within grain boundaries.

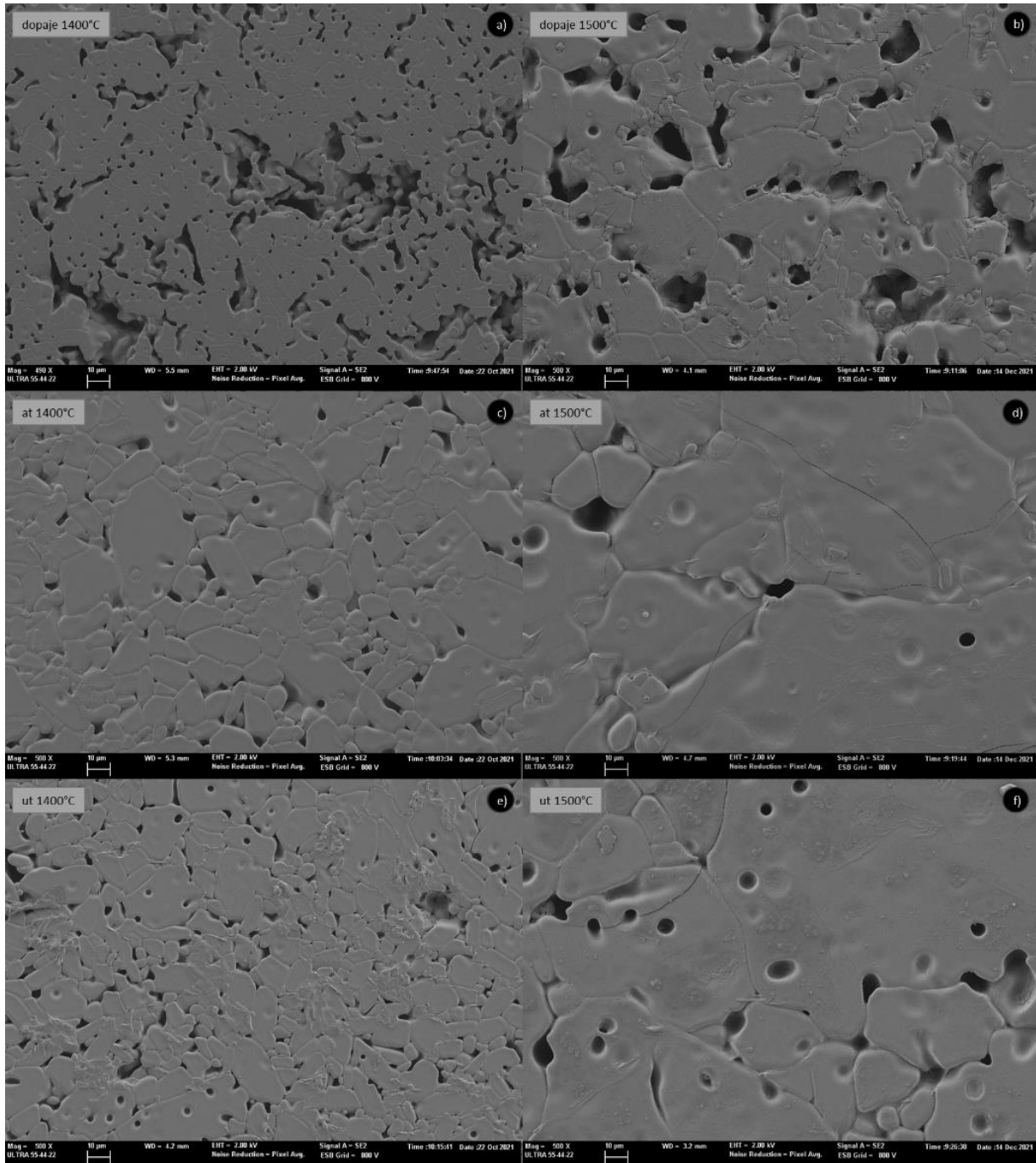


Figure 23 - FESEM captions of *dopaje*, *at* and *ut* powder samples sintered by conventional method at 1400°C and 1500°C.

No FESEM data is obtained for the microwave sintered samples. The observable samples being embrittled by the sintering could not be prepared for this characterization.

5. CONCLUSION

Through the work carried out during this project, it is possible to draw the conclusions shown below:

- The main objective of the study was to determine if sintering of magnesia titanate ceramic powders using microwave oven was possible. Different sintering parameters, such as temperature, power and duration of microwave exposure were tested on different powders. The preparation of the samples, as well as the microscopic nature of the materials also had an influence on the sintering results. The *dopaje* powder which did not have a good powder size distribution had its mechanical properties reduced and its densification cut short, resulting in a sparse microstructure.
- The influence of electric and magnetic fields on the sintering of MgO-TiO₂ powders needed to be clarified. For magnetic fields, the sintering is a failure with an impossibility to exceed 300°C and thus to progress in the sintering of the sample. On the other hand, the control of the power of the microwave ovens by electric field was not simple either. The sintering of the raw parts is unstable with heating rates difficult to control, even with the use of susceptors. The dielectric properties of the powders fluctuate throughout the heating process leading to very high heating rates, often accompanied by non-uniform sintering within the part even when exceeding 1000°C. Negative effects on mechanical properties have even been shown when reaching too high temperatures. In addition, many samples did not maintain their integrity during sintering, resulting in sample breakage or melting, leaving little product to characterize and no suitable applications at this time. If the microwave sintering technology is to be applied to the magnesia-titanate mixture, it is necessary to control the heating and all its parameters with extreme precision.
- Regarding the impact of the sintering mechanisms, namely densification and grain growth, on the mechanical properties and microstructure of the parts, it has been figured out for conventionally sintered samples. Densification alone does not seem to explain the increase in mechanical properties and suggests the effect of grain growth on the properties, which could be verified if toughness values are obtained. It is necessary to validate these hypotheses for this same material when sintered by microwave. For the case of dielectric properties, the measurements carried out during the process make it possible to affirm the influence of the various phases on the capacity of the part to heat more or less easily.
- To compare the two conventional and non-conventional methods, the samples sintered by microwaves, with a heating time twelve times lower and at a temperature several hundred degrees lower, reach the same mechanical properties as the samples sintered by conventional way. Microwave sintering is a plausible way to synthesize parts made of ceramic materials, with lower energy consumption and shorter process times than existing industrial methods.

6. BUDGET

The different prices of laboratory equipment used for this study are given in the Table below. All this equipment is used and amortize during several years but it must be considered as a necessary investment made by the university. The energy consumption to work with the equipment is estimated too.

Table 8 - List of equipment.

qt	Description	Price equipment (€)
1	Cutting saw	
1	Resin coating machine	63000
1	Polishing machine with discs	
1	Isostatic Press	4800
1	Magnetic hotplate	200
2	Conventional furnace	25000
1	Microwave oven	50000
1	Precision scale	8000
1	Archimede's set	
1	DRX	80000
1	FESEM	
1	Laser Diffraction	32000
1	Powder size measurement	
1	Nanoindentation equipment	23000
Total investment		286000

Table 9 - Energy consumed.

Hours of use (h)	Description	Power (W)	Energy consumption (kW.h)
2	Cutting saw	750	1,5
3	Resin coating machine	1000	3,0
15	Polishing machine with discs	570	8,6
3	Isostatic Press	500	1,5
6	Magnetic hotplate	1020	6,1
8	Conventional furnace	4500	36,0
3	Microwave oven	800	2,4
1	Precision scale	15,5	0,02
2	Powder size measurement	200	0,4
10	Nanoindentation equipment	150	1,5
Total energy			61,0
Energy cost (€/kW.h)			0,0855
Energy cost (€)			5,21

The following tables show estimations costs labor, equipment and material. As a conclusion, the global cost of the project is given in the last table.

Table 10 - Labor costs.

Unit	qt	Description	Unit price (€/unit)	Price (€)
Labor costs				
h	4	FESEM labor	20	80,00
h	12	DRX labor	80	960,00
h	160	Project director	24	3840,00
			Sub-total	4880,00

Table 11 - Equipment costs.

Unit	qt	Description	Unit price (€/unit)	Price (€)
Equipment cost				
ud	3	Beaker 100mL	0,96	2,88
ud	1	Metal clamps	2,55	2,55
ud	1	Metal spatula	2,89	2,89
ud	2	Ceramic crucible	3,20	6,40
ud	1	Latex glove box	4,39	4,39
ud	7	Polishing discs	200,00	1400,00
			Sub-total	1419,11

Table 12 - Material costs.

Unit	qt	Description	Unit price (€/unit)	Price (€)
Material costs				
g	50	Resin powder	0,087	4,35
kg	0,5	MgO powder	20	10,00
kg	0,5	TiO ₂ powder	20	10,00
			Sub-total	24,35

Table 13 - Global cost of the project.

Category	Cost (€)
Energy cost	5,21
Labor cost	4880,00
Equipment costs	1419,11
Material costs	24,35
Total (without taxes)	6328,67
IVA (21%)	1329,02
Total cost of the project	7657,70

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