

Sintering of cerium oxide based materials by microwave heating

Hussein Hammoud

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THÈSE

Présentée par

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Spécialité : Science et Génie des Matériaux

Sintering of Cerium Oxide based materials by Microwave heating

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There are more possible roads to knowledge, but scientific logic allows us to be wrong or right with complete confidence.

This thesis is only a beginning of my journey.

It is dedicated to my parents.

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Introduction

Nowadays, the management of nuclear waste is one of the most important challenges and questions due to the increase of the nuclear production of energy. In the year 2000, the spent fuel being produced was about 220'000 tonnes and is growing by 10'000 tonnes each year (Greenpeace International). For example, there are over 435 commercial nuclear power reactors operable in 31 countries, its total capacity is about 375'000 MWe, and there are about 70 more reactors under construction. One solution is that radiotoxic nuclear wastes containing minor actinides (americium, curium and neptunium) can be recycled for usage in accelerator driven systems and can reduce the time to obtain the original uranium to 1000 years instead of 100'000 years. The figure 1 shows the production of nuclear power in 2013.



Figure 1: The nuclear power produced by some countries in 2013.

In order to transmute the actinides, different options exist. One of them is the production of conventional fuel pellets, which has the issue of a rather heavy use of mechanical devices and the production of powders. Other options are new types of fuel, such as particles, which offer a simplified fabrication route. Here the Sphere-Pac concept is promising. In order to produce fuel particles for this concept, three tasks should be carried out. Firstly, the dissolution of spent fuel in an aqueous reprocessing step, this leads to a nitrate solution containing the actinides. With that a feed solution containing the actinides and the chemical ingredients has to be produced, this will later allow a gelation process, where the spheres are formed. The chemical process here is the internal gelation, which is driven by a temperature increase. Secondly, the temperature increase is realised within a microwave cavity. Therefore the microwaves have to be transferred into the glovebox, which contains all the radioactive solutions, to perform the internal gelation technique for the production of the xerogel drops (spheres). Finally, the collected gelled spheres have to be sintered. A good option here is the

sintering by microwave heating in order to densify it at lower temperature with less loss of actinides due to the evaporation. These dense spheres will be filled together in the cylindrical cladding (pin), which results in the so called sphere-Pac fuel. The pins will then be used in the transmutation system, such as a conventional fast reactor, or a subcritical version, allowing higher minor actinide contents, called accelerator driven systems (ADS)

The process requires a controlled and dust-free environment. The aqueous route is ideal to fulfil this demand. Having reached the solid phase, after gelation and drying, when it comes to sintering, the treatment by microwave technology was recommended as a good candidate and a suitable technique. In the research on nuclear fuels, ceria is used as non-radioactive simulant for plutonium [1]. The synthesis of millimetric sphere shaped CeO₂ xerogel particles (see figure 2) by microwave assisted internal gelation has been studied [2]. The washing and the drying of the solution which is produced by the digestion of the nuclear wastes are the first stages for a complete process. Hence, the porous spheres produced must be further densified by microwave sintering. Several studies have investigated the use of microwave technology for the internal gelation at a frequency of 2.45 GHz [3-5].



Figure 2: The cerium oxide gelled spheres collected in water (Laboratory for Nuclear Materials, PSI).

Since the eighties, the elaboration of ceramics by microwave heating was the target of several studies in the area of ceramics. Microwave technology is currently used as an alternative route to conventional processing techniques in order to treat different kinds of materials. The sintering process of ceramics is one of the applications of microwave heating which in general has more advantages compared with conventional sintering technique, such as rapid heating process, uniform heating within the specimen which provides a homogenous physicomechanical properties and its ability to modify the microstructure and the chemical reaction pathways due to its selective heating [6, 7].

Actually, the motivation of this thesis is mainly the evaluation of the use of microwave technology and its applicability in the densification step of this procedure and then following-up the sintering process of cerium oxide.

In addition, there is a major gap in understanding the gain provided by microwave sintering compared to conventional sintering. The studies found in literature concerning the sintering of ceria based materials didn't include the microwave sintering of pure ceria. This gap presents a real challenge not only in the fundamental research area but also in industrial scale. Moreover, it is an additional reason that motivates us to contribute to this challenge. Hence, several objectives are integrated in thesis work to perform the task.

Firstly, the influence of the porosity for ceria up to 1000°C should be studied by determination of the thermal and dielectric properties of a series of model samples of ceria which were sintered conventionally in varying range of porosity.

Secondly, the ability of microwave sintering of ceria should be evaluated and compared to the conventional sintering.

Thirdly, the development of a setup which couples a classical furnace with microwave resonator using the cavity perturbation method for the determination of the dielectric properties of ceria at high temperature is necessary.

Finally, the experimental data should be introduced in Multiphysics solver in order to study the interaction of the electromagnetic field with ceria spheres and the temperature, guiding to understand the sintering process.

Given this current context, we have developed a system to determine the dielectric properties of ceria and made a comparison study between microwave sintering in single mode cavity and conventional sintering by a classical dilatometry for two different powder granulometry. In addition, a simulation study by COMSOL Multiphysics solver which couples electromagnetic and heat transfer and treats the different parameters of ceria as inputs has been included to this work in order to quantify the effect of electric field on the sintering.

This work has been funded by CCEM Project MeAWaT. A part of this work was made at the laboratory of Materials science and Technology (EMPA, Thun, Switzerland) in collaboration with Paul Scherrer Institute (PSI, Villigen, Switzerland). The other part of this work has been developed at the Ecole des Mines of Saint Etienne (Saint-Etienne, France) in collaboration with SIMAP laboratory (Grenoble, France).

This manuscript is structured in five chapters which are presented as follows:

- Chapter 1: is dedicated to the interaction of matter with electromagnetic radiation, the sintering basics, the properties of cerium oxide and some studies concerning its sintering.
- Chapter 2: is dedicated to the experimental setup developed for the determination of the dielectric properties of ceria and the different methods used for the determination of thermal and physical properties.
- Chapter 3: concerns the results of the thermal and dielectric properties of ceria and additional their connection with the rules of mixture (pores and matter).
- Chapter 4: presents the comparison study of sintering of ceria pellets by the two different techniques: conventional and microwave sintering. Moreover, the effect of particle size of the powder is also reported in this section.
- Chapter 5: is dedicated to the multiphysics simulation using COMSOL. The effect of different factors such as neck and particle sizes and the packing effect on the electric field are reported in this part to understand the electromagnetic effect on the sintering.

Finally, the conclusions achieved through this thesis and some prospects for related future research, are presented in this part.

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Chapter 1: Background

1.1 Interaction of electromagnetic radiation with matter and microwave heating

1.1.1 Interaction of microwave radiation with matter:

The microwave energy is an electromagnetic energy which has a range of frequencies between 300 MHz and 300 GHz, corresponding to wavelength range between 1 mm and 1 m. These waves are called also centimeter waves. Moreover, the typical frequencies used for the materials processing are: 0.915, 2.45, 5.8 and 24.125 GHz which are the industrial, scientific and medical radio bands (ISM). The typical frequency for microwave oven used by 90% of American homes is 2.45 GHz which is equivalent to a wavelength of 12.24 cm in free space. On the other hand, the microwave systems operated at 915 MHz are well used by the industrial and commercial market because the conversion of the electric power into electromagnetic power in these systems is higher than the conventional technique (the efficiency exceeds 82% instead of 70%). From the economical point of view, the microwave technology has been shown to reduce the cost and deliver a good performance comparing to the classical technique. The figure 1.1 shows the electromagnetic spectrum and their applications.



Figure 1.1: The electromagnetic spectrum (left) and the typical microwave and wireless applications (right) [1].

An electromagnetic wave consists of a magnetic wave which propagates perpendicularly to an electric wave. We are not interested in our study to the magnetic interaction with the matter but only to the electric interaction with it.

When the electromagnetic (EM) waves encounter the matter, three possible behaviours (figure 1.2) can results:

- 1- If the electromagnetic waves are completely reflected, the material is **opaque**.
- 2- If the waves are transmitted through the matter without the loss in energy, the material is **transparent**.
- 3- If a fraction of the waves are absorbed, the material is an **absorbent** and will heat when an electromagnetic field exists. Hence, in the AC field at high frequency, the interaction between the EM field as photons and the matter composed of uncharged and charges particles such as ions (cations and anions) and electrons are the origin of a heating through the material. Actually, this mechanism is based on the interaction between the dipoles of the object and the electric field where the charges form induced dipole moments that tend to align with electric field in competition with thermal effects. On the other hand, if the system presents permanent dipole moments, the alignment of these dipoles is due to electrical torque and it is influenced by the thermal effects as well. Moreover, if the field is non-uniform, a field gradient will be presented and will cause the dielectrophoresis forces in the treated system [2]. These forces do not require charged particles and depend strongly on the electrical properties, shape and size of particles. In case of ceramics, the main factors that contribute to microwave heating are ionic and electrical conductivity, degree of porosity, particle size and point defects [3].

It is important to note that in case of metals, an electric current is created at the surface and therefore the majority of the energy is reflected and just a very small part will be absorbed by the metallic material whereas this energy is much more efficient for a ceramic material where the penetration depth (see the equation 1.7) is generally greater than the dimension of the material.



Figure 1.2: (a) transparent, (b) opaque and (c) absorbent material [4].

1.1.2 Dielectric materials: complex permittivity and loss tangent:

When the matter is exposed to an electric field excitation, it acts through an electric displacement field \vec{D} . It is related to the electric field \vec{E} by:

$$\vec{D} = \varepsilon \vec{E}$$
(Eq.1.1)

where ε is the dielectric permittivity of the material.

When the applied electric field is sinusoidal, \overline{D} depends on the angular frequency ω and the permittivity of the material becomes complex $\varepsilon^*(\omega)$. It can be written:

$$\varepsilon^{*}(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$$
(Eq.1.2)

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are respectively the real part and the imaginary part of the permittivity.

The real part of complex permittivity is related to stored energy within the material and the imaginary part to the dissipated energy within it. Thus, we can define a loss tangent ($\tan \delta$) as the ability of the matter to absorb the electromagnetic energy and to transform to heat energy. It is related to the dielectric losses and given by:

$$\tan \delta = \frac{\varepsilon'(\omega)}{\varepsilon'(\omega)}$$
(Eq.1.3)

It is known that the heating of the material is better when its loss tangent is important. On the other hand, another mechanism associated to the electrical conductivity can be presented where the free charges create an electrical current and provide heat energy by Joule Effect. We can define the total dissipated factor $\mathcal{E}_t^{"}$ as the sum of two contributions: the dielectric losses and the conductive losses.

$$\varepsilon_{t}^{"} = \varepsilon^{"} + \frac{\sigma}{\omega}$$
(Eq.1.4)

where σ is the electrical conductivity of the material.

In case of insulators such as ceramics, the dielectric losses have the main contribution on the total dissipated losses whereas in case of conductors (metals and semiconductors) the loss mechanism is associated to the conductivity σ .

It is important to note that in case of magnetic materials such as magnetite (Fe_3O_4), another loss mechanism will present and contribute to the microwave heating process through its interaction with the magnetic field.

1.1.3 The main physical quantities of microwave-matter interaction:

The matter itself has specific elements which are the origin of the phenomenon. As we mentioned in the previous section, the free charges are related to the electrical conductivity σ and the fixed charges to the complex permittivity ε^* . These charges align by the action of the electric and/or magnetic field [5]. In the case of ceramic materials like CeO₂, the absorption of microwaves is low and due in general to the physical barriers such as the defects and the grain boundaries. Hence, these barriers can resist to the charge flow by generating the space charge [6].

The main parameters that describe and determine the uniformity and the efficiency of the heating by microwaves are:

1- The dissipated power P (W.m⁻³):

The quantity of the electromagnetic energy converted each second into heat energy per one cubic meter of a nonmagnetic material is given by Equation 1.5:

$$P = (\sigma + 2\pi f \varepsilon_0 \varepsilon^{"}) |E|^2$$
(Eq.1.5)

where σ id the electrical conductivity (S/m), |E| is the electric field norm (V/m), f is the frequency of the radiation (Hz), ε_0 is the permittivity of free space and ε is the loss factor or the imaginary part of the complex permittivity of the matter.

2- The penetration depth d (m):

A part of the electromagnetic wave penetrates into material and transforms typically to heat energy. This heat energy decreases and is expressed by an attenuation factor α given by equation 1.6:

$$\alpha = \frac{2\pi}{\lambda} \sqrt{\frac{\varepsilon'\left(\sqrt{1 + \tan^2 \delta}\right) - 1}{2}}$$
(Eq.1.6)

where λ is the wavelength of the radiation ε' is the real part of the complex permittivity and $\tan \delta$ is the loss tangent which is equal to $\frac{\varepsilon'}{\varepsilon'}$.

The penetration depth is the distance at which the power becomes 1/e (about 37%) of its value at the surface. It is defined by the relationship with α [7]:

$$d = \frac{1}{2\alpha} = \frac{\lambda}{2\pi\sqrt{\varepsilon'}} \tan\delta$$
(Eq.1.7)

For a typical frequency of 2.45 GHz

$$d = 1.974 \frac{\sqrt{\varepsilon'}}{\varepsilon'} (cm)$$
(Eq.1.8)

For example, it is equal to 7 cm for SiC and 100 cm for Zirconia [8, 9]. The calculated value for ceria is about 13 m.

3- Thus in a unit of volume, the variation of the temperature per unit of time depends on the dissipated power and can be expressed as [10]:

$$\frac{\Delta T}{\Delta t} = \frac{2\pi f \varepsilon_0 \varepsilon_{eff} \left| E \right|^2}{\rho C_p}$$
(Eq.1.9)

A several types of dielectric polarisation can exist during the interaction:

- Electronic polarisation: it is presented for the majority of the frequencies and it is less efficient for very high frequency.
- Ionic polarisation: this type of resonance is activated only in the infrared range of frequencies.
- Dipolar polarisation: it is also called molecular polarisation and is created in general at low range of frequencies in the presence of an external electric field. It is typically the main contribution during the microwave heating.
- Space charge polarisation: it requires very low frequencies and it is well known in physics of semiconductors.
- Interfacial polarisation: this polarisation is presented only in case of heterogeneous materials.

The figure 1.3 presents the relaxation curves of Debye in order to show the dependence of the two parameters (the dielectric constant ε and the loss factor ε) on the frequency. It shows that the different dielectric polarisations become weak for high frequency. On the other side, the loss factor which is the main parameter for the dissipation of the electromagnetic energy in the matter, decreases when the frequencies are higher than the frequency range of the dipolar polarisation.



Figure 1.3: The response of the dielectric constant (a) and the loss factor (b) in a large range of frequencies [11].

1.1.4 Difference between direct and indirect/hybrid microwave heating.

In order to get a good microwave heating, two ways of microwave heating can be used depending on the materials properties.

a- Direct heating: the principle of this heating is to put a sample (the target for heating) directly in microwave applicator (figure 1.4.a). Then, the result of the interaction between the microwave and the matter leads to the heating. In general, this type of

heating becomes more efficient at high temperature especially for a low absorbent material, such as the most of the ceramic materials.

b- Indirect heating: the principle of this heating is to use a good absorbent material (susceptor) which is exposed to microwave. Then, it is heated up and consequently heats the target material by infrared radiation (figure 1.4.b). This type of heating is similar to the conventional heating and is used in case of a transparent or low absorbent material.

Actually, a hybrid heating is an indirect one but in addition the sample becomes absorbent at a certain temperature, where the direct heating takes place.

Microwave heating had a success in the sintering field for a variety of ceramics, metals and composites materials. The difference between this technique and the conventional one resides in providing a volumetric heating, direct transfer of energy and rapid heating [12]. Comparing to the conventional heating, it reduces the energy consumption and time required; particularly for high temperature range where in general heat losses increase strongly with the temperature [13]. Hence, the microwave technique offers uniform heating that delivers better mechanical properties with lower environmental hazards, which are not observed in conventional treatment [5, 13].



Figure 1.4: Types of microwave heating

1.1.5 Microwave generators and cavities (applicators):

In the microwave processing field, it is known that the main tools for the microwave process are: microwave generators and microwave cavities.

1.1.5.1-Microwave generators:

Based on the applications [14], in general we can find four kinds of microwave sources and therefore four different generators:

- a- Magnetron: it is a microwave source which is the most usable and has a range of frequency between 1 and 30 GHz.
- b- Klystron: it is used as an amplifier for high frequencies (up to 100 GHz) and as oscillators for microwave relay but it is now limited for some applications such the modern particle accelerators.
- c- Gyrotron: it was developed in 1958 by Twiss and Schneider [15] the advantage of this microwave source is its high power (1 MW) and its high frequency (up to 300 GHz). It is generally used for plasma heating.
- d- Solid state generators: the invention of solid state transistors and its used in radios were the origin of the solid state microwave generators and it was proposed as a better alternative to the magnetrons. Its advantages are various comparing to magnetrons. It produces a very stable signal and it is operated at very low voltage. It has better shelf-life than magnetron and it is less noisy because the creation of microwave by solid state generators is based on the transistors instead of vacuum tubes in magnetrons. In addition, the solid state microwave has a range of frequencies whereas the magnetron has a fixed frequency [14].

1.1.5.2-Microwave cavities (applicators):

In order to optimize the energy produced by the generator and to get a better microwave absorption by the sample, a microwave cavity is required. It is metallic box which has special shape (most of them are rectangular) and dimensions. Depending on the dimensions, we can distinguish in general two main types:

- a- Single mode cavity: the feature of a single mode cavity is that only one propagation mode is available in the frequency range selected. It is important to note that an empty cavity (unloaded) with canonical shape such rectangular or cylindrical, has an available exact analytical solutions for the electric and magnetic field. When loaded the analytical solution has to be redeveloped to take into account the influenced of loaded material (shape and material properties) [16-17]. It is used in general for homogeneous heating of sample smaller than 1/8 of the wave length. These applicators are used in general in the fundamental research domain.
- b- Multimode cavity: in comparison to single mode cavity, a multimode cavity presents many propagation modes on a small frequency range delivered by solid state generator or at fixed frequency imposed by magnetron. The energy will be fed in the mode where the exciting frequency is matched. Consequently, when the sample has a large volume, more modes can be found therefore the heating becomes more efficient. Moreover, the distribution of the fields in this cavity is very complex which requires a wave stirrer in order to get a uniform electromagnetic field. These applicators are more used in industrial area where the amount of materials is important.

1.2 Solid state sintering

1.2.1 Definition:

The fabrication of ceramics by sintering process appears for a very long time about 12000 years ago (Jomon pottery in Japan) [18], it is considered as one of the oldest technique to make the ceramic components.

Solid state sintering in powder metallurgy is a process at a high temperature below the melting point that can elaborate a ceramic piece starting from the ceramic powder by bonding together its particles where the diffusion mass transport is activated. Hence, this process produces the ceramic components which have different microstructures such as porosities, grain size... It is not easy to find a simple definition of sintering but according to a definition given by Fang [19], the sintering is:

"A thermal treatment for bonding particles into a coherent, predominantly solid structure via mass transport events that often occur on the atomic scale. The bonding leads improved strength and lower system energy".

1.2.2 Stages of sintering:

Based on the evolution of the microstructures during the sintering process, it is normally described through three stages:

- a. Initial stage: this stage is preceded by an important early step where weak bonds between the particle contacts are developed due the green fabrication (often by compacting the powder under the pressure). Hence, the growth of the necks during the initial stage becomes rapid and the relative density achieves 65% in general.
- b. Intermediate stage: during this stage, the system forms a solid section crossed by a network of interconnected pores and the cylindrical pores shrink. The stack of particles can be described by a model of truncated cuboctahedron suggested in 1961 by Coble [20]. The elimination of the opened pores is activated during this step and the relative density can reach more than 90%.
- c. Final stage: this stage begins when the closed pores start to be removed and the grain boundaries to move by the diffusion mechanism. The densification becomes higher but its velocity decreases when the separation of the pores and the grain boundaries happens. The existence of a gas in solid phase can make the end of this process very difficult due to the opposite reaction of the gas which is the main blocking effect of the completed sintering. The evolution of sintering during the different stages is presented in figure 1.5.



Figure 1.5: The different stages observed during the sintering [19].

1.2.3 Basic principles and driving forces for sintering:

In thermodynamics, a change in surface energy of the system is established during the sintering. It is the main result of the interfacial energy which is the driving force of this transformation. The reduction in free energy dE between two particles in case of consolidated powder when the total surface area changes by dA, is given by equation 1.10:

$$dE = \gamma_{sv}.dA$$
(Eq.1.10)

where γ_{sv} is the surface energy at the interface between two phases (solid/solid and solid/gas). According to differential geometry theorem [21], if we consider that a volume element dV is removed from the system with the radii of curvature *a* and *b*, the equation 1.10 becomes:

$$\frac{dE}{dV} = \gamma_{sv} \cdot \frac{dA}{dV} = \gamma_{sv} \cdot \left(\frac{1}{a} + \frac{1}{b}\right)$$
(Eq.1.11)

The chemical potential μ , which drives matter transport and presents the thermodynamic works needed for the reduction of the free surface energy under the stress, is given by the equation 1.12:

$$\mu = \Omega \frac{dE}{dV}$$
(Eq.1.12)

where Ω is the atomic or molar volume. This relation is usually complex for polycrystalline ceramics because its pores are in contact with the grain boundaries [22]. For example, at triple

point where the pores are supposed to be spherical, Raj could simplify the expression to equation 1.13 [23]:

$$\mu = \Omega\left(\frac{2\gamma_{sv}}{p} + \frac{2\gamma_{gb}}{g}\right)$$
(Eq.1.13)

where p, g (which replace a and b in eq. 1.11) and γ_{gb} are respectively the radius of the pores, the diameter of the grains and the specific energy of the grain boundary.

The region between the particles formed during sintering is called neck region. The blue arrow in figure 1.6 shows the neck size x. The free surface energy is always lower at grain boundaries compared with solid-gas interface; during sintering process the surface area of the system have to be reduced by the benefit of the increase in grain boundary surfaces and therefore improve the densification [24].

In solid state sintering, the surface energy of the interfaces of solid/solid is lower than the solid/gas. Therefore, in order to improve the sintering, the decrease of the surface area of the interfaces solid/gas by the coalescence of the particles is needed.



Figure 1.6: The topologic change and neck evolution between two spherical particles during the sintering process.

The diffusion is the movement of the atoms in such direction and such rate and it results from the reduction in surface energy during the process. In solid state, the diffusion is slower than in liquids or gases and requires high temperature. This phenomenon is related to the kinetic behaviour of the sintering. Moreover, many laws of shrinkage were developed to explain this aspect and the relationship between the pores and the global volume [25, 26]. The forces applied to the solid/gas interface can be represented via the expression of the pressure by the well-known Laplace equation:

$$dP_{s/g} = P_s - P_g = \frac{2\gamma_{sv}}{r}$$
(Eq.1.14)

where P_s and P_g are the pressure in solid and gas respectively and the *r* is the local curvature of the surface.

Therefore, it results as:

- a- If $dP_{s/g} > 0$, the matter of the solid is under compressive stress. It means that the saturated vapour pressure is locally high and the concentration of the defects is less than the equilibrium state.
- b- If $dP_{s/g} < 0$, the matter of the solid is under tensile stress. It means that the saturated vapour pressure is locally low and the concentration of the defects is greater than the equilibrium state.

We can distinguish in a system of two particles six different mechanisms of diffusion in which three of them produce a microstructural change without shrinkage and are called nondensifying mechanisms (1, 2 and 3 in figure 1.7) and three of them induce densification (4, 5 and 6). Also, we have 3 types of volume diffusion (2, 5 and 6 in figure 1.7) then the surface diffusion (1), the grain boundary diffusion (4) and the last one is the vapour transport (3).



Figure 1.7: Six mechanisms of matter transport during the sintering [27].

It should be noted that the grain boundary (4) and the lattice (5) diffusions from the grain boundaries to the neck are the most important for the densification. The other mechanisms are responsible for the neck growth and the grain coarsening, they lead to a significant reduction of the sintering rate and the pores content.

On the other hand, it is also important to understand the main diffusion phenomena and their contributions to the sintering process and the effect of the material properties (powder, microstructure, grain size ...) on the total process. Unlike liquids and gases, the atoms cannot move easily in solid state and require a high temperature in order to activate the diffusion phenomena by increasing its kinetic energy. Thus, the possible diffusional paths expected through the solid at atomic scale, are shown in figure 1.8. It is known that the interstitial diffusion happens when the bonding between the atoms and their surrounding environment is weak and it is in general faster than the vacancy diffusion [27, 28].



Figure 1.8: Possible diffusional events by atomic motion: direct or self-exchange (a), ring type of rotation (b), vacancy exchange (c) and interstitial mechanism (d) [28].

Finally, the mechanisms of sintering are the result of the different diffusional events at atomic scale and are observed at large scale as a matter transport and as a volume reduction of the system. Moreover, the surface diffusion is a non-densifying aspect, and depends on the change of pressure associated to convex surface of the particle, and the concave surface of the neck. On the contrary, the volume and the grain boundary diffusions are known as densifying aspects. From a kinetic point of view, the neck growth (x) for each elementary mechanism (1, 2, 4 and 5) can be related to the grain size (a), the sintering time (t) and the physical parameters (table 1.1).

Sintering mechanism	Neck growth	Scale exponent α
Lattice diffusion from the	$_4 16D_l\gamma_sV_ma$	
grain boundary to neck (4)	$x = \frac{1}{RT}t$	3
Grain boundary diffusion from	$_{6}$ $48D_{b}\delta_{b}\gamma_{s}V_{m}a^{2}$	
the grain boundary to neck (5)	$x^{\circ} = \frac{1}{RT} t$	4
Surface diffusion from particle	$_{7}$ 56 $D_{s}\delta_{s}\gamma_{s}V_{m}a^{3}$	
surface to neck (1)	$x' = \frac{1}{RT}t$	4
Lattice diffusion from particle	$_{5}$ 20 $D_{l}\gamma_{s}V_{m}a^{2}$	
surface to neck (2)	$x^{*} = \frac{1}{RT}t$	3
D_s , D_b and D_l are the surface, grain boundary and lattice diffusion coefficients		
δ_b and δ_s are diffusion thickness of grain boundary and surface diffusion		
γ_s is the solid surface energy and V_m is the molar volume of the solid		

Table 1.1: Neck growth for various sintering mechanisms at initial stage [24].

1.2.4 The influence of the powder properties on the sintering:

The main factors which are generally taken into account during the sintering of ceramic materials and can lead or delay the process, are the grain size and the internal point defects of the matter.

1.2.4.1-Grain size

a) In the kinetic study of the sintering, the grain size is considered to be a very important parameter to increase or decrease the sintering rate. A relationship between the grain size and the densification rate and sintering time was suggested in 1950 [29]. Regarding the sintering of two kinds of powders with radii a_1 and a_2 , where $\frac{a_2}{a_1} = \lambda$, the relation between the sintering times t_1, t_2 to reach a given densification and λ , is given by:

$$t_2 = t_1(\lambda)^{\alpha}$$

(Eq.1.15)

where α is an exponent; its values are defined in Table 1.1.

b) Thus, the general sintering relation for the neck growth can be expressed as:

$$\left(\frac{x}{a}\right)^n = F(T)a^{m-n}t$$
(Eq.1.16)

For a given sintering state (x/a = constant) of different sizes, $a^{m-n}t$ must be constant and therefore $\alpha = n - m$. For example, the value of α is equal to 3 for lattice diffusion and takes different values according to the main mechanism (see table 1.1).

c) The densification rate is inversely proportional to the cube of the grain size for the lattice diffusion; its expression during the intermediate stage is [30, 31]

$$\frac{d\rho}{dt} = \frac{42D_l\gamma_s V_m}{RTa^3}$$
(Eq.1.17)

where ρ is the relative density.

In the case of grain boundary mechanism, the densification rate is inversely proportional to the fourth power of the grain size and is given by the equation 1.18:

$$\frac{d\rho}{dt} = \frac{427D_b\delta_b\gamma_s V_m}{8RTa^4} \left(\frac{1}{P_v}\right)^{1/2}$$
(Eq.1.18)

where δ_b is the diffusion thickness of grain boundary diffusion and P_{ν} is the fractional porosity at time t.

According to the different equations presented in this section, it is clearly seen that the sintering process is strongly influenced by the grain size and shape as well as by the temperature.

1.2.4.2- Point defects

In ceramics, there are usually three types of point defects, Frenkel, Schottky and electronic defects.

- a- Frenkel defect is a point defect in ceramics. It is a defect pair of an interstitial atom and vacancy (figure 1.9 (b), in black the cationic vacancy).
- b- Schottky defect is also a point defect and it forms in case of stoichiometric pair of cation and anion vacancies (see the figure 1.9 (a), in black the cationic vacancy, in red the anionic vacancy).
- c- The electronic defect forms when the intrinsic electronic disorder is present. In ceramics, the formation of free electrons and holes is the origin of this defect.



Figure 1.9: Schematic of Schottky (a) and Frenkel (b) defects [32].

Moreover, there are other kinds of defects which are called linear and surface defects. The linear defects are related to the dislocations presented in the ceramic structure which require a high strength to move. This aspect is possible when we apply a large force and stress on the ceramic. On the other hand, the origin of the surface defects is the missing bonding, the cracks and the geometric shape due to stress concentration.

Finally, all these defects can influence the behaviour of the sintering process. In addition, the presence of additives (like dopant) and the porosity in the bulk ceramic which are introduced during the fabrication is also an important parameter for an efficient sintering.

1.2.5 Activation energy and diffusion coefficient:

In thermodynamics, the concept of activation energy is the most important concept to determine the rate of a reaction under various conditions. The matter transport during the sintering can be described by a relationship that relates the matter flux to the transport coefficient and the driving force. In general, the diffusion coefficient which is a fundamental parameter is presented in the expression of the transport coefficient (equation 1.17). The approximation Fick's first law for diffusion in one direction is expressed as [33]:

$$J = -\frac{Dc}{RT}\frac{d\mu}{dx}$$
(Eq.1.19)

where J is the flux, D is the diffusion coefficient, c is the concentration per unit volume, x the direction along the diffusion and μ is the chemical potential.

Moreover in order to move and diffuse from a position to a neighbouring position, the atom requires certain energy. The path between two positions (starting and ending positions) is expressed by the activation energy. In the presence of driving force $\frac{d\mu}{dx}$, the existence of activation energy during the forward jump is more frequent than the backward jump which means that the atoms can diffuse easier in the direction of the driving force. Now, the energy barrier concerning the diffusion between two sites is influenced by the driving force. It results that the activation energy ΔE_A is much smaller in case of forward jump rather than backward jump. Thus, the probabilities of a forward jump (P_f) and the backward jump (P_b) is this case is given by:

$$P_{f} = \upsilon \exp\left(-\frac{\Delta E_{A} - \frac{d\mu}{dx}\frac{\tau}{2N}}{kT}\right)$$
(Eq.1.20)

$$P_{b} = \upsilon \exp\left(-\frac{\Delta E_{A} + \frac{d\mu}{dx}\frac{\tau}{2N}}{kT}\right)$$
(Eq.1.21)

where k is the Boltzmann constant, N is the Avogadro's number, τ is the interatomic distance and ν is the frequency of the atom (in solid $\nu \approx 10^{13}$).

The variation between these two expressions gives the real movement between atoms (net movement) ΔP_{f-p} . Comparing the difference between the two previous equations to equation 1.19, taking into account the equivalent unit of each parameter and considering only the first order terms of the obtained results, it becomes:

$$\Delta P_{f-p} \approx \frac{\upsilon \tau}{RT} \exp\left(-\frac{\Delta E_A}{kT}\right) \frac{d\mu}{dx} = (s^{-1})$$
(Eq.1.22)

Hence, the relation between the flux and the real movement is given by:

$$\Delta P_{f-p} = \frac{-J(g / s.cm^2)}{c(g / cm^3).\tau(cm)} = (s^{-1})$$
(Eq.1.23)

Thus, the relationship between the diffusion coefficient and the activation energy can be written by the following equation:

$$D = \upsilon \tau^2 \exp\left(\frac{-\Delta E_A}{kT}\right)$$
(Eq.1.24)

It is clear to conclude from the equation 1.21, the dependence of the diffusion mechanism and the activation energy. It is also important to note that the thermal energy due to the presence of high temperature is a supplied energy for the atoms to overcome the activation energy barrier of the system.

1.2.6 Experimental methods to determine the activation energy:

The main methods to determine experimentally the activation energies for nonisothermal sintering are the constant heating rate method (CHR) and the master sintering curve concept (MSC).

1.2.6.1- Constant heating rate (CHR)

This method was developed by Wang and Raj [34, 35], needing the shrinkage versus temperature and by using the relation given below:

$$\ln\left(T.\frac{d\rho}{dt}\right) = -\frac{-Q_A}{RT} - \ln g^{\alpha} + f(\rho) + C$$
(Eq.1.25)

where $Q_A = N.\Delta E_A$, *C* is a constant and the other parameters are the same defined in section 4. If we assume that the grains have the same size and the function of relative density is constant, we can simplify the equation 1.21 to:

$$\ln\left(T.\frac{d\rho}{dt}\right) = -\frac{-Q_A}{RT} + B$$
(Eq.1.26)

where *B* is a constant. Now, from the curve $\ln\left(T, \frac{d\rho}{dt}\right)$ versus 1/T a fixed heating rate and a

fixed density, we can deduce the activation energy which is equal to the slope of all these points (each rate and density).

1.2.6.2- Master sintering curve (MSC)

This technique was developed by Sun and Johnson and was based on the combined stage sintering model [36, 37]. The concept of this technique is to determine the densification of the sample for different thermal cycles. It links the linear shrinkage rate to the diffusion coefficients and to the microstructure. The linear shrinkage rate is given by the equation 1.23:

$$-\frac{dL}{Ldt} = \frac{\gamma \Omega}{kT} \left(\frac{\theta_l D_l}{g^3} + \frac{\theta_b \delta_b D_b}{g^4} \right)$$
(Eq.1.27)

where *L* is the initial length of the sample, $\frac{dL}{dt}$ is the linear change rate in one dimension, θ_l and θ_b are the geometric factors concerning the lattice diffusion and grain boundary diffusion respectively. Now, if we assume that the system has an isotropic shrinkage and only

one diffusion mechanism is dominated (lattice diffusion), we can simplify the equation by converting the linear rate to shrinkage rate:

$$\frac{k}{\gamma\Omega\delta_b D_0} \int_{\rho_0}^{\rho} \left(g(\rho)\right)^{\alpha} d\rho = \int_0^t \frac{1}{T} \exp\left(-\frac{Q_A}{RT}\right) dt$$
(Eq.1. 28)

where D_0 is the coefficient of diffusion. The left part of the equation describes the microstructural behaviour (density and grain size) whereas the right part depends on the sintering conditions (time and temperature).

Now, we assume that the right side of the equation is:

$$\int_{0}^{t} \frac{1}{T} \exp\left(-\frac{Q_{A}}{RT}\right) dt = \mathcal{G}(t, T(t))$$
(Eq.1.29)

The relation between $\mathcal{G}(t,T(t))$ and ρ is called the Master Sintering Curve, and the calculation of the activation energy can be done by finding the minimum deviation between the curves representing these two functions.

Now, we present in table 1.2, the values of the activation energies during conventional (CS) and microwave (MW) sintering calculated by Zuo et al [38] for alumina Al_2O_3 and zinc oxide *ZnO* using the two methods we have discussed in this section.

Method		Al_2O_3	ZnO
	Relative density	60-85	70-90
CHR	range (%TD)	528 ± 22	221 ± 7
	CS (KJ/mol)	440 ± 8	307 ± 8
	MW (KJ/mol)		
	Relative density	55-99	65-99
MSC	range (%TD)	538	214
	CS(KJ/mol)	534	289
	MW (KJ/mol)		

Table 1.2: Values of sintering activation energies for Al_2O_3 and ZnO using two methods.

From the table 1.1, it is clear that the values obtained through the two methods are mostly in good agreement and roughly similar. The activation energy determined by CHR method was for intermediate stage while that determined by MSC method was from the full densification stage. Actually, the results are very similar due to the fact that the shrinkage stage corresponds mainly to the intermediate stage where the dominant diffusion mechanism is presented.

1.2.7 Microwave effects:

During the sintering process, an additional force that have been claimed to accelerate and improve the diffusion mechanism is the ponderomotive force. Many studies [39-42] and explications were done in order to understand the contribution and the role of this microwave ponderomotive force which induces a migration of vacancies that leads to a mass transfer. Hence, the origin of this force is the interaction between the electromagnetic field and the free space charges of vacancies. The acceleration of the sintering of ionic materials results from the fact that the vacancies movement on the surface is more important than in the bulk. This explanation was proposed by Rybakov and Semenov in 1994 for nonthermal effect of microwave in case of ionic crystal [40, 41]. Four years later, they worked with Booske in a

common study based on the same hypothesis to explain the microwave effect in case of solid state ionic plasmas [42].

On the other hand, some experimental studies were carried out for zinc oxide and zirconia under a hybrid heating that combines the conventional and microwave heating. They show the dependence of the sintering rate and the density on the proportion of microwave power from the total heating power (see figure 1.10) [43, 44]. In other terms, the selective nature of microwave heating and its volumetric aspect induce a faster temperature rise and a vacancies concentration gradient within the target material which can improve the sintering process. It is important to mention that the temperature was measured at the upper surface of the pellet sample.



Figure 1.10: Normalized linear shrinkage of zirconia plotted as function of sintering temperature and the microwave power [43]. The sintering enhancement increases with microwave power.

In accordance with these considerations, Whittaker demonstrated in his work in 2005 concerning the diffusion in ceramics that the mass transport mechanism evolves preferentially along the electric field vector [45] where in another study regarding the orientation of pores under microwave heating has showed an elongation of the pores in the direction of a linearly polarized microwave field [46] (see figure 1.11). Brosnan et al have observed in his study concerning the sintering of alumina a reduction of sintering temperature [47]. The temperature was 1280°C in the presence of microwave whereas it reached 1480°C for a pure conventional heating. Basing on this study, Raj et al [48] considered that the contribution of the ponderomotive force on the sintering process is negligible in case of oxide materials. On the other hand, the calibration method of temperature in the Brosna's work raises a doubt about the validity because the value of the emissivity used in microwave oven was calculated in classical furnace. Thus, the hypothesis of Raj et al about the low effect of the ponderomotive force needs evidence and it raises a doubt. Moreover, he also suggests an explication of the microwave effect based on the dielectric losses concerning the grain boundary region. Raj explains that there is a difference in temperature between the core of the grain and its boundary, and this difference is the origin of the higher diffusion rate [48]. Johnson has

examined this concept with care and he showed that this difference for alumina is very low to contribute a significant effect on the global process $(10^{-8} \,^{\circ}\text{C})$ [49]. Another study shows an interesting effect of the microwave field at the grain boundary region where a huge electric field norm was obtained. It is a new approach that describes the microwave effect as energy gradient which leads to an important mass transfer based on the ponderomotive force and the creation of the plasma [50].



Figure 1.11: Histogram showing the pores orientation in case of microwave (a) and conventional sintering (b) of zirconia ceramics [46]. The number of pores oriented perpendicular to the electric field is more important (angle 0 and 180°) whereas those parallel have less amount (angle 90°).

From a theoretical point of view, several models have been proposed to explain the nonthermal ponderomotive effect, these models are based on the phonon excitation, the concentration gradient at grain boundary and the heat aspect. Regarding the phonon model, the radiation energy couples at low microwave frequency elastic lattice oscillations can generate a non-thermal phonon distribution that enhances ion mobility and therefore the diffusion rates [51, 52]. In 2012, a theoretical model was proposed by Rybakov et al [46, 53], and has been confirmed by the experiments, in which it describes the movement of pores and the densification by numerical simulation. In 2013, Olevsky et al [54] showed in their simulation work that the electromigration flux is maximum near the inter-particle contact (see figure 1.12). Additionally, they show that the compressive stress is proportional to the intensity of the electric field at the neck region and inversely proportional to the ratio of diffusivities of the grain boundary and surface.

The figure 1.12 presents the distribution of the electric field between two particles having a diameter of $20 \,\mu\text{m}$.



Figure 1.12: Concentration of the electric field at the neck region between two particles (particles radius = $10 \mu m$) [54].

According to Rybakov et al, the motion of the vacancies is influenced by an applied electric field, and then the flux of vacancies J is given by [55]:

$$J = -D^{(V)}\nabla C_V + D^{(V)}C_V \frac{qE}{kT}$$
(Eq.1.25)

where C_V is the concentration, q is the effective electric charge of the vacancies, E is the electric field norm and $D^{(V)}$ is the diffusivity. This equation takes into account the two sorts of vacancies, the diffusion and the drift parts.

However, under microwave sintering conditions the magnitude of the drift part exceeds the diffusion part by 2-3 orders [55]. The concentration of vacancies accumulates in thin layer near the surface when the electric field oscillates between two opposite directions where it drives the vacancies into the bulk. Hence, the evolution of the porosity Θ due to ponderomotive force was also reported (figure 1.13) in this simulation work. According to the simulation results obtained, the ponderomotive microwave effect contributes significantly to the sintering process.



Figure 1.13: Evolution of porosity due to ponderomotive effect (a), capillary stresses (b), and their combined effect (c) [55]. τ is the characteristic time of densification.

It is important to know that the grain size = 10^{-6} m, the initial value of porosity and electric field are respectively 0.4 and 30000 V/m.

Finally, the microwave effect have been studied since around 20 years and the various studies especially those through the simulation approaches show an effect of microwave on the sintering. The influence of this effect can be negligible or important depending on the case, so it is easy to be evaluated. The nonthermal effect of microwave sintering is an additional force that leads in general to a better sintering process.

1.3 Cerium dioxide (ceria)

1.3.1 Structural and physical properties of ceria

Ceria or CeO₂ has a fluorite structure, space group Fm3m. The oxygen anions form a simple cubic structure, wherein the cations of cerium (IV) occupy the half of the cubic sites. In other words, we can reverse the role between the cations and anions, and then, Ce^{4+} cations form a face centred cubic subnetwork and O²⁻ anions occupy all the tetrahedral sites (see figure 1.14). The lattice parameter of ceria is equal to 5.410 Å, the cerium Ce⁴⁺ has an ionic radius of 1.03 Å and the radius of the interstitial site is 1.01 Å [56, 57].

Ceria has important redox properties. Indeed, it has a very good oxygen storage capacity. This explains its use in electrochemical sensors to measure the oxygen pressures [58]. Its colour is pale yellow and it is probably due to charge transfer Ce^{4+} / O^{2-} .



Figure 1.14: unit cell of CeO_2 , Ce^{4+} in green and O^{2-} in red.

Moreover, ceria has the redox couple Ce^{3+}/Ce^{4+} , which makes it effective for the oxidation of hydrocarbons to carbon dioxide [59] and as photochemical bleaching in some luminescent materials [60]. In addition, it is used as catalyst carrier especially for the automotive emission gases [61]. Its hardness and compact design make it a good cleaning and polishing agent for glasses [62]. It is also known as decolorized of classical glass. Under an oxygen pressure lower than 10^{-3} Pa, ceria presents another structure than the faces centred cubic structure such the body centred cubic structure whereas it doesn't have a phase transition even at very high temperature [63]. It is also used as UV filter (skin cancer), as electrolytes in SOFC (solid oxide fuel cell) technology and as non-radioactive uranium dioxide simulant, for the nuclear waste recycling technology [64, 65]. Some physical properties of ceria are listed in table 1.3.

Physical property	Value
Density	7.22 g/cm ³
Melting point	2750 К
Specific heat	460 J/Kg.K
Thermal conductivity	12 W/m.K
Refractive index	2.1 (visible) 2.2 (infrared)
Relative dielectric	11
constant (0.5-50 MHz)	
Young's modulus	165x10 ⁹ N.m ⁻²
Hardness	5-6 GPa
Poisson's ratio	0.3

Table 1.3: Some physical properties of pure CeO₂ [63].
1.3.2 Thermodynamic aspect

As we have mentioned in the last section, the stoichiometric ceria has no phase transition even at very high temperature whereas the non-stoichiometric ceria has different phases under specific conditions of pressure and temperature. We present the phase diagram of the ceria in figure 1.15 below. It shows that for oxygen pressure in the range of 10^{-9} up to 10^{-3} Pa [66]:

- Only one phase is presented for a temperature higher than 953 K and a stoichiometric variation x in the range of 0-0.2.
- Several intermediate phases C_xO_{2x-2} can be presented for a temperature lower than 953K and for x less than 0.2.
- Some phases can be presented for x close to 0.3 and for a temperature greater than 1073K.



Figure 1.15: phase diagram of cerium dioxide [67].

1.3.3 Defects and vacancies

The defects are presented when the CeO₂ is reduced to CeO_{2-x} as a Ce³⁺. According to Kröger-Vink notation [68], as Ce³⁺ has one negative charge compared to the classical lattice, therefore, it is typically written as Ce'_{Ce} . Many studies show that these substitutional negative

defects are balanced by Ce^{3+} which are moved to interstitial sites or by oxide ion vacancy V_{o} [69]. Recently, it is well known that oxygen vacancies are the main compensating defects in such nonstoichiometric CeO_{2-x} [70]. Faber et al have showed in their study using x-ray diffraction that the quantity of interstitial Ce is not more than 0.1% of the total defect concentration in CeO_{1.91} [71]. The reduction of Ceria is usually written:

$$2Ce_{Ce} + O_{O} = \frac{1}{2}O_{2}(gas) + 2Ce_{Ce} + V_{O}$$

(Eq.1.26)

Moreover, we can dope ceria either with lower valency metal oxide to introduce more oxide vacancies or with higher valency metal oxide to remove the vacancies. Hence, the value x depends only on the oxygen partial pressure P_{O_2} if we assume that the defects don't interact between each other [63]. And then, in case of undoped ceria:

$$x = c.(P_{O_2})^{-1/6}$$

(Eq.1.27)

And for doped ceria:

$$x = c.(P_{O_2})^{-1/4}$$
(Eq.1.28)

where $x = \frac{[Ce_{Ce}]}{2}$ and c is constant.

1.3.4 Electrical conductivity

The model presented in the previous section concerning the oxygen vacancies and electrons is also applicable for the determination of electrical conductivity of ceria σ_i . In general, it can be expressed for a solid having charged species a_i which has number of charges z_i and concentration c_i as:

$$\sigma = \sum_{i} e z_i c_i \mu_i$$
(Eq.1.29)

where *e* is the elementary charge and μ_i is the mobility of charged species. For ceria, the total conductivity which is the sum of electronic and ionic conductivities is written:

$$\sigma_{t} = \sigma_{e} + \sigma_{i} = e\mu_{e}z_{e}\left[e^{i}\right] + e\mu_{V_{O}}z_{V_{O}}^{"}\left[V_{O}^{"}\right]$$
(Eq.1.30)
36

By taking into account the concept of electroneutrality (equation 1.31) and the equilibrium constant (equation 1.32):

$$\begin{bmatrix} e' \end{bmatrix} = 2 \begin{bmatrix} V_o \\ 0 \end{bmatrix} \text{ and } K = \begin{bmatrix} e' \end{bmatrix}^2 \begin{bmatrix} V_o \\ 0 \end{bmatrix} (P_{o_2})^{1/2}$$
(Eq.1.31) (Eq.1.32)

In practical [72, 73], according to the $(P_{O_2})^{-1/n}$ laws, the conductivity must depend on the oxygen pressure with n = 4 or 5 and, by combining the explication concerning the additional ionic equilibrium of oxygen vacancies, σ_t is proportional to $(P_{O_2})^{-1/4}$ whereas theoretically it is proportional to $(P_{O_2})^{-1/6}$.

Actually, the properties of ceria have an important role in the microwave process especially its ionic conductivity. The influence of the ionic conductivity on the microwave process will be presented in chapter 4 where the dielectric properties of ceria will be reported.

1.3.5 Studies concerning the sintering of ceria

We have found a few studies regarding the conventional sintering of ceria and even lesser regarding the microwave sintering of it. The studies concern the conventional and microwave sintering of ceria are presented in this section.

Regarding the sintering of ceria, a study has been done recently using high temperature environmental scanning electron microscope in situ HT-ESEM [74]. This technique shows the evolution of grain growth and pore elimination rate and the change in the grain boundaries with a resolution of 10 nm. The figure 1.16 shows the progression of conventional sintering at 1400 $^{\circ}$ C for different heating time. Thus, it was also possible to determine kinetic parameters such as grain growth, grain boundaries velocities and pore elimination rates.



Figure 1.16: Evolution of ceria sintering versus the real heating time [74].

Zhou et al have studied the effect of the redox reaction of ceria nanopowders on the sintering behaviour [75]. They show that at high sintering temperature ($1500-1700^{\circ}C$), CeO₂ transforms into Ce₂O₃, and delivers oxygen in gaseous form. In addition, the loss of mass due to the oxidation-reduction decreases with a wide increase in particle size. The dependence of the preparation powder method on the improvement of the sintering was reported by Heintz and his co-worker in 1986 [76]. It shows that the choice of the dispersion medium and centrifugation recovery improve the sintering by 8% for ceria prepared from hydrazinate oxalate compared oxalate alone.

Moreover, regarding the sintering of doped ceria Ahmad et al, shows recently in 2015 that the density, grain size and lattice parameter change significantly for Mg-doped and Sr-doped ceria with sintering temperature [77]. The values of relative density and the grain size for the different samples and temperatures are listed in the table 1.4.

Sample	Temperature	Relative	Grain size
	(°C)	density %	(µm)
CeO ₂	1200	86	5.9
CeO ₂	1300	90	5.7
CeO ₂	1400	93	5.5
$Ce_{0.99}Sr_{0.01}O_{1.995}$	1300	91	3.8
Ce0.99Sr0.01O1.995	1400	94	3.0
Ce _{0.99} Mg _{0.01} O _{1.995}	1400	92	6.3

Table 1.4: Values of grain size and relative density for different samples.

On the other hand, it was not possible to find in literature a study concerning the microwave sintering of pure ceria. Some authors have studied the behaviour of doped ceria under microwave sintering.

A study concerning ceria nanopowders in the presence of poly vinyl pyrrolidone (PVP) shows that a full density is achieved via microwave assisted hydrothermal technique. The important of this work is that the sintering temperature is reduced to 1070 °C in air and the sintering time to 10 minutes [78]. The variation of the densification rate as function of temperature and PVP amount is presented in figure 1.17.



Figure 1.17: Densification rate as function of temperature and molar ration of PVP amount [78].

Moreover, a multiple elements doped ceria under a rapid microwave sintering has been studied by Chang et al [79]. They have obtained a short processing time and lower temperature and then it was possible to modify the grain boundary resistance and the vacancies mobility of oxygen for the different ceria-based electrolyte.

Another work by Acharya [80] presents a comparison between conventional heating and microwave heating of dysprosium doped ceria nanopowder. The microwave sintering gives a high density material with homogenous grain growth and grain size of 400 nm whereas the conventional sintering produces nonhomogeneous grain growth and grain size in range of 1100 up to 1400 nm. The ionic conductivity obtained during the microwave sintering was higher and the activation energy was lower than in conventional sintering.

1.4 Conclusion

The comparison of the different works presented in this chapter and in addition the basic aspects of sintering by microwave process show an interest to use of microwave in order to improve the sintering and a need to understand the electromagnetic effect on ceria. Thus, in this work, we will try to find an adaptable system to determine such ceria microwave properties and therefore to sinter it in better conditions. The simulation work is also necessary to understand the electric field effect on the sintering of ceria.

Résumé en français : Généralités et bibliographie

Le frittage des matériaux par chauffage micro-ondes est un procédé très complexe dans lequel des interactions et des phénomènes multi physiques ont lieu. La compréhension de ce procédé est indispensable dans la vision du développement de cette technologie. Dans ce chapitre, les généralités du procédé d'élaboration et de consolidation de matériaux pulvérulents par frittage ainsi que la modélisation de la diffusion de matière et l'interaction de la matière avec les micro-ondes sont présentées. Les recherches qui concernent le frittage conventionnel et micro-ondes des céramiques d'une manière générale ainsi que les propriétés physico-chimiques de l'oxyde de Cérium sont aussi présentées : Il en résulte qu'un faible nombre d'études relatives au matériau Cérine ont été trouvées.

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Chapter 2: Dielectric and thermophysical characterisation methods

In this chapter, the elaboration of the cerium oxide samples with different densities is presented first. Then the experimental setups and associated methods to determine the effective complex permittivity (or effective dielectric properties) and the thermal properties of cerium oxide (CeO₂ ceria) are described. Moreover during the sintering process, the temperature increases from room temperature up to the ideally sintering temperature. Also, since during the densification of the sample shrink and the microstructure changes from a porous green body of weakly bounded individual particle to a solid monolithic microstructure, it is also necessary to evaluate the effect of the temperature but also the effect of the porosity (distributed air volume fraction) on the permittivity and on the thermal conductivity and thermal diffusivity in order to allows to model as accurately as possible the microwave assisted sintering. The resulting experimental values will be presented in Chapter 4. These values will be further used in Chapter 6 as inputs in the electromagnetic heating simulation by a finite element (FE) solver, in an attempt to quantify the volumetric heat distribution within ceria in the course of microwave assisted sintering.

2.1 **Preparation of ceria pellets by powder metallurgy**

A commercial powder of cerium dioxide (CER (IV)-OXID 99.9%, Aldrich), with a particle size less than 5 μ m, and with theoretical density 7.13 g/cm³ was used. The as-received powder was mixed with additive binders (PVA and PEG) used in ceramic powder technology before the compaction. Pellets were pressed uniaxially in a tungsten carbide die (see figure 2.1) with 12 mm diameter with different values of pressure. The height of the green samples was fixed to 2 mm for further thermal analysis and 18 mm for dielectric measurements.



Figure 2.1: Photo of the tungsten carbide die used for the preparation of the samples. The specimens were formed in an electromechanical uniaxial press (INSTRON 5584). An Intron's Bluehill software was used for the control and the data acquisition. In the following step the pellets were heated up to 600°C and maintained for three hours in order to remove the binders. The green densities of the series were: 56.22% for serial 1, 59.47% for serial 2, 59% for serial 3, 59.08% for serial 4, 59% for serial 5, 62.25% for serial 6 and 69.26% for serial 7. Then the pellets were heated in air at 5°C/min up to sintering temperatures (1050, 1250, 1500 and 1600°C) which were maintained for various dwell time (0, 1, 3 and 4 h) in order to cover a porosity range from 3.68 up to 44.33 vol %. For each series three to five samples were prepared, only one of them was used for thermal properties measurement (see table 2.1). The porosity was determined using Archimedes' method. After sintering, the different series of samples with their forming conditions and their densities are presented in the table 2.1.

Serial Number	Pressure (MPa)	Sintering Temperature (°C)	Dwell time (hours)	Relative density (%) of samples for the measurement of thermal properties	Relative density (%) of samples for the measurement of the dielectric properties	Standard deviation (%)
1 (4 samples)	30	1050	4	55.67	56.59	0.48
2 (4 samples)	50	1250	0	59.29	62.40	1.46
3 (4 samples)	50	1400	0	65.50	66.87	0.67
4 (3 samples)	50	1500	0	73.63	-	1.75
5 (4 samples)	50	1500	1	-	87.42	2.48
6 (5 samples)	50	1500	3	89.92	90.27	2.25
7 (4 samples)	300	1600	3	96.32	95.48	0.41

Table 2.1: Series of ceria samples with their conditions and final densities.

The figure 2.2 shows the two different sizes of samples, the short one is used for thermal measurement and the long one is used for for dielectric measurement.



Figure 2.2: Photo of two samples of ceria.

2.2 The dielectric measurement methods

Among the classes of methods developed for the determination of the dielectric permittivity, some are based on resonators others on open space or also on transmission lines measurements. Available methods are numerous and cover a large range of frequencies from DC up to the terahertz region.

These methods have been used for the characterization of different types of materials such as wood, ceramics, plastic, liquids, and also living tissues [1-3]. The selection of the most suitable method is directed by considering a priori the type of materials (strong or weak absorbent), its state (liquid, monolithic solid, powdered solid, etc....), the accuracy of the measurement required. This choice is further limited by the frequencies range and the temperature range of interest.

In this section a brief introduction of two methods which were used in this work will be presented. The first is based on an open coaxial structure ("dielectric probe kit"); it allows the evaluation of the material under test (MUT) over a broad and continuous frequency range. The second, more sensitive and precise, exploits only a discrete set of resonating frequencies fixed by the geometry of a metallic enclosure (resonating cavity or resonator).

2.2.1 Coaxial probe method:

2.2.1.1-The setup:

The measurements are done using the open end of a coaxial probe (fig 2.3) which is connected to a vector network analyzer (VNA 8720D Agilent/ HP).

This method relies on the changes in phase and the amplitude of the reflection coefficient (the ratio between the emitted to the reflected microwave signal) in presence and absence of the sample at the open end of the coaxial line. The effective complex dielectric permittivity is automatically calculated by the proprietary Agilent software [4, 5].



Figure 2.3: The probe kit from [4], a draw of a cylindrical sample is added to show how the measurement was made.

The measurements are made at room temperature for a dense sample (95.5% t.d) for a range of frequencies from 200 MHz to 20 GHz. The calibration using the three standard kits? in this range of frequencies was made at the beginning to optimize the noise and improve the measurement. The whole system is presented schematically in the figure 2.4.



Figure 2.4: Schematic of the end-of-coax probe method (R is the reflected power).

2.2.1.2-Accuracy and limitation of the method:

This method requires and assumes a perfect contact surface between the probe and the sample. It is adapted essentially to liquids and perfectly flat homogenous solid. This method belongs to the broad band methods and lacks sensitivity when measuring low loss material (loss tangent < 0.5) as in the case of Ceria. This method is less accurate at high frequency. For

regular cases, the typical accuracy of this method is expected about 5% for both, real and imaginary part of the dielectric permittivity. This method was selected because it is simple, doesn't require a complicated setup and covers a large range of frequency.

Two additional issues come from the sample preparation: first cerium oxide samples produced by powder compaction and sintering remain porous and biphasic (air and matter). Second, the surface resulting from sintering can be warped and rough whereas the measurement requires surfaces as flat as possible. Therefore, the roughness must be less than $\pm 2.54 \mu m$ (100 μ in) [4].

2.2.1.3-Sample surface warping and roughness characterisation:

In order to reduce the error of our measurement using the probe kit, we analyze in this section the topography of the sample using a 3D laser confocal microscope (Keyence) before and after the polishing and the surface of probe face. Thus, we polished the sample's surface using a simple ceramographic procedure (SiC paper grit 2000, followed by a carefull washing to avoid the presence of SiC residue. The figures 2.5 and 2.6 show the roughness at the surface of an as-sintered sample (95.5% t.d) and then for the polished sample respectively.



Figure 2.5: Surface topology for the densest (95.5%) sample as sintered: 3D map

The surface topology of the sample's surface shows a significant roughness of about 3.33 μ m, a wave shape of surface is seen in the figure 2.5. It is important to note that the presence of thin pics in this figure is the consequence of the artifacts due to the detection of the laser radiation on the surface. The measurements were repeated at least twice.



Figure 2.6: Surface topology for the polished sample: 3D map.

The surface topology of the polished sample in the figure 2.6 shows a flat surface where the wave shape disappears, the measured roughness is equal to 0.29 μ m. Therefore, after the polishing, the roughness Ra decrease from 3.33 μ m to 0.29 μ m which is required one for a good measurement.

The 3D surface map in figure 2.7 shows that the probe has a low roughness; the measured value of roughness was 0.97 μ m (the surface seen in blue presents the polymer part of the coaxial piece while its metal part is presented in red). Therefore, we don't expect a significant error on the obtained values of ε' due to the roughness. Nevertheless, the error on the measurement can be due the contact between the probe and the sample.



Figure 2.7: Surface topology for the probe face: 3D map.

2.2.2 Resonant cavity method

As previously said, in order to determine the dielectric properties as function of temperature, we need to develop a device to perform these measurements. In a first step the device and the issues will be presented and secondly the description of methodology will be exposed.

2.2.2.1- Description of the setup:

The measurement setup consists of five parts:

- 1) A sample holder (quartz crucible $Ø_{in}9.7-Ø_{out}12 \text{ mm x } 60\text{mm}$), inserted in a quartz tube ($Ø_{in}13-Ø_{out}17 \text{ mm}$), with atmosphere control
- 2) A high temperature MoSi₂ tubular furnace (SuperThal Mini MS26, Kanthal, Sweden) powered by a DC source (TDK Lambda 1500W)
- A water cooled cylindrical microwave resonator (Aluminum, Ø_{in}85 mm x 17mm height) with two openings (Ø_{in} 17mm) connected to a Vector Network Analyser (HP8720D)
- 4) A linear stage (A-LST020D, ZABER) assuring the translation of the sample from the furnace to the microwave resonator.
- 5) A LabViewTM interface (fig 2.12)



Figure 2.8: High temperature dielectric measurement system (furnace + resonator) (EMPA, Thun).

The figure 2.8 shows the coaxial cable (blue), the K-thermocouple (orange), on the upper part of the bloc of the the furnace which is related to the cavity in the bottom.

In order to facilitate the measurement of the effective complex permittivity, an automation program under LabViewTM was created to control the furnace temperature and the microwave measurement. This program consists of three routines:

- 1) A PID heat controller (*proportional-integral-derivative* controller).
- 2) The transfer of the sample from the furnace to the measurement resonator.
- 3) The calculation of ε_r and ε_r using an analytical model (see section 2.2.2.4).

Typical two operational steps of the measurement system are schematized at figure 2.9: At each desired temperature the bloc furnace-cavity is briefly moved vertically to place the sample in the microwave resonator and the change in reflection coefficient (S11) is measured. The furnace is moved back to the initial position, and until the next targeted temperature is reached. Typically 100°C steps are used up to 1000°C, at each temperature a dwell time of 10 min is observed before the sample is transferred and measured.



Figure 2.9: Schematic shows the developed system for the dielectric measurement.

2.2.2- Temperature control by PID:

The thermal conductivity of a powdered sample can be three orders of magnitude inferior to a bulk sample of the same material. In the vertical furnace configuration used, heat losses by convection and radiation are significant. The heating schedule of the sample is lagging compared to that of the furnace; moreover the sample temperature is expected to stay always inferior to that of the furnace. The use of a thermocouple closed to the sample is not compatible with the microwave measurement.

So the sample temperature can only be estimated by running firstly a calibration experiment with two thermocouples placed next to the sample without performing the microwave measurement. The positions of these two thermocouple wires on the sample are presented in the figure 2.10, the first one is close to the up side (position 1) of the cylindrical sample, and the second one is close to cylindrical surface (position 2).

During the measurement, this calibration is used to estimate the effective temperature onto the surface of the sample based on the furnace temperature. The temperature difference obtained after 10 minutes at each step is less than 5° C through the sample (between position 1 and position 2) itself and less than 15° C between the sample (position 2) and the furnace.



Figure 2.10: Schematic shows the positions of the two thermocouple wires on the sample

This temperature difference is the minimum that we could get and its effect on the measurement remains acceptable (less than 15° C). An example of this calibration is shown in figure 2.11 for a sample having a low densification (56.5% t.d). The figure 2.11 shows a low difference in temperature between both thermocouple positions close to the sample, and a temperature offset from the target temperature larger for lower temperatures than at higher temperatures.



Figure 2.11: The variation of the temperature in time for three different positions of the thermocouples.

In order to control as well as possible the temperature schedule, we have developed a LabVIEW interface. A PID specific procedure was developed to control in a way which obliges the system to follow certain instructions. Here, in case of heating, we generate an output signal which is the electric current of the furnace. This controller takes into account the temperature of the sample and compares it to the required instruction (the target). The values of the three tuning parameters are fixed after several trials to get an optimized and suitable heating procedure.

This gives us a fast slope of heating and a good stability at the dwell with a very small fluctuation. Hence, the values which were used are:

- 20 for the proportional gain.
- 3 seconds for the integral time.
- 30 seconds for the derivative time.

A print screen of the LabVIEW interface used is presented in the figure 2.12.



Figure 2.12: The LabViewTM interface used during the measurement.

The figure 2.12 shows the different parameters that can be modified before the beginning of the measurement: the maximum temperature, number of steps, the PID gains

When the hot sample is transferred into the water cooled microwave resonating cavity its temperature is falling. The figures 2.13 and 2.14 show the exact recorded point at which the dielectric measurement was taken at around 100°C and 1000°C respectively. The measured temperature concerning the first step was 89°C which is 11°C less than the target temperature (100°C). Whereas, for the last step (1000°C) where the heating of the furnace has been

limited to 960°C due to the furnace safety voltage, the corresponding temperature was 940°C which is 20°C less than the furnace temperature and 60°C less than the target temperature (1000°C). It is important to know that for the other heating steps the difference in temperature was less than 15°C.



Figure 2.13: The variation of temperature around 100°C and the point at which the measurement was done (in red circle).



Figure 2.14: The variation of temperature around 1000°C and the point at which the measurement was done in red circle.

2.2.3-Principle of the method, its setup and its range of applicability:

a- Principle:

The resonant cavity method is limited to only few discrete frequencies corresponding to the Eigenmodes of the resonator. Moreover, this method is more appropriate to low loss material such as ceria [6].

The reflection coefficient (S11) which is the ratio of the reflective wave power to the incident one was measured using a VNA (frequency interval 1.5-2.7 GHz, number of point 1601, linear sweep 0.8 s). One port calibration is carried out before the measurement [7]. The shift of the resonant frequency and the change in quality factor were extracted from the measured S-parameters based on a method proposed by Kajfez [8].

The principle of the measurement is based on the fact that the introduction of a sample in a resonator affects its resonance. The changes in the resonance frequency position and full width half maximum (FWHM) are related to the position, the volume and effective dielectric properties of the sample (see figure 2.15). The figure 2.15 presents the variation of the reflection coefficient S11 as function of frequency in case of empty cavity (in black), with quartz tube (in red) and with a ceria sample (in green).



Figure 2.15: a) Change in resonance frequency due to the presence of the sample. b) definition of resonance frequency (ω_0) and FWHM ($\Delta\omega$)

From these results the quality factor and the resonant frequency mode can be easily determined (figure 2.15 b). Indeed, the minimum power reflection coefficient gives the resonant frequency ω_0 and the full width half maximum $\Delta \omega$ (FWHM) give the quality factor Q of the cavity (Equation 2.1):

$$Q \approx \frac{2\omega_0}{\Delta\omega}$$
Eq. 2.1

b- Range of applicability:

One major assertion is the Eigenmode to be considered. If the cavity loading is negligibly small (filling factor $<10^{-3}$), we can assume that the Eigenmode doesn't change when the sample is introduced. In our case, the volume fraction of the sample into the the cavity (or filling factor) is significant (in our case 6.10^{-2}), then we can expect to be out of the validity range of the cavity perturbation method and even that totally different Eigenmode set might result. In the present work an attempt of results analysis is based on the theory of the cavity perturbation method. The effect of the sample/cavity volume ratio has been studied in order to investigate the accuracy of the measurement of this technique. It has been reported that this factor has a significant influence on the measurement of the dielectric permittivity and loss tangent [9-11]. The verification of the mode shifting in the cavity should be carefully addressed to ensure reliable results (see §2.2.2.4b).

2.2.2.4- Resonance measurement and calculation of \mathcal{E}_r and \mathcal{E}_r using model for TM₀₁₀ mode:

*a- Permittivity calculation attempt using cavity perturbation and TM*₀₁₀ *mode*

The table 2.2 shows the measured values of resonance frequencies and calculated quality factors for the empty cavity and the cavity loaded with four standard materials of known geometries and dielectric properties. The variations in quality factor and resonant frequency are related to the dielectric properties of the samples. The next step is to solve the inverse problem starting from the experimental values relation to find out the permittivity.

Sample	Resonance frequency (GHz)	Quality factor	
Empty cavity	2.634	1048.45	
Diamant MBD4	2.496	102.02	
Al	2.246	119.98	
SiC F100	2.334	32.95	
SiC F360	2.342	41.31	

 Table 2.2: Values of the resonance frequencies and quality factors of the empty cavity and with the 4 standard samples at room temperature

To extract the effective complex permittivity of the samples materials (the dielectric constant ε_r and the loss factor ε_r) from these experimental values, we try first to apply the cavity perturbation theory based on the TM₀₁₀ mode. For the empty cavity this TM₀₁₀ mode is found at 2.634GHz (close enough to the frequency of interest 2.45GHz).

The mathematical model based on the cavity perturbation model used for the calculation of the dielectrical permittivity for a TM_{010} cavity was suggested by McNeal et al. The complex permittivity is given by equations 2.2 and 2.3 [12]:

$$\varepsilon_{r} = 1 + 0.539 \cdot \frac{V_{c}}{V_{s}} \frac{f_{0} - f_{s}}{f_{0}}$$
(Eq.2.2)
$$\varepsilon_{r} = \frac{0.539 \cdot V_{c}}{2\varepsilon_{r} V_{s}} (\frac{1}{Q_{s}} - \frac{1}{Q_{0}})$$
(Eq.2.3)

where f_0, f_s, Q_0, Q_s are respectively the resonance frequency and the quality factor of the TM₀₁₀ mode of the cavity without and with sample. V_c, V_s are respectively the volumes of the cavity without and with the sample.

 Q_0 of the cavity depends on the initial conditions of the measurement (the initial temperature of the cavity and the calibration of the VNA).

The calculated values of the dielectric properties using $TM_{010}(\varepsilon \text{ cal and } \varepsilon \text{ cal })$ and those by the dielectrometer (ITACA-Dimas system) ($\varepsilon \text{ ref and } \varepsilon \text{ ref })$ for standard samples are presented in the table 2.3.

Sample	εˈref	ε "ref	ε cal	ε "cal
Diamant MBD4	3.15	0.01	3.16	0.002
Al	11.41	0.13	7.08	0.02
SiC F100	9.06	1.48	5.70	0.10
SiC F360	8.15	1.04	5.58	0.08

Table 2.3: Values of the standards samples (by ITACA-Dimas dielectrometer system) and calculated dielectric properties using cavity perturbation for the TM_{010} mode at room temperature.

Typically, the measurement error using the swept-frequency method is less than $\pm 5\%$ for ε_r and $\pm 15\%$ for ε'' due to the technique itself [8], whereas the repeatability of the calculation was satisfactory in which the error was less than $\pm 1\%$ for both parameters. Additionally, at high temperature, this measurement accuracy might be further limited by the existence of convection phenomena of air during the measurement stage. Except for diamond powder (Diamant MBD4) the values obtained by using this approach are about the half of the reference values for the real part and about 1/10 for the imaginary part. This confirms the limitation of the cavity perturbation method for large filling factor especially marked for high permittivity materials.

b- Effect of the volume fraction of the cavity filled by the sample: filling factor

In order to examine the continuity of frequency shift due to the presence of the sample, a series of measurements was made while a cylindrical sample of ceria with a total height of 20 mm is inserted gradually in the cavity in 2mm steps.

The figure 2.16 shows the variation of the resonance frequency as function of the penetration of the sample inside the cavity (from 0 mm where the sample is just outside until 20 mm where it runs through the whole cavity).



Figure 2.16: The shift in resonance frequency versus the height insertion of the sample (0 to 20 mm).

From 0 to 8mm insertion height, the resonance frequency decreases as expected due to the addition of matter. As the sample is pushed further a discontinuity occurs and suddenly the frequency decreases. As the sample is inserted coaxially to the cavity, it occupies the region of the strongest E-field of the TM_{010} mode, any increase of the sample insertion height should result in a further decrease of the resonance frequency. The discontinuity in the frequency shifts shows that as more than half of the sample is inserted, the TM_{010} mode is no longer supported by the system. The origin of the resonance line measured by the VNA has to be

attributed to another mode type or a combination of modes set, induced by the presence of the sample.

c- Modelling of electric field

In order to visualize the effective electric field distribution in the presence of the sample, we have modelled the cavity with and without the sample. A model of our cavity was performed in QuickWave 3D simulator (QWED, Poland) which is based on the conformal Finite Difference Time Domain (FDTD) method. The figure 2.17 presents the real cavity and its model in QuickWave simulator.



Figure 2.17: The microwave system for dielectric measurement (image at left), the part marked in orange is the resonant cavity and its draw in QuickWave (image at right).

The resulting distribution of the electric field in the cavity is presented in figures 2.18 and 2.19. The details concerning the QuickWave software and the concept behind are presented in appendix.



Figure 2.18: The distribution of the electric field in the empty cavity corresponding to TM_{010} .



Figure 2.19: The distribution of the electric field in the cavity loaded with the sample. The field symmetry with two nodal planes perpendicular to the cylinder axis ressembles that of a TM_{012} mode.

The figure 2.18 shows that for the empty cavity, the electric field has the distribution expected for of TM_{010} mode (the electric field vectors are parallel to z axis in the whole cavity). The electric field distribution displays similarities with that of the TM_{012} mode (figure 2.19) once the sample is loaded in the cavity (the electric field vectors are parallel to z axis and inward close to both flat sides and around the sample and then go obliquely at the upper and lower sides of the sample. It appears that the introduction of a sample such as Ceria, the resonant mode TM_{010} is no longer supported and replaced by a mode with a symmetry rather related to TM_{012} mode.

2.2.2.3-Calculation of ε_r and ε_r using TM₀₁₂ mode and hybrid mode:

Given the results of 2.2.2.2 we present another tentative of applying the cavity perturbation method, based on this time on the TM_{012} mode, as given by the equation 2.4 and 2.5 below [13]:

$$\frac{f_0 - f_s}{f_0} = \left(\varepsilon_r - 1\right).A.B.G.\frac{V_s}{V_c}$$
(Eq.2.4)

$$\frac{1}{Q_s} - \frac{1}{Q_0} = 2\varepsilon_r^{"}.A.B.G.\frac{V_s}{V_c}$$
(Eq.2.5)

The A, B and G coefficients depend on the cylindrical Bessel functions and the dimensions of the cavity and the sample. In case of cylindrical cavity and mode TM012, these coefficients are defined by equations 2.6, 2.7 and 2.8[14].

$$A = J_0^2 (2.405 \frac{R_s}{R_c}) + J_1^2 (2.405 \frac{R_s}{R_c})$$
(Eq.2.6)

$$B = 1 + \left[\frac{L}{2\pi . H_s}\right] . sin\left(\frac{2\pi . H_s}{L}\right) . cos\left(\frac{4\pi . H_c}{H_s}\right)$$
(Eq.2.7)
And $G = (0.2178) . \left(\frac{c_0}{f_0 . R_c}\right)$
(Eq.2.8)

where $H_c, R_c, V_c, H_s, R_s, V_s$ are respectively the length, the radius and the volume of the cavity without and with the sample. *L* is the length of coupling which is 3 mm in our case. The value of f_0 of this mode for an empty cavity was calculated theoretically using the equation 2.9 which depends basically on the height and the diameter of the cavity.

$$f_0(TM_{012}) = \frac{c_0}{2\pi} \sqrt{\left(\frac{2.405}{R_c}\right)^2 + \left(\frac{2\pi}{H_c}\right)^2}$$
(Eq.2.9)

Hence, the value of f_0 is equal to 21.59 GHz. As this value is out of the limit range of our VNA frequencies, the calculation of Q_0 is not possible and therefore the calculation of $\mathcal{E}_r^{"}$ as well. However, we present in table 2.4 the values of $\mathcal{E}_r^{'}$ calculated by using the theoretical value of f_0 for empty cavity and the value of resonance frequency resulting from the loaded cavity obtained from the VNA measurement.

Sample	εref	εˈcal
Diamant MBD4	3.15	956.1
Al	11.41	968.6
SiC F100	9.06	964.2
SiC F360	8.15	963.8

Tableau 2.4: Values of the reference (ITACA-Dimas dielectrometer system) and calculated \mathcal{E}_{r} at 2.45 GHz in TM₀₁₂ mode at room temperature.

As the values obtained differs about two orders of magnitude as compared to the reference values, this model is not satisfactory. Consequently the perturbation method cannot be correctly applied, neither for TM_{010} mode nor for TM_{012} mode. At this point it is tempting but formally incorrect to compare the quality factor and the resonance frequency shift for TM_{010} mode and TM_{012} mode. In the next session, we present however this empirical approach based on a "TM loaded" method to determine the dielectric properties.

2.2.3 TM loaded empirical method

By using a 'hybrid method' that compares the resonance frequency of TM_{010} mode in the empty cavity mode and assumes a TM_{012} for the loaded cavity, we will try to demonstrate that using the resonance frequency and the quality factor it is possible to evaluate the dielectric properties. This method consists to use the values obtained in TM_{010} (resonance frequency and quality factor) as inputs in the calculation model of TM_{012} (Eq. 2.4 and 2.5). The values obtained are presented in table 2.5.

Sample	ε ref	ε ref	ТМ	TM	TM010 E cal	$TM_{010} \varepsilon$ cal
			loaded ε cal	loaded ε cal		
Diamant MBD4	3.15	0.01	3.8	0.02	3.16	0.002
Al	11.41	0.13	12.5	0.13	7.08	0.02
SiC F100	9.06	1.48	9.44	1.32	5.70	0.10
SiC F360	8.15	1.04	9.1	1.04	5.58	0.08

Tableau 2.5: Values of the reference (ITACA-Dimas dielectrometer system) and calculated dielectric properties at 2.45 GHz in TM₀₁₀ mode and TM loaded at room temperature.

As the values obtained by TM loaded method, are found by chance very close the reference values, we will use this method in our calculation of the permittivity of the ceria samples.

2.2.4 Back to the concept of the modes and the verification of the mode shifting in the cavity (TM loaded):

In the theory of resonant cavities, the modes and associated resonance frequencies are determined by the shape the size and the conductivity of the metallic resonator. Each eigenmode corresponds to a standing wave with a specific electric- and magnetic field intensity distributions. Non-magnetic samples should be placed in the region of the highest electric field for optimal interactions and energy transfer.

In our work, the empty cavity was designed to be excited in the mode TM_{010} (see fig. 2.18) When loaded, this mode is no longer supported (see fig. 2.19). Formally the essential assumption of the cavity perturbation method requiring the same mode to considered for the cavity empty and loaded is no longer fulfilled [3, 9, 10, 11], explaining why the calculation leads to values far away from the expected results (see table 3.3).

Taking a chance and considering the mode TM_{012} but feeding the equation with the values of the TM_{010} for the empty cavity (2.70 GHz) instead of the frequency of the TM_{012} (equal to 21.59 GHz).Following this empirical calculation the values obtained at room temperature for four standard samples happen to be very close to the reference values. The reason for this unexpected result remains to be clarified.

We present in the figure 2.20 and 2.21, the variation of ε_r and ε_r calculated by the two models as function of the reference values as well as a linear calibration curve relating directly the experimental frequency and quality factor with the reference values for the real and imaginary parts of the permittivity.

The figures 2.20 and 2.21 show linear relations between the reference values and the value calculated by cavity perturbation methods based on either TM_{010} or "TM loaded" methods.





Figure 2.20: The variation of ϵ ' in both methods as function of the reference values (a). And direct calibration method showing the linear dependence of resonance frequency versus ϵ ' of the reference materials (b)





Figure 2.21: The variation of $\mathcal{E}_r^{"}$ in the two methods as function of the reference values (a). And direct calibration method showing the linear dependence of the inverse quality factor versus ε " the reference materials (b)

The straight lines in case of TM loaded seem similar to the first bisector. This behaviour shows that the TM loaded seems more suitable for our calculation than the pure.

In summary, we have shown that as the cavity perturbation is not directly applicable to our system. To extract the complex permittivity, we have explored three alternatives: applying the TM₀₁₀ method outside of its validity, and use a further correction with the associated calibration curve (Fig 2.20 & 2.21), apply a direct calibration, or apply the "TM loaded" approach with an optional calibration.

2.3 The thermal properties measurement methods:

As we mentioned at the beginning of this chapter in order to understand the heating processing during the sintering, to master it and to model it, we need to determine the thermal properties as function of temperature and density; especially the thermal conductivity and the specific heat capacity.

The techniques we have used are known and simple. Actually, the thermal conductivity λ was determined indirectly by measuring the thermal diffusivity α in argon using the Laser Flash Analysis (LFA 457 Microflash, Netzsch, Germany) [15], and the specific heat c_p, by using a Differential Scanning Analysis (DSC 404 C, Netzsch, Germany).

I will present in the first instance, the two methods used for the measurement of α and c_p and then the relation between these two parameters and λ .

2.3.1 The measurement of the thermal diffusivity α by Laser Flash Analysis:

This method developed by Parker in 1961 [16], it consists to send a heat pulse on the face of a cylindrical sample which has small dimensions. The temperature is measured on its upper side by an infrared detector. Then, the analysis of the temperature variation as a function of time provides the calculation of the thermal diffusivity. The measurement was made at EMPA (The Swiss Federal Laboratories for Materials Science and Technology) in Dübendorf, Switzerland.

In our case, the pulse source is a laser source and the both sample sides were coated with graphite spray to ensure uniformity of the heat over the entire surface. In order to optimize the systematic error, a first measurement is made with a reference material (Pyroceram 9606) which has low thermal diffusivity. This material is known as having a very low dispersion of the measurement in the range of 2.3 to 2.7 % [17]. The thermal diffusivity was determined from 5 measurements at each temperature for each sample. The diffusivity was measured under argon flow (50ml/min) from room temperature up to 1000°C (100°C by step).

The figure 2.22 shows the different parts of the Laser Flash Analysis machine used during the measurement.



Figure 2.22: The transversal section of the machine (Netzsch LFA 457).

2.3.2 The measurement of the specific heat capacity c_p by Differential Scanning Analysis:

This technique consists to measure the difference in heat exchange between a sample and a reference (in this case the sapphire). This difference in heat flux through the measuring cell (containing the sample) and the reference one is the source of information about the parameter. The measurement can be carried out in air or under an inert controlled atmosphere to prevent any kind of reaction in handling.

Using a low amount of Ceria powder (187.3 mg) the heat capacity was determined in the same gas flow condition as in LFA, with 15°C/min heating rate. The uncertainty of DSC method is less than 1% [18].

The measurement is done in three steps:

- 1) A baseline measurement where the sample holder is empty.
- 2) A standard measurement with a "standard sample", here, we use the sapphire.
- 3) A sample measurement where the sample holder contains the ceria powder (187.3 mg).

A Proteus Netzsch Thermal Analysis software was used to control the set point temperature, the heat flow measurement and to display the live results on the screen.

The figure 2.23 presents the different elements needed for the measurement by DSC technique.



Figure 2.23: The principle of the DSC technique.

The relationship in equation 2.10 shows how the c_p of the samples is calculated, knowing the c_p of standard sample, the corresponding masses m_i and the potential difference (*DSC_i*) between the different signals.

$$c_{p} = \frac{m_{\text{standard}}}{m_{\text{sample}}} \cdot \frac{DSC_{\text{sample}} - DSC_{\text{Bas}}}{DSC_{\text{standard}} - DSC_{\text{Bas}}} \cdot c_{\text{p,standard}}$$
(Eq.2.10)
where *i* represents the baseline measurement, the standard and the sample.

2.3.3 The calculation of thermal conductivity λ :

The thermal conductivity λ is calculated by a simple relation (equation 2.11) between c_p , α and the density ρ :

$$\lambda = \alpha \cdot \rho \cdot c_p$$
(Eq.2.11)

where λ in W/m.K c_p in J/Kg.K α in m²/s ρ in Kg/m³

2.4 Conclusion:

In this chapter, we presented the method of the preparation of the different samples, then the different issues and the methods we have faced and performed in order to get a better calculation of the dielectric properties of cerium oxide. Moreover, in our methodology we took into account the limits due to the temperature measurement and the sample dimensions and we examined it by different approaches such as experimental and simulation studies. Thus, a TM loaded method which was the most appropriate one for our measurement was used as an empirical method for the calculation. In the other hand, the thermal measurement for the different thermal parameters was done using classical methods.

Like the complex dielectric permittivity and the thermal diffusivity, the thermal conductivity is calculated from room temperature up to 1000°C and for a large range of fractional porosity (different samples densities) from 3.7 up 44.3%. Their results will be presented in chapter 4.

Résumé en français : Méthodes de détermination des propriétés thermophysiques et diélectriques de la Cérine

La méthodologie de mise en forme et d'élaboration de matériaux à base d'oxyde de Cérium par métallurgie des poudres ainsi que les méthodes de détermination des propriétés diélectriques (ε' , ε'') et thermo-physiques (c_p , κ , λ) de ces matériaux en fonction de la température sont présentées. En outre, afin de comprendre l'effet de la température et la porosité sur l'interaction du champ électromagnétique sur la Cérine en cours du frittage et donc déterminer ses propriétés diélectriques jusqu'à haute température (1000°C), nous avons développé une méthode expérimentale basée sur la théorie de perturbation appliquée à une cavité résonnante. Les étapes et les outils de développement de cette méthode sont aussi présentés en détails dans ce chapitre.

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Chapter 3: Dielectric and thermophysical properties of cerium dioxide

As we mentioned in the chapters 2 and 3, the determination of the dielectric and thermal properties are necessary to understand the heating by microwave. In addition, the follow-up of the densification of xerogel sphere having elementary fine particles and the variation of the physical properties of ceria as function of temperature and porosity for the simulation study are the main objectives of this part. Therefore, the effect of porosities is reported and it provides the needed elements for the sintering process and as inputs for modelling.

In this chapter, the CeO_2 powder was characterized and the pattern will be shown at the beginning. We present also the experimental determination of the thermal and dielectric properties of conventionally sintered cerium dioxide (CeO₂) samples.

On the other hand, the experimental results are compared to the theoretical models found in the literature.

3.1 Characterization of the raw ceria powder

The XRD analysis (operated by the diffractometer Bruker D8 Discover) is a method that can identify the physico-chemical properties of materials (crystallized) and the crystal structure of the analyzed specimen.

XRD analysis were made on the powder to identify the crystalline phases and determine whether heating up to 1000 °C had an effect on the structure.

The figure 3.1 shows the XRD patterns of three treatments of ceria powder:

- 1) The powder used to elaborate the different samples (CER (IV)-OXID 99.9%, Aldrich).
- 2) A repeatability of the experiment.
- 3) The powder which was heated up to 1000°C to determine the stability of ceria structure.



Figure 3.1: XRD patterns of the different powders and the fluorite structure of ceria.

The XRD patterns obtained for all the powders present the fluorite phase of ceria (CeO_x). It is clear from the presented peaks that the powders keep its stable fluorite structure.

There are two kinds of ceria powders used in our study:

- 1- The micro-powder having 99.9% of purity and a particle size smaller than 5 µm was used for the determination of the physical properties of ceria and it was also used in the comparison study between the microwave sintering and the conventional sintering.
- 2- The nano-powder having 99.9% of purity and a particle size smaller than 25 nm was used in this study for the comparison with micro powder and also to account for the microwave interaction with nano particles coming from a sol-gel process.

3.2 Microstructure for porous and dense materials by Scanning **Electron Microscopy**

the microstructure by SEM (Hitachi S-4800 (CFE), EMPA, Thun) Firstly, of the ceria micro-powder is shown in figure 3.2.



Figure 3.2: SEM micrograph of ceria powder on TEM cell.

The powder shows a formation of agglomerates due to the coalescence of the grains. These agglomerates have a size between 0.1 and $2 \mu m$.

The microstructure of five specimens were observed by Scanning Electron Microscopy (SEM) (JSM-6400) after cutting samples according perpendicular and parallel planes to the pressure axis and several polishing steps up to a final one of $1 \mu m$ were made.

The results for both kinds of planes were similar: No differences of pore fraction and pore shape were identified (see figure 3.3). In figure 3.3, we present the microstructures of a dense sample (89.92%) for the two kinds of planes.



a)

b)

Figure 3.3: SEM micrographs showing a) perpendicular and b) parallel cross section to the pressure axis of the dense sample 89.92%.

In figure 3.4, five examples of microstructures observed for sintered samples only for perpendicular surfaces to the pressing axis are shown.

After heat treatment at 1250°C (figure 3.4a) very low shrinkage was observed after sintering, and porosity (59.29%td) has an irregular shape due to the high porosity, while homogenously distributed and interconnected. Then, a sample treated at 1400°C with a relative density of

65.5 % (figure 3.4.b) was observed and it shows a high tortuosity at this porosity fraction. For a higher densification (1500°C; 73.63%td), porosity remains interconnected; while its contours are smoothed (figure 3.4c). For much higher densification (82.63%td), it appears some non-homogenous densification, indeed some zones appear denser with closed porosity surrounded by zones with higher porosity ratio but in which porosity stays open (figure 3.4d). And finally, close to the theoretical density (1500°C; 89.92%td), pores close and adopt a spherical shape, corresponding to the final stage of sintering (figure 3.4e). In conclusion, the pore content decreased during the sintering process and their "elliptical" shape disappeared progressively at high densification where it became closed with a spherical shape.





Figure 3.4: SEM micrographs showing five samples a) 59.29% b) 65.5% c) 73.63% d) 82.63% e) 89.92%

The figure 3.5 shows the variation of the relative density of ceria sample from 67% to 83% as function of time. The heating rate was 25K per minute up to 1500 $^{\circ}$ C.



Figure 3.5: Curve of densification of ceria sample at 25K/min.

In order to determine the mean grain size, the intercept method was used through SEM images.

3.3 Effective permittivity

In this section, we present the results concerning the complex dielectric permittivity by the two methods presented in the chapter 2. In addition, a theoretical model suggested by Maxwell-Garnett which depends on the porosity is also presented.

3.3.1 Determination of the real part of dielectric constant ε_r' by coaxial probe method

The VNA displays \mathcal{E}_r as function of frequency. The figure 3.6 shows the variation of the real part of the dielectric constant at room temperature the sample (95.5% t.d) before the polishing.



Figure 3.6: Variation of ε' for the densest sample of ceria versus the frequency.

As this material has a low loss tangent, the calculated ε falls out of the applicability of the method and have to be discarded. Moreover, due to instrumental sensibility, at high frequency the measurement needs a correction and this explains the wavy shape seen. The variation of ε in function of the frequency is presented in figure 3.7 for the polished sample.



Figure 3.7: Variation of ε' for the densest sample after polishing versus the frequency.

Here the calculated value for ε' at 2.45 GHz is 21.14 close to 23 as reported in the literature [1]. This small variation is due to the better contact between the interface of the sample and the probe and the presence of the air at the interface.

However, this method provides acceptable results for only one parameter ε at room temperature. In the next section we will show the results obtained by our device up to high temperature, but firstly we will develop the Maxwell-Garnett model which describe the permittivity of a ceramic composite material.

3.3.2 Effective permittivity, Maxwell-Garnett model (taking into account the porosity)

The effective permittivity in this case depends strongly on the content, and can be well presented by using the Maxwell-Garnett [2] model given in equation 3.1. It is based on the polarization induced by an external electric field in a medium where spherical inclusions were dispersed.

$$\frac{\varepsilon_{eff} - \varepsilon_s}{\varepsilon_{eff} + 2\varepsilon_s} = p \frac{\varepsilon_i - \varepsilon_s}{\varepsilon_i + 2\varepsilon_s}$$
(Eq.3.1)

where ε_s is the permittivity of the solid particles (cerium dioxide in our case), ε_i is the permittivity of the spherical inclusions (air), ε_{eff} is the effective permittivity of the medium and *p* is the volume fraction of the spherical inclusions. In our case, the medium was ceria and inclusions were considered as air gas. This relationship can be rearranged:

$$\varepsilon_{eff} = \varepsilon_s \frac{1+2\chi}{1-\chi}$$
(Eq.3.2)
With $\chi = p \frac{\varepsilon_i - \varepsilon_s}{\varepsilon_i + 2\varepsilon_s}$
(Eq.3.3)

Because the permittivity has a complex form with a real and imaginary parts ($\varepsilon = \varepsilon' - i.\varepsilon''$) both values are considered evolving as equation 3.2. This is the simplest model and we should keep in mind that it overlooks the effect of the size of the pores and the size of the particles.

3.3.3 Dependency of dielectric properties (real part) on porosity at room temperature

We present in the figure 3.8 the comparison of the experimental data at room temperature with Maxwell-Garnett model (Eq. 3.2). The values of ε' decrease linearly from 18.24 to 10.5 while the porosity increases from 4.5 up to 43.5% vol.

In the figure 3.8, the upper curve represents the model using 23 as value for the full dense dielectric constant coming from the literature [2]. And the lowest curve represents the same model using the extrapolated value of ε at full densification from our experiments 19.55

(presented in section 3.4). Therefore the results are in relative good agreement with model for the full range of porosity.



Figure 3.8. Variation of the relative dielectric properties (real part) ε' vs. the fractional porosity at room temperature and the Maxwell-Garnett models.

The experimental curve has a linear model between the two theoretical models presented in the figure 3.8.

3.3.4 Dependency of dielectric properties on temperature and porosity

The results concerning the dielectric properties as function of temperature and porosity which were obtained by cavity perturbation method are presented in this section. The real and imaginary parts of the dielectric properties are reported in the figure 3.9 (a and b) in 3D plot in order to show the effect of temperature and porosity on these parameters.

It shows the dielectric properties (real (a) and imaginary (b) parts) from room temperature up to 1000 °C versus the fractional porosity for all prepared samples (from 55.6% to 95.5% td). The relative dielectric constant varies linearly with temperature and is higher for the denser specimens (figure 3.9a). On the other side, the loss factor (or imaginary part of permittivity) does not change significantly below 700 °C, but it becomes very high when the temperature increases (figure 3.9b). Moreover, it becomes higher, when the density was close to the sample which presents high porosity ratio.



Figure 3.9: Variation of the relative dielectric properties a) real and b) imaginary parts vs. the fractional porosity and the temperature.

The ε_{eff} increases slowly with temperature and inversely proportional and quickly with porosity (figure 3.9a), ε_{eff} depends much more on the temperature, especially at high temperature from 750-800°C (figure 3.9b).

The dielectric permittivity (ε) as function of fractional porosity at room temperature has been modelized using a polynomial function (equation 3.4). Its value for full dense sample can be determined from this function. It gives for a full dense sample (p=0) ε_d equal to 19.55.

$$\varepsilon' = -160.643 p^3 + 45.354 p^2 - 7.437 p + 19.55$$

(Eq. 3.4)

With *p* : volume fraction of porosity.

The temperature dependence of the loss factor can be explained by the effect of the ionic conduction of oxygen at elevated temperature. Yamamoto et al [3] show that ceria can modify its stoichiometric composition by reduction the Ce^{4+} to Ce^{3+} accommodating about 14% of oxygen vacancies at 800°C.

Yahiro et al [4] show that the ionic conductivity of ceria has a different behaviour at high temperature (figure 3.10). The variation of the ionic conductivity of ceria in air as function of the temperature and the amount of samarium oxide is presented in figure 3.10. The dots that have a triangle shape with its half black present the pure ceria (see the red arrows).



Figure 3.10: Arrhenius plots of the ionic conductivities for different materials, **A** for ceria [4].

The figure 3.10 shows that around 750°C the ionic conductivity of ceria becomes important. Hence, this change can explain the large increase (figure 3.9b) of the loss factor at this temperature.

Therefore, the microwave heating of ceria materials is possible especially since the temperature reaches 750°C whereby the loss factor becomes important.

3.4 Thermal properties

In this section, we present the results concerning the thermal properties by the methods presented in chapter 2. In addition, several theoretical models concerning the dependency of the effective thermal conductivity on the porosity are also presented.

The relationship between the thermal conductivity λ and the different thermal parameters is given by the equation 3.5:

$$\lambda = \alpha \cdot \rho \cdot c_p$$
(Eq.3.5)

Where c_{p} , α and ρ are respectively the specific heat capacity, the thermal diffusivity and the density of the material.

3.4.1 Effective thermal conductivity, theoretical models of porosity dependence

For the composite materials or the materials which have many phases, the thermal conductivity depends widely on the volume fraction, the type of the phases, the geometry of the pores, their distribution and the influence of the grain boundaries [5].

Here, we present some models which were found to correlate well the thermal conductivity of such porous ceramics materials. First of all we present models based on pore content, and secondly we present model which depends on pore content and shape.

a) The Francl et al. model suggested the following equation (Eq. 3.6) for ceramics materials having isometric and anisometric pores randomly arranged [6]:

$$\frac{\lambda}{\lambda_0} = 1 - p$$
(Eq.3.6)

Where λ and λ_0 are respectively the thermal conductivity of a porous ceramic materials and the full dense ceramic material and *p* is the volume pore fraction.

On the basis of the Odelevskii equations [7], Aivazov and Domashnev [8] obtained the following equation 3.7 to represent the thermal conductivity of porous titanium nitride. In this case they suggest a factor m to represent the pore distribution and the pore shape in the specimens.

$$\frac{\lambda}{\lambda_0} = \frac{1-p}{1+m.p}$$
(Eq.3.7)

where m is a linear function of porosity (Eq. 4.8) for $m \ge 0$.

$$m = a.p$$

After substitution in the equation 3.7, it results the equation 3.9:

$$\frac{\lambda}{\lambda_0} = \frac{1-p}{1+a.p^2}$$
(Eq.3.9)

Where $a \ge 0$, this value was found equal to 6 for titanium nitride, and 10 for polycrystalline graphite [9].

b) The Maxwell model consider a matrix of materials made of spheres which are enough small that do not interact thermally with the continuous solid phase [10]. Therefore, he proposed for low volume fraction of porosity *p*:

$$\frac{\lambda}{\lambda_0} = 1 + \frac{3.p}{\left(\frac{\lambda_1 + 2.\lambda_0}{\lambda_1 - \lambda_0}\right) - p}$$
(Eq.3.10)

Where λ_1 is the thermal conductivity of the inclusions, in our case we take the value 0 for the air. Therefore the equation 3.10 can be transformed in equation 3.11:

$$\frac{\lambda}{\lambda_0} = 1 - \frac{3.p}{2+p}$$
(Eq.3.11)

c) Moreover, Rayleigh suggested a model for large volume fraction where the interaction between the spheres is small and the position of it is at the intersections of a cubic lattice [11].

After substituting the value of the air thermal conductivity directly we obtain:

$$\frac{\lambda}{\lambda_0} = 1 - \frac{3.p}{2 + p - 0.39225 p^{10/3} + \dots}$$
(Eq.3.12)

As the interaction of the spheres is usually neglected, the model of Maxwell is still better and simpler.

d) However, for non-spherical inclusions, Maxwell's equation was modified in order to show the contribution of the thermal conductivity tensor. In case of long cylinder porosity parallel to z-axis, this tensor is composed by three components, the one which is parallel to z-axis is given by equation 3.6 and the other two components for x- and y-axis, supposed equals, are given by equation 3.13:

$$\frac{\lambda_{xx}}{\lambda_0} = \frac{\lambda_{yy}}{\lambda_0} = 1 - \frac{2.p}{1 + p + (0.30584.p^4 + 0.013363.p^8 + ...)}$$
(Eq.3.13)

e) Also, for complex inclusions, in case of unconsolidated granular beds, equation 3.14 allows a relationship between conductivity and porosity [7, 12].

$$\frac{\lambda}{\lambda_0} = \frac{(1-p)}{1+(\alpha-1).p}$$

(Eq.3.14)

in which α includes a shape factors.

$$\alpha = \frac{1}{3} \sum_{i=1}^{3} [1 - g_i]^{-1}$$
(Eq.3.15)

The *shape factors* g_i satisfy the relation $g_1 + g_2 + g_3 = 1$ and are equal to 1/3 for spheres. Then, in our case $\alpha = 1.5$ for spherical inclusions and the equation is simplified to the equation 3.11. These several models show the variety of interaction possible between the porosity and the thermal conductivity: pore content and pore shape seem to be the most important parameters.

Besides these basic models, several known models have been developed such as Bruggeman [13], Cheng-Vachon [14], Hamilton-Crosser [15], Meredith-Tobias [16] and Lewis-Nielsen model [17]. These models (Table 1) were not used for our results because the first models fit well with the experimental data.

Model	Terms of use
Bruggeman	Ideal system, non-interacting spherical/spheroidal particles in
	homogeneous medium
Cheng-Vachon	Discrete phase in continuous matrix, particle distribution
Hamilton-Crosser	Sphericity of particles (the sphericity is defined as the surface area of a
	sphere with the same volume as the particle divided by the surface area
	of the particle)
Meredith-Tobias	Large volume fractions of the discrete phase and a narrow size range
Lewis-Nielsen	Grain size, geometry and particles packing

Table 1: List of some thermal conductivity models and their applicability [18].

3.4.2 Dependency of thermal properties on temperature and porosity

In order to study the variation of the thermal properties of ceria needed in the simulation part of this work and to understand the effect of densification on the thermal diffusion, we have determined the specific heat capacity, thermal diffusivity and thermal conductivity of cerium oxide up to 1000°C.

3.4.2.1 Specific heat capacity and thermal diffusivity

The change in heat capacity versus temperature is shown in figure 3.11: up to 500°C the heat capacity increases with temperature and remains constant above this temperature. This is in good agreement with the literature [19] and this evolution can be modelled by a polynomial fit given by equation 3.16:

$$c_p = 0.3062 + 6.69 * 10^{-4} * T - 1.34 * 10^{-6} * T^2 + 1.15 * 10^{-9} * T^3 - 3.56 * 10^{-13} * T^4$$

(Eq. 3.16)

This polynomial function has a similar behaviour as expected for ceramic oxide materials [20].



Figure 3.11. Heat capacity for the CeO₂ powder in argon.

The thermal diffusivity of six kinds of samples from 55.67 to 96.32 % t.d. are shown in figure 3.12. Diffusivity decreases logarithmically with temperature and increases with relative density, moreover it increases linearly to the reverse of temperature as theoretically expected (fig. 3.12).



Figure 3.12: Variation of the thermal diffusivity versus the inverse of temperature for 6 different samples (different densities).

3.4.2.2 Thermal conductivity

The temperature and porosity dependence of the thermal conductivity up to 1000°C is shown in figure 3.13. For high porosity content it decreases slowly with temperature and faster for low porosity content. Clearly the thermal conductivity increases with increasing density and decreases with increasing temperature: for example the thermal conductivity decreases from 13 to 3 W/m.K for the densest sample (96.32%td) from room temperature up to 1000°C, as described in the literature [19].



Figure 3.13: Variation of the thermal conductivity λ vs. the fractional porosity and temperature.

As we have seen in the results before concerning the thermal conductivity, the contribution of the porosity seems to be more important than the temperature, globally during the heating processing. In fact, for the ceria powder used in this study, sintering starts above 1000°C, the figure 3.13 shows that the thermal conductivity decreases strongly up to low values before the beginning of densification and slightly increases as the sample densifies.

For all samples at room temperature, the thermal conductivity as function of fractional porosity has been fitted to a polynomial function (equation 3.17). The thermal conductivity at full density λ_0 can be determined from this function. It gives for a full dense sample (p=0) λ_0 equal to 15.157 W/m.K.

$$\lambda = -160.643p^3 + 45.354p^2 - 7.437p + 15.157$$
(Eq. 3.17)

With *p* : Fractional porosity.

The same methodology was used for determining λ_0 at 500 and 1000°C. The obtained values are respectively: 6.05 and 2.70 W/m.K as expected when the temperature increases, λ decreases related to phonon scattering [21, 22], described by the equation 3.18:

$$\lambda = \frac{1}{a.T+b}$$
(Eq. 3.18)

With *T* the temperature in Kelvin (K) and a, b are constants expressed respectively in $(W^{-1}.m)$ and $(W^{-1}.K.m)$.

The figure 3.14 presents the variation of $1/\lambda$ versus the temperature.



Figure 3.14: Variation of $1/\lambda$ as function of the temperature.

The figure 3.14 shows a linear variation of the $1/\lambda$ versus the temperature which has a good agreement with the previous model in equation 3.18.

A comparison with Aivazov & Domashnev's model (equation 3.9) which is well known for low range of porosities, using different values of *a* parameter at room temperature, are presented in figure 3.15. Here, the experimental data and the theoretical models of the relative thermal conductivity λ/λ_0 , for different values of *a* (0, 1, 10, 15) are presented. According to the model, for lower values of porosity (less than 0.27), when *a* parameter increases the model moves from linear variation with very low slope to high slope for high values of *a* parameter. Comparing the several models, it appears that the Maxwell's model (equation 3.11) for spherical inclusions and small volume fraction *p* and the model for complex inclusions in case of unconsolidated granular beds (with α =1.5 equation 3.14) are equivalent (figure 3.15). The two last models are very close to Rayleigh's model (equation 3.12).



Figure 3.15: Variation of the relative thermal conductivity λ/λ_0 versus the fractional porosity at room temperature from our experiments (black) compared with different models from [6-12].

Comparing with experiments, the nonspherical-z component (or the linear model a=0, equation 3.6) is more suitable at low porosity values less than 0.27. Beyond this value the relative thermal conductivity decreases more rapidly than the various models (Maxwell, Rayleigh, anisotropic components and for high values of *a* parameter).

Remind that at room temperature and high densification (greater than 73% t.d) the pores appeared with spherical and elliptical shape. Here, the experimental results obtained up to 27% vol. porosity are closed to the linear model (Eq.3.6) which concerns the porous materials having spherical shape of pores. However for lower densification the results depart from the linear model. This trend could be related to the pores shape which is far from the shape suggested in these models.

Moreover, for high temperature the results at 500°C and 1000°C (figure 3.16) show a similar behaviour as at room temperature for all domains of porosity. Comparing to the two models presented in figure 3.16 (nonspherical-z and nonspherical-x,y), the relative thermal conductivity fits well with the nonspherical x-y model at low values of fractional porosities less than 0.27.



Figure 3.16: Variation of the relative thermal conductivity λ/λ_0 versus the fractional porosity at room temperature (black) 500°C (cyan) and 1000°C (red) compared with two models.

3.5 Conclusion

Finally, we can conclude that during the conventional sintering of ceria powder materials, the microstructure evolves especially the grain and pores sizes and their shape. Actually, the pore content decreased during the sintering process and their "elliptical" shape disappeared progressively at high densification where it became closed with a spherical shape. The thermal conductivity depends on the porosity and temperature but more on porosity. Moreover, the ratio λ/λ_0 was also affected by the tortuosity of the pores and especially for high fractional porosity (greater than 0.27).

The dielectric properties have been studied up to 1000°C, the results showed that the loss factor (ϵ '') depends on the temperature and is strongly affected in porous sample, while the dielectric constant (ϵ ') was more affected by the porosity content than the temperature. Moreover, the pores shape have no influence on ϵ ' and our results are in good agreement with Maxwell-Garnett model.

The dielectric constant (ϵ ') obtained at room temperature by the coaxial probe method has a good agreement with the results obtained for the densest sample and the literature.

In order to enrich both models (Aivazov & Domashnev and Maxwell-Garnett), it will be interesting to take into account not only the pores content but also their shape. For microwave assisted sintering of cerium oxide, heating (which is related to ε ") is independent of the densification excepted for the initial state (the most porous state) of the process. Microwave heating above 750°C, is possible due to the ionic conduction of ceria.

Résumé en français : Propriétés diélectriques et thermo-physiques du dioxyde de cérium (Cérine)

Les résultats qui concernent la dépendance des propriétés thermiques et diélectriques de la Cérine en fonction de la porosité et la température ainsi que leur lien avec la microstructure des matériaux frittés sont présentés. Une discussion est menée sur l'effet de la température et la porosité sur les propriétés thermiques, en particulier la diffusivité thermique (λ) . Les résultats expérimentaux sont comparés aux différents modèles théoriques de la littérature concernant essentiellement des lois de mélange. De la même façon les résultats expérimentaux concernant les propriétés diélectriques de la Cérine au cours de la densification pendant le traitement thermique sont analysés et comparés au modèle de Maxwell-Garnett. Les résultats obtenus concernant les propriétés diélectriques et les paramètres thermiques, ont montré la dépendance de (ε ') et (ε ") de l'oxyde de cérium sur la température et la porosité des échantillons. En plus, ces résultats ont montré que le chauffage micro-ondes de la Cérine est possible en particulier au-dessus de 750 ° C où la conduction ionique de l'oxyde de cérium devient importante.

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Chapter 4: Conventional and microwave sintering of cerium oxide

As we have mentioned before, the main objective of the project was to use the microwave technology in the new setup for the waste recycling, starting from the production of xerogel ceria spheres, then the debinding and finally the sintering. In previous studies, the first two steps were performed and therefore the last step needs to be validated in this work. In addition, due to the lack of research studies concerning the microwave sintering of ceria, this work could have a significant contribution in this field.

In this chapter, the different setups used for the conventional sintering (the dilatometer) and for the microwave sintering (single mode applicator) and the assembly used for the determination of the emissivity and the relative density of cerium oxide will be presented. In addition, the experimental results concerning the sintering behaviour of ceria pellets prepared from two different powders (micro-powder and nano-powder) are also presented. We have chosen a nano-powder in order to be close to the powder state obtained in xerogel spheres. Moreover, the results concerning the evolution of the different grain morphologies of the sintered specimens will be shown in this chapter.

4.1 Preparation of ceria pellets from micro and nano powder

With the aim to know the effect of the grain size of ceria on the microwave and conventional sintering, several pellets of ceria were formed in two steps from two different powders (micrometric and nanometric powders). The powders were firstly pressed uniaxially in a tungsten carbide die with 8 mm diameter at low pressure, then, an isostatic pressure at 300 MPa was applied to obtain homogenous samples which have less flaking defects at the edges. The problem of flaking is not negligible for studying the optical dilatometry of the specimens. The height of the sample was fixed at 4 mm. The micropowders used are the same powders described in the first section of chapter 3 whereas the nanopowders was also an commercial powder of cerium dioxide (CER (IV)-OXID 99.9%, Aldrich), with a particle size less than 25 nm, and with theoretical density 7.13 g/cm³.

The figure 4.1 presents two different pellets of ceria from micrometer and nanometer powders after the debinding in air at 600°C.



Figure 4.1: The ceria pellets (8 mm x 4 mm) from micropowder and nanopowder

4.2 Conventional sintering method

The purpose of a dilatometric study in the perspective of sintering is to analyze the sample shrinkage phenomenon. Hence, a conventional sintering was carried out in a dilatometer (Setsys 16/18, SETARAM, France). It is a technique which is able to follow the change in height of a cylindrical sample throughout a specific thermal cycling. A photo taken for the dilatometer and the ceria sample before running the measurement is presented in figure 4.2.



Figure 4.2: Photo of the dilatometer used during the conventional sintering at the Ecole des Mines of Saint-Etienne.

It is important to know that the original data recorded by the dilatometer contains noise information which comes from the thermal expansions of the sample holder and the sample itself. Therefore, the dimensional variations of a dense alumina sample which is called "white measurement" in the same thermal cycle and has a similar height as the test sample, must be deducted from original results, so a corrected curve describing the shrinkage profile densification of the sample can be obtained.

4.3 Microwave sintering method

The microwave sintering of ceria pellets was carried out in the laboratory SIMAP in Grenoble, France. The setup used in this work is a single mode cavity was implemented during the PhD work of Sylvain Charmond [1] and has been modified to be reliable to the sintering follow-up of alumina (which has a low loss factor like ceria) during the PhD of J. Croquesel [2]. It is able to heat a cylindrical pellet of different materials (especially ceramics) and therefore sinter it. On the other hand, as it is important in this study to compare the sintering by microwave heating to the conventional one, different tools have been used and will be presented in this section.

4.3.1 The setup

The microwave cavity which was developed by the French company SAIREM, has a standard waveguide WR340 (86.36 mm x 43.18 mm) working in TE_{01} mode at a frequency of 2.45 GHz. Its main parts can be describes as:

a) The main part (brass central piece): has a length of 160 mm and a cylindrical opening of 52 mm of diameter centered along the large faces (see figure 4.3.a). In order to avoid the electromagnetic leakage, a lead of 91 mm is placed with a central lid (figure 4.3.b). Moreover, the test sample is placed in the center of this part which is water cooled circulating by a water flow. A beam splitter is fixed next to the camera which is located with 90° against the sample. The radiation coming from the sample during the heating passes under the beam splitter whereas the images detected by the camera are obtained by reflection.

The figure 4.3 presents the main part of the cavity where the sample is located.



Figure 4.3: The central part of the cavity. The cavity is opened in (a) and the sample is placed in the centre. In (b) the cavity is closed by the lid.

- b) The piston holder (short-circuit): in order to reflect the incident electromagnetic waves, this part (the piston) has an aluminium wall which is conductive. The position of the piston can adjust over a distance of 130 mm in order to modify the position of the maximum of electric field inside the central part where the test sample is placed (figure 4.4). This piston has a motor controlled by a PID developed under LABVIEW program. The regulation follows the temperature measured by a pyrometer on the surface of the sample in order to get the same protocol defined in the conventional heating.
- c) The iris holder: it contains an iris in copper that has an aperture of 3 cm in z direction. This piece is important in the microwave applicator because it can increase the electromagnetic power in the applicator by reflecting a part of the electromagnetic waves arriving from the piston (from the other side of the cavity). It is located at the same side of the generator (figure 4.4) to let the waves pass through its aperture. It can move along z-axis over a distance of 79 mm.

The figure 4.4 presents the cavity used during the experiments.



Figure 4.4: Photo of the central part of the cavity. The cavity is opened in (a) and the sample is placed in the centre. In (b) the cavity is closed by the chimney.

d) Impedance adapter (AI 3S M WR340): This piece was developed by SAIREM, France and it is actually a simple section of standard waveguide equipped with three movable stubs (figure 4.5) located between the generator and the cavity (applicator).

The important of this piece is that in case of low dielectric loss materials such as alumina and ceria which need a high electric field magnitude, the losses in the cavity coming from the interaction of the waves with the iris which have a huge contribution to the delivered power can be higher by using this adapter. Therefore, the electromagnetic power arriving to the sample which has a low dielectric loss is efficient especially at low temperature whereby the dissipated power is usually very low.



Figure 4.5: Photo of the impedance adapter (three stubs) placed between the generator and the cavity.

4.3.2 The materials used and the methods of measurement

In order to follow the shrinkage of the ceria samples as function of temperature and time in the microwave heating conditions, several materials and program were used and a calibration protocol was applied in advance to integrate the emissivity of ceria in LABVIEW program to have the corresponding temperature during the heating.

4.3.2.1 The thermal isolation material

As the thermal isolation is quite necessary in the microwave heating, many materials have been tested during the PhD of Jérémy Croquesel [2]. A material called "Fiberfrax Duraboard" (type 1600, Unifrax Corp, Niagara Falls, USA) which has a good resistance of temperature up to 1600°C and a little disturbance of the electric field. Moreover, this insulator has a very low thermal conductivity that makes it very resistive to thermal shock when the sample is heated up with high heating rate and in case of free cooling. This insulating material was used by Brosnan et al in their work concerning the microwave sintering of alumina [3].



The ceria sample a)



Figure 4.6: Photo of a ceria sample inside the insulator in the cavity (a), SEM micrograph of the Fiberfrax Duraboard 1600 taken by J. Croquesel [2].

The insulator Fiberfrax Duraboard used is shown in the figure 4.6a and a SEM micrograph of it is presented in figure 4.6b. The Fiberfrax Duraboard material is made up of long needled fibers of alumina and silica.

4.3.2.2 The measurement of temperature by pyrometer

Because, the thermocouple wire used usually for the measurement of the temperature interacts with the electric field and therefore disturbs the microwave heating [4], the temperature in this work was measured by a pyrometer which provides a contactless measurement. The pyrometer (IGAR 12 LO) used is integrated with optical fiber that communicates the signal to the controller box. It works over a temperature range from 450°C up to 1700°C in two modes of measurement monochromatic or bichromatic and has an accuracy of 0.7%. The test made by Andrey Guyon [5] concerning the bichromatic mode of

measurement in direct microwave heating shows a missing of the signal, so, our measurements were made in monochromatic mode. A calibration by inductive heating was done in order to provide the variation of the emissivity of ceria as function of temperature to LABVIEW program. The obtained values of the emissivity will served as inputs to adjust automatically the measurement by the pyrometer. The protocol and the details concerning the calibration will be presented in the section 4.3.2.4.

The monochromatic pyrometer measures the luminous flux and therefore the temperature using the laws of thermal radiation. Hence, the temperature T of a radiative source (the hot sample) can be determined by a relation between the emissivity at a special wave length ε_{λ} and the temperature T_{λ} which is the temperature of the black body having the same luminance of the source. This relation is called the approximation of Wien and is given by the equation 4.1:

$$\frac{1}{T_{\lambda}} - \frac{1}{T} = -\frac{\lambda . k}{h.c} Ln(\varepsilon_{\lambda})$$
(Eq.4.1)

with k the Boltzmann constant, h the Planck constant, c the speed of light and λ is the wavelength at which the temperature is measured.

4.3.2.3 The detection of the sample surface during the heating by CCD camera

The detection of the shrinkage of the sample by optical dilatometry during the heating is performed using camera CCD 8 bits (1280x1024 pixels). This camera has a lens head of 180 mm which allows taking photos for the top surface of the sample through the chimney. The figure 4.7 presents a photo of ceria sample surface taken by the camera during the microwave heating.



Figure 4.7: Example of image detected by the camera for ceria sample at 1400°C.

A photo of the sample's surface (figure 4.8a) is recorded at each second during the thermal process. Then, an algorithm for the detection of the sample's edges was developed [6] in LABVIEW and it has been applied on each photo (figure 4.8 (b-e)) to calculate the radius of the sample (see red circle in figure 4.8f).



Figure 4.8: Method for the detection of the shrinkage developed by Daniel Żymełka [6].

This method presented in the figure 4.8 has a good advantage because it is a contactless measurement that doesn't affect the magnitude of the electromagnetic field and therefore the microwave heating of ceria sample.

4.3.2.4 The calibration protocol of the temperature

It is necessary to use to use a calibration system which has the same configuration as the real microwave heating. The system was developed during the PhD thesis of J. Croquesel [2] and it consists to heat a ceria sample by electromagnetic induction in the same conditions of the microwave cavity.

Ceria pellets (φ 13 mm x1.5mm) were uniaxially pressed (P= 200 MPa) and have a similar density as the samples to be sintered. This pellet was placed on a metallic piece in the Fiberfrax isolator inside the copper coil which is connected to the generator (figure 4.9a). The electric current passes through the coil and creates a variable magnetic field which is the source of the electrical induction in the metallic piece (figure 4.9b) under the ceria pellet. The metal heats up by joule effect coming from the heat dissipation of the electric current and conducts the heat to the pellet. The ceria is heated up by conduction and its radiation at its upper face will be detected by the pyrometer through a small hole in the upper part of the isolator to avoid any radiation coming from the metal. A thermocouple was measuring the temperature on the lower face of the pellet through a hole in the metal (see figure 4.9.b)





Figure 4.9: The calibration system (a), the pierced metal piece in the Fiberfrax isolator (b).

In the figure 4.9a, we can see a thermocouple type S (on the left lower corner), the pyrometer (above), the generator (right side) and the calibration cell covered by a pierced Fiberfrax piece inside the copper coil. The pierced metal where the thermocouple wire will go in is presented

in the figure 4.9b. The thermocouple wire does not interact with the magnetic field and does not heat.

Therefore, the apparent emissivity of ceria was obtained as function of temperature (from 500 up to 1400°C) by correcting each value of the temperature measured by pyrometer to the corresponding value by thermocouple. The calibration protocol has been done for ceria pellets (Φ 13 mm x h1.5 mm pressed at 200 MPa) formed from micro-powder as well as from nano-powder.

The variation of the apparent emissivity as function of temperature for ceria (micro-powder) and (nano-powder) is presented in the figure 4.10. The standard deviation for both variations is less than 3 % which was too small to be clearly appeared in this figure. This precision in the standard deviation makes the variation of emissivity acceptable and reasonable.



Figure 4.10: The variation of the apparent as function of temperature for ceria sample made of micropowder (blue) and nano-powder (red).

The apparent emissivity of micropowder increases with temperature from 0.095 up to 0.17 whereas it has a low variation in case of nanopowder with a low drop at around 700°C. The difference in emissivity variation between the two powders can be influenced by the presence of oxygen vacancies which depend on the ratio of Ce^{4+}/Ce^{3+} [7]. The drop seen in case of nanopowder can be due to the presence of free charges due to the increase of the conductivity at around 700°C and these charges can be mobilized by the induction heating (effect of electromagnetic field).

The fitting model corresponding to the variation in the figure 4.10 of micro-powder is given by the equation 4.2 and was provided in the LABVIEW protocol for the temperature measurement by pyrometer.

 $\varepsilon = -1.2210407*10^{-18}T^{6} + 6.4174631*10^{-15}T^{5} - 1.3679985*10^{-11}T^{4} + 1.5161650*10^{-8}T^{3} - 9.0997962*10^{-6}T^{2} + 2.7625075*10^{-3}T - 2.3266744*10^{-1}$
This polynomial model of apparent emissivity was served as inputs in the simulation which will be presented in chapter 5.

The fitting model corresponding to the variation of nanopowder in the figure 4.10 is given by the equation 4.3:

$$\begin{split} \varepsilon &= -4.2531945^{*}10^{-18}\text{T}^{6} + 2.5620945^{*}10^{-14}\text{T}^{5} - 6.3066627^{*}10^{-11}\text{T}^{4} + 8.0836724^{*}10^{-8}\text{T}^{3} \\ &\quad -5.6587399^{*}10^{-5}\text{T}^{2} + 2.0392940^{*}10^{-2}\text{T} - 2.7770658 \end{split}$$

(Eq.4.3)

4.4 The measurement of the density

The initial and final densities of the green and sintered samples and the relative density during the heating cycle were determined by two methods in order to follow the variation of the densification.

4.4.1 The geometrical method

The bulk density of ceria samples is determined geometrically from the measurement of the dimensions and the mass of the sample. In case of cylindrical pellets having a bulk density ρ_{ceria} , it is given by the equation 4.4.

$$\rho_{ceria} = \frac{4m}{\pi d^2 h} (g.cm^{-3})$$
(Eq.4.4)

with *m* the mass of the pellet, *d* its diameter and *h* its height.

The relative density is calculated relatively to the theoretical density of the material ρ_{th} which equal to 7.13 g/cm³.

$$\rho = \frac{\rho_{ceria}}{\rho_{th}}$$
(Eq.4.5)

4.4.2 The density calculated from the shrinkage during the sintering

4.4.2.1 Conventional dilatometry

From the final density calculated for the sintered sample and its height, it is possible to calculate the relative density at each moment by the relation:

$$\rho(t) = \frac{\left(1 + \alpha \frac{h_f - h_0}{h_0}\right)^2 \cdot \left(1 + \frac{h_f - h_0}{h_0}\right)}{\left(1 + \alpha \frac{h(t) - h_0}{h_0}\right)^2 \left(1 + \frac{h(t) - h_0}{h_0}\right)} \rho_f$$

(Eq.4.6)

where α is the shrinkage anisotropy factor defined by:

$$\alpha = \frac{\left(\varphi_f - \varphi_0\right).h_0}{\varphi_0.\left(h_f - h_0\right)}$$
(Eq.4.7)

with h_0 , h_f , φ_0 , φ_f are respectively the initial and final height and initial and final diameter of the sample. $\rho(t)$, ρ_f and h(t) are respectively the instantaneous, final density and instantaneous height.

4.4.2.2 Optical dilatometry

Contrary to the conventional dilatometry, the optical dilatometry is able to measure the diameter and not the height. Therefore, the instantaneous density can be calculated by the equation 4.8:

$$\rho(t) = \frac{\left(1 + \frac{\varphi_f - \varphi_0}{\varphi_0}\right)^2 \cdot \left(1 + \frac{1}{\alpha} \frac{\varphi_f - \varphi_0}{\varphi_0}\right)}{\left(1 + \frac{\varphi(t) - \varphi_0}{\varphi_0}\right)^2 \left(1 + \frac{1}{\alpha} \frac{\varphi(t) - \varphi_0}{\varphi_0}\right)} \rho_f$$

(Eq.4.8)

with $\varphi(t)$ the instantaneous diameter of the sample.

4.5 Experimental study: Conventional versus Microwave sintering

The densification of ceria pellets made from two different powders during the conventional and microwave sintering for a heating rate of 25K/min will be presented in this section. Moreover, the sintering curves of ceria pellets made from micro-powder for three different heating rates (25, 20 and 15 K/min) will be presented in the case of microwave

sintering (MS) and be compared to the conventional sintering (CS). In addition, the microstructures of different sintered samples are also presented in this section.

4.5.1 The densification curves of ceria

This part concerns the effect of grain size of ceria on the sintering during the two heating techniques conventional (CS) and microwave (MS) and the effect of heating rates on the sintering.

4.5.1.1 Micrometric versus nanometric during conventional and microwave sintering

The densification curves were obtained using the two dilatometry's techniques presented in sections 4.2 and 4.3. The curves of two different kinds of ceria samples (micrometer M and nanometer N) were carried out in the same experimental conditions (heating rate of 25K/min, dwell time of 5 minutes at 1500°C and a free cooling down to the room temperature).

The figure 4.11 shows the variation of the relative density as function of temperature for two samples of ceria M and N during the conventional sintering (CS).



Figure 4.11: The variation of the relative density as function of temperature during conventional sintering (CS) for ceria samples M and N at 25K/min.

The figure 4.11 shows that the sample N starts to densify from 950°C with a large rise whereas the sample M has a low rise starting from 1100°C. Moreover, the sample N shrinks from 58% up to 89% of relative density whereas the relative density of the sample M increases from 67% to 83%. This can be explained that as the sintering happens during the intermediate stage where the elimination of the opened pores is activated, the sample N can act much more than the sample M due to the depending of the sintering rate on the grain size. The sintering is inversely proportional to the grain size which makes the densification in case of sample N more important. In addition, the diffusion at atomic scale is also more important and has an influence on the global densification.

Now, the figure 4.12 shows the variation of the relative density as function of temperature for two samples of ceria M and N during the microwave sintering (MS).



Figure 4.12: The variation of the relative density as function of temperature during microwave sintering (MS) for ceria samples M and N at 25K/min.

As seen during the conventional heating, the same effect of the initial grain size is obtained in terms of densification during microwave heating. The figure 4.12 shows that the sample N starts to densify from 1000°C with a very large rise whereas the sample M begins at around 1250°C as observed in CS (figure 4.11). In this process, the sample N shrinks from 59% up to 86% of relative density whereas the relative density of the sample M increases only from 63% to 69%. The final densities obtained for the samples N are slightly different compared to conventional heating (86% in MS instead of 89% in CS) in both cases whereas it becomes very different for samples M (68 % in MS and 83% in CS). It appears that the grain size has a significant effect on the interaction between microwave and the green specimen, indeed, the M sample presents a low shrinkage during MS.

It is important to mention that the curves seen in figure 4.12 are obtained after correction of temperature signal and shrinkage measurement. These errors are coming from the bad detection of the edges by the camera during the microwave sintering and from the accuracy due the measurement of temperature by the pyrometer.

4.5.1.2 Densification of ceria samples M

Now, we compare the densification as function of heating rates for two M specimens of ceria. The curves of the densification concerning two samples M of ceria during the conventional sintering are presented in the figure 4.13.



Figure 4.13: Variation of the relative density as a function of temperature during conventional sintering (CS) for ceria M at different heating rate.

The figure 4.13 shows that the final density obtained for a heating rate of 20K/min, the initial densification increases from 65% up to 80% which is about 15% of difference and the same difference has been obtained for the sample at 15K/min from 66% as initial value of relative density up to 81%. Therefore, the results show a weak influence of the heating rate on the final densification during the conventional sintering.

Now, the densification concerning two samples M of ceria during the microwave sintering is presented in the figure 4.14.



Figure 4.14: Variation of the relative density as a function of temperature during microwave sintering (MS) for ceria M at different heating rate.

For the microwave heating, the densification increased from 66.5 up to 70% for a heating rate of 20K/min. For a heating rate of 15K/min, the final relative density was 70.5% which corresponds to an increase of 0.5% comparing to the previous heating rate. Therefore, the results show a low influence of the heating rate on the final densification during the microwave sintering for M samples.

In microwave sintering like in conventional sintering, the results show a weak dependency of the heating rate with the densification. However, the conventional sintering has a significant effect on the final densification whereby the sample has a higher densification.

4.5.2 Comparison of the microstructures of sintered ceria samples

In order to study the evolution of grain morphology for the two different sintering process and two different ceria powders, SEM analysis of polished and etched surfaces was made and the results are presented in this section.

Firstly, we present for M and N powders the SEM micrographs of two ''before sintering'' samples and then for each one, the grain morphology by conventional and microwave sintering. The results are presented in the figure 4.15.



Figure 4.15: SEM micrographs of ceria samples a) M pressed 67%, b) M CS 83%, c) M MS 69%, d) N pressed 59%, e) N CS 89% and f) N MS 86%. The samples in b, d, e and f are polished and etched.

The green sample M which is less porous than the N sample, has a grain size less than 2 μ m whereas the N sample is largely less than 200 nm. The sintered M sample in case of microwave sintering has a larger grain size (4.0 μ m) than in case of conventional sintering (1.9 μ m), despite its high porous content 69% compared to 83% for CS. It is clear that the

sintered N samples present a grain growth which is much larger than the M samples in both sintering process. Moreover, the coarsening is more activated in case of microwave sintering for N samples. The final relative density is slightly higher in case of CS 89% (9.8 μ m) instead of 86% (10.9 μ m) for MS. Now, the SEM results for the different heating rates of M samples in the CS and MS are presented in figure 4.16, in order to identify the effect of heating rate on the sintering and microstructure.





(f) MS 15K mean grain size = $3.9 \pm 0.3 \mu m$

Figure 4.16: SEM micrographs of polished and etched M ceria samples; a) 25K/min CS 83%, b) 25K/min MS 69%, c) 20K/min CS 80%, d) 20K/min MS 70%, e) 15K/min CS 81% and f) 15K/min MS 70.5%.

The grain size is higher in case of microwave sintering, for example at 15K/min the mean grain size is $3.9 \,\mu\text{m}$ in case of MS instead of $1.6 \,\mu\text{m}$ in case of CS. Moreover, the grain size has very weak dependence on the heating rate and it is not significant in the small range (15, 20, 25K/min) we have selected.

4.6 Conclusion

The microwave applicator system developed at the laboratory SIMAP was used for the sintering by microwave heating of ceria samples. The two different kinds of ceria samples were tested and the results show that the samples performed with nanometric powder (N) lead to higher densification than the samples performed with micrometric powder (M). This behavior was obtained also for conventional heating technique. Moreover, in case of microwave heating, during the sintering, the grain coarsening is more activated and especially for nanometric powder

Finally, the microwave process seems to have more influence on the grain growth than on the densification for ceria based materials. Moreover, high heating rates (15 up 25K/min) have low effect on the final density but it has a significant effect on the grain size.

Résumé en français : Frittage de la Cérine par chauffage conventionnelle et par chauffage micro-ondes

Dans ce chapitre, une étude comparative entre le frittage conventionnel et celui par chauffage micro-ondes de deux poudres de Cérine (micrométrique et nanométrique) est présentée. Dans un premier temps nous avons décrit les équipements utilisés et plus précisément le montage développé pour le frittage par chauffage micro-ondes ainsi que les matériaux à fritter. Une calibration particulière pour la mesure de l'émissivité des matériaux au cours de son chauffage a également été mise en place pour déterminer le plus précisément la température des matériaux. Ensuite, les résultats obtenus par les deux techniques expérimentales de frittage sont discutés. Ces résultats ont montré que le chauffage par micro-ondes agit sur le grossissement des grains de la Cérine plus que le chauffage conventionnel. D'autre part, le chauffage classique a un avantage sur l'amélioration de la densification finale alors que les vitesses de chauffage ont un faible effet sur la densité finale mais plutôt un effet remarquable sur la taille des grains.

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Chapter 5: Microwave effect on model and ceria particles: a simulation study

Today, despite numerous efforts it is still unclear how the local electromagnetic and thermal field gradients can influences the mass transfer mechanisms involved during sintering such as grain boundary diffusion and surface diffusion. Hao et al [1] suggest in their work about the microwave heating effect a model that includes the reduction in the formation energy of vacancy at the neck surface. Rybakov et al [2, 3] suggest a model to explain the nonthermal effect by a ponderomotive force which combines the diffusion mechanism and the electromigration fluxes of vacancies. On the other hand, Johnson shows in his work [4] that for grains diameters less than 3 μ m, the grain boundary diffusion predominates over volume diffusion for all sintering stages. Though microwave technology can be used for the selective and rapid heating of many different classes of materials, [5]. On the other hand, the availability of user-friendly softwares makes it attractive to address multi-physics problems such as microwave assisted sintering, in which the electromagnetic interactions are coupled to heat and mass transfer [6].

In this chapter, we present a single mode resonant microwave cavity (2.45 GHz) loaded with either spherical model then ceria particles. A weakly coupled Electromagnetic-Thermal (EM-thermal) solver is used iteratively to determine how the microscopic geometry (local curvatures between the particles, grain size and neck size) modifies the electromagnetic field, and in turn the thermal field in the particles and also to quantify the microwave effect for a realistic process. The modelling is performed with the conformal Finite Element (FE) solver COMSOL Multiphysics. The dielectric and the thermal properties of cerium oxide (ceria) particles up to 1000°C used in the simulation have been determined in our previous published study [7]. Despite the existence of several softwares used for electromagnetic simulation, our choice of COMSOL Multiphysics was due especially to its ability to couple different physics (in this case electromagnetic and heat transfer) and its user-friendly interface.

5.1 The different concepts of model and the materials parameters

The main elements needed for the modelling using COMSOL Multiphysics can be divided in three categories:

- a) The physical scenario and the geometry.
- b) The materials properties.
- c) The mesh.

5.1.1 The physical scenario and the geometry

The scenario consist of a single mode resonating cavity based on a 260 mm segment of a rectangular waveguide WR340 (86mm x 43mm) delimited by a short circuit on one side and a symmetrical inductive rectangular iris (65mm x 43mm) on the other side. The resonance of interest is a TE_{103} mode close to 2.45 GHz. The different physics (called modules in the software) such as electromagnetic module which is solved in frequency domain and the heat transfer in time domain are coupled together.

The figure 5.1 presents the geometry and the different elements of the cavity.



Figure 5.1: Geometry of the cavity and its elements (distance in meters).

The cavity is loaded with spherical ceria samples (\emptyset 0.1-3mm) surrounded by a crucible, centered in one electric field maxima (see figure 5.2). The cavity walls are set at perfect metallic conductor. The microwave input power is fixed at 1000 W and the heating time at 2000 s. The simulation process can be described as an iterative process where the multiphysics problem follows the different steps mentioned below:

First, an electromagnetic stationary calculation was made everywhere in the cavity and within the sample taking into account the dielectric properties (Equation 5.1) of the sample to provide the energy absorbed. The boundary conditions applied to the cavity walls supposed that they are perfectly conductors (Equation 5.2). Then, the energy absorbed by the sample acts as a local heat source (Equation 5.3). The heat transfer in the solid is also included in this study (see Equation 5.4). The losses coming from the radiation of the sample surface are given by the Equation 5.5. Finally, the heat flow (Equation 5.6) assumed for the air was also included. The heat transfer and the heat losses were calculated in a time domain whereas the electromagnetic study was in frequency domain.

In this study, we were interesting to quantify the electric field in the whole cavity and the dissipation energy due to electric field contribution in the sample. The relative permeability of the different objects (sample, crucible ...) was fixed at 1; therefore the calculated losses are resulting from dielectric losses and the losses by conduction.

Now, we present the different equations used which relate the different physics involved:

$$\nabla \left(\boldsymbol{\mu}_{r}^{-1} \nabla \boldsymbol{E}\right) - \boldsymbol{k}_{0}^{2} \left(\boldsymbol{\varepsilon}_{r} - \frac{\boldsymbol{j}\boldsymbol{\sigma}}{\boldsymbol{\omega}\boldsymbol{\varepsilon}_{0}}\right) \boldsymbol{E} = 0$$

(Eq.5.1)

Equation 5.1 represents the wave propagation equation in the whole cavity.

$$\vec{n} \wedge \vec{E} = \vec{0}$$

(Eq.5.2)

Equation 5.2 represents the boundaries conditions at the cavity walls where the electric field is parallel, due to perfect conductive of constitutive material.

$$P = (\sigma + 2\pi f \varepsilon_0 \varepsilon_{eff}) |E|^2$$
(Eq.5.3)

The electromagnetic dissipation in the materials is defined by equation 5.3

$$\rho c_{p} \frac{\partial T}{\partial t} + \rho c_{p} u \nabla T = \nabla (k \nabla T) + Q_{s} \qquad \rho c_{p} \frac{\partial T}{\partial t} = \nabla (k \nabla T) + P$$
(a)
(Eq.5.4)

Equation 5.4 (a) represents the general heat transfer in the solid (sample), and in our case, because sample is static the resulting equation becomes Eq.5.4 (b)

$$-\boldsymbol{n}.(-\boldsymbol{k}\nabla\boldsymbol{T}) = \boldsymbol{\varepsilon}\boldsymbol{\sigma}\left(\boldsymbol{T}_{amb}^{4} - \boldsymbol{T}^{4}\right)$$
(Eq.5.5)

Equation 5.5 represents the radiative losses in the materials (ceria sample and alumina crucible).

$$\rho_{f}c_{pf}\frac{\partial T}{\partial t} + \rho_{f}c_{pf}u_{f}.\nabla T = \nabla .(k_{f}\nabla T) + Q_{f} \qquad \rho_{f}c_{pf}\frac{\partial T}{\partial t} = \nabla .(k_{f}\nabla T)$$
(a)
(Eq.5.6)

Equation 5.6 (a) represents the heat transfer in the air (the fluid) by conduction and convection. In our case convection is not taken into account and because air does not heat by microwave therefore the heat propagation equation becomes Equation 5.6 (b).

with |E| the electric field norm, f the frequency, σ is the electrical conductivity of ceria, ε_r the relative dielectric permittivity of ceria, $\varepsilon_{eff}^{"}$ the imaginary part of the dielectric constant of ceria, k, k_f the thermal conductivity of ceria and the air respectively, c_p, c_{pf} the specific heat capacity of ceria and the air respectively, u, u_f the velocity field of ceria and the air, ε the emissivity of ceria, Q_f , Q_s the heat source for the air and the ceria respectively. Q_f is equal 0 (case of air) and Q_s to P (case of ceria).

The figure 5.2 and 5.3 present for empty cavity the maxima of the electric field magnitude in the two planes xy (seen from the top) and zy (seen along the whole cavity) respectively.



Figure 5.2: Maxima of the electric field magnitude in xy plane.



Figure 5.3: Maxima of the electric field magnitude in zy plane.

The distribution of the electric field in the cavity shows that it has three regions where the electric field magnitude is maximal. The highest norm obtained was 49300 V/m. Moreover, the sample position was fixed in the middle region as seen in the two figures 5.2 and 5.3 and the E-field direction is along z axis (the height of the cavity).

5.1.2 The materials properties

The cavity walls have been imposed to be perfect electric conducting metal. The crucible material is based on porous alumina material. Its dielectric properties were very low in order to get as highest electric field magnitude as possible in the sample region.

The table 5.1 presents the thermal and the dielectric parameters of the porous alumina crucible used it the study.

Relative permittivity	Specific heat capacity (J/Kg.K)	
1	990	
Emissivity	Thermal conductivity (W/m.K)	
$5.1307 {10}^{-19} * {T}^{6} - 3.7659 {10}^{-15}{T}^{5} + 1.0469 {10}^{-11}{T}^{4} -$		
$1.339710^{-8}T^3 + 7.585810^{-6} * T^2 - 1.846910^{-3} * T +$	$1.537610^{-4} * T + 0.25152$	
1.0369		

Table 5.1: Thermal and dielectric parameters of porous alumina crucible.

Now, the dielectric and thermal properties of ceria which were determined in the chapter 3 are presented in table 5.2.

Relative permittivity	Specific heat capacity (J/Kg.K)
$7.9519 + 0.0087 * T - j * (1.4354 10^{-14} * T^{5} - 4.4388 10^{-11} * T^{4} + 5.2856 10^{-8} * T^{3} - 2.9991 10^{-5} * T^{2} + 8.0780 10^{-3} * T - 0.8058)$	$5.42110^{-7} * T^{3} - 1.438910^{-3}T^{2}$ $+ 1.2612 * T + 62.208$
<i>Emissivity</i> $1.46310^{-7} * T^2 - 0.000310^{-3} * T + 0.221$	<i>Thermal conductivity (W/m.K)</i> -1.157*log(<i>T</i>)+8.7001

Table 5.2: Thermal and dielectric parameters of cerium oxide.

5.1.3 The mesh

The selection of mesh element is important in such finite element solver because these elements are responsible for the provided information delivered by the software. Hence, the mesh element must be less than $\lambda_g/5$ in which λ_g is the guide wavelength and it is equal to

17.3 cm. The reason is due to the discretization of the wave in order to ensure a better accuracy in the calculation. Otherwise, the results will depend strongly on the mesh.

The mesh was tested using many calculations in order to fix and optimize the mesh size in the sample region. It is important to know that the y axis is the axis through the length of the cavity, the z axis is the one through its height and the x axis is the one through its width.

Actually, the mesh elements were divided into three sizes depending on the concerned objects:

1- The maximum element size concerning the cavity was fixed at Lz/6 (7.2 mm); with Lz is the height of the cavity.

The fully meshed cavity model is presented in the figure 5.4.



Figure 5.4: The mesh applied to model cavity.

2- The mesh concerning the crucible object was fixed to be less than 5 mm by using the automatically mesh (fine) provided by COMSOL.

The fully meshed crucible model is presented in the figure 5.5.



Figure 5.5: The mesh applied to model crucible is in blue.

3- The maximum element size concerning the spherical sample was fixed at r/10 in volume; with r is the sample radius. Moreover, a different element size was applied to the sample surface (or boundary) in order to get more accuracy at the curvature region. Its value was r/15.

The fully meshed of sphere model is presented in the figure 5.6.



Figure 5.6: The mesh applied to model spherical sample.

On the other hand, four calculations of a model sphere with $100\mu m$ of radius are presented in figure 5.7 in order to quantify the effect of the mesh size on the electric field norm along y axis.



Figure 5.7: The variation of electric field magnitude through a spherical sample along y axis.

The figure 5.7 shows the variation of the electric field magnitude for a spherical sample of ceria having $\varepsilon'=10$ and $\varepsilon''=0.01$ (called model particle). The element size of the mesh inside the sample has three maximum values 0.5r, 0.2r and 0.1r and in the fourth calculation the surface meshing was imposed to be r/15 (0.066r) with 0.1r inside the sphere. It is clear from the figure 5.7 that the accuracy is similar inside the centre of the sample for 0.1r and 0.2r (in blue and red) whereas the curve concerning the 0.5r (green triangles) is different. Moreover, the one with 0.1r and the imposed mesh at the surface (in purple) provides more precision at the interface as it appears lower on the left vertical line. We have chosen therefore the fourth mesh protocol which has these elements sizes:

- 1- 0.1r as maximum for the volume of the sample
- 2- r/15 as maximum for its surfaces
- 3- Lz/6 as maximum for the cavity which is about 7.2 mm.
- 4- 5 mm as maximum for the crucible.

Moreover, the mesh was adapted at the interface of the different objects so it goes progressively from one object to another as seen in the figure 5.8.



Figure 5.8: The variation of element size of the mesh in the plan yz across a sphere having a radius of 0.1 mm (the scale varies from 9.6 mm to 6.7 μ m). The scale is in meter.

5.2 The electric field interaction with model particles

The objective of this calculation is to quantify the effect of particle size on the electric field magnitude and therefore define the optimal size in order to limit the calculation time. In this section, we present the results concerning the effect of particle size for a configuration of cavity without crucible for one spherical model particle and in case of three particles. Moreover, **the radiative losses are not taken into account in this configuration** whereas the thermal conduction in solid and fluid is allowed. This part of our work aims to study the local interaction of the electric field with the particles and the heating due to pure microwave heating.

5.2.1 The effect of particle size

The spherical sample which has $\varepsilon'=10$ and $\varepsilon''=0.01$ and the thermal parameters of ceria, is placed in the centre of a region of high electric field magnitude (see section 5.1.1). The radius varies from 0.01 to 1 mm due to the limits of dimensions of the software. The variation of the electric field norm along the (x, 0, 0) and (0, y, 0) axis are presented in figure 5.9, both are perpendicular to the E-field axis and along (0, 0, z) axis is presented in figure 5.10 which is parallel to E-field.



Figure 5.9: The variation of electric field norm in the sample along x and y axis for four different sample radii (0.01, 0.1, 0.5 and 1 mm).



Figure 5.10: The variation of electric field norm in the sample along z axis for four different sample radii (0.01, 0.1, 0.5 and 1 mm).

When the size of the particle increases the norm of E-field increases from 10300 V/m as the maximum obtained at the centre of the smallest particle to 10350 for the largest one. Moreover, the E-field gradient through each particle is larger in x and y axis compared in z axis, it will affect the heating. The spikes seen in this figure are just an artefact due to the discretization principle in the Finite Element method.

The distribution of the temperature of one ceria model particle for the four different radii is presented in figure 5.11. In this calculation, the thermal losses at the cavity walls are null and these losses for all other surfaces are conductive.



Figure 5.11: The variation of sample temperature along three axes for four different sample radii (0.01, 0.1, 0.5 and 1 mm) after 2000 s.

The temperature increases slightly with the size of the particle by only 6° C. The temperature across each particle along the three axes doesn't show any thermal gradient. The variation of temperature observed close to the surface of particle inside the gas domain is due to the conductive losses from sphere surface to air.

5.2.2 The effect of ε' and ε''

In order to quantify the influence of dielectric properties in a microwave heating process, a spherical sample with 1 mm of radius is placed at the same position as before, the centre of a region of high electric field magnitude (see section 5.1.1). The values of ε ' and ε '' were varied and therefore the loss tangent *tan* δ , are presented in the table 5.3:

ε' for a fixed ε''=0.1	tan δ for a fixed ε ''=0.1	ε'' for a fixed ε'=10	tan δ for a fixed ε '=10
1	0.1	0.001	0.0001
10	0.01	0.01	0.001
100	0.001	0.1	0.01
-	-	1	0.1
-	-	10	1

Table 5.3: values of ε ' and ε '' and tan δ used during the calculation.

Firstly, the variation of the electric field norm as function of ε '' is presented in the figure 5.12 along the three axes as they were similar. Then, the distribution of the corresponding temperature is presented in the figure 5.12. As the wavelength in the sample λ_s depends on the ε ' by the relation $\lambda_s = \lambda_g / \sqrt{\varepsilon}$, therefore the mesh size in the sample has a value less than the condition mentioned in section 5.1.2. For example, the value of λ_s in case of ε '=100 is equal to 1.7 cm which is greater more than 5 times of the element size 0.1 mm.



Figure 5.12: The variation of electric field norm in the sample along the axes for five different values of ϵ '' (0.001, 0.01, 0.1, 1 and 10).



Figure 5.13: The variation of temperature in the sample along the axes for five different values of ϵ '' (0.001, 0.01, 0.1, 1 and 10) after 2000s.

The figure 5.12 shows that the variations of the electric field norm were very similar for the four cases when $\varepsilon'' \leq 1$. For these cases, the magnitude of the electric field is about 10300 V/m and it decreases strongly from 10300 to 7800 V/m for a high value of $\varepsilon''=10$. The figure 5.13 shows that due to high value of ε'' , the temperature of the sample becomes high about 600°C, whereas for $\varepsilon''=1$ the temperature decreases down to 150°C and finally for lower values of ε'' the heating of the model particle is not efficient (less than 40°C). However, for all values of ε'' , the temperature remains constant inside the particle which is expected because the losses are not taken into account.

On the other hand, the variation of the electric field norm as function of ε ' is presented in the figure 5.14 along the three axes as they were similar.



Figure 5.14: The variation of electric field norm in the sample along the axes for three different values of ϵ ' (1, 10 and 100).

It shows that the variation of the electric field increases strongly from 500 to 40500 V/m when ε ' decreases from 100 to 1. The drop of the electric field norm inside the particle depends much more on ε ' than on ε ''. This is reasonable as ε ' is related to the capacity of the matter to store electromagnetic energy.

The distribution of the corresponding temperature is presented in the figure 5.15.



Figure 5.15: The variation of temperature in the sample along the axes for three different values of ε ' (1, 10 and 100) after 2000s here ε '= ε * in notation.

For a fixed ε '' value (0.01), the temperature of the sample starts to become important (around 110 °C) for ε '=1 which is due to the loss tangent, here $\tan \delta = 0.01$ (see chapter 1). Hence, the heating of model particle will be significant when the loss tangent will be greater than 0.01. Moreover, as excepted ε ' has an influence on the electric field magnitude whereas ε '' affects the heating and therefore the parameter $\tan \delta$ presents the contribution of these two parameters.

5.3 The electric field interaction and the heating of three ceria particles without thermal losses

In this section, we present the results concerning the effect of neck size (X) of three ceria particles and then the effect of packing configuration in a cavity without crucible. Once again, the radiative losses are not yet taken into account in this configuration, only conductive losses are presented.

5.3.1 The effect of neck size

Three spherical samples (0.1 mm of radius) are placed at the position on which the centre of the system has the same position as in case of one sphere. The ratio neck size over

grain size (X/R) has three different values: 0 in case of no neck between the particles, 0.1 and finally 0.2. The three particles are rearranged along y axis which is the axis along the length of the cavity (see figure 5.16). The values of ε 'and ε '' used in the following section of this chapter are those determined for ceria materials, defined in table 5.2 (see section 5.1.2). For example, at room temperature ε '=10.5 and ε ''=0.02.



Figure 5.16: Schematic presentation showing the position of the system of three spheres (0.1 mm of radius) and the axes in Y configuration.

The figure 5.17 presents the electric field norm along a cross section in xy plane which passes across through the middle of the three particles.



Figure 5.17: The variation of electric field norm in cross section in xy plane axis for X/R=0.2.

The electric field magnitude in the particles varies from 7000 to 10000 V/m and becomes very high near the surface 20000 V/m. For more precision, the figures 5.18, 5.19 and 5.20 present the variation of electric field magnitude along x, y and z axis.



Figure 5.18: The variation of electric field norm along x axis for three different neck sizes (0, 0.1 and 0.2).



Figure 5.19: The variation of electric field norm along y axis for three different neck sizes (0, 0.1 and 0.2).



Figure 5.20: The variation of electric field norm along z axis for three different neck sizes (0, 0.1 and 0.2).

The figure 5.18 shows that the electric field along x axis decreases significantly from 8800 V/m at the centre of the system (the central particle) to 8200 V/m when the ratio neck size over grain size (X/R) increases from 0 to 0.2. In terms of power, this variation corresponds to about 13% of the total dissipated power, using the equation 5.2. Moreover, a similar gradient of electric field norm through the sample for the three cases of X/R ratio is presented and it is about 300 V/m.

The figure 5.19 which presents the variation along y axis through the three ceria particles. It shows the similar behaviour as in x axis at the centre of the central particle: the presence of neck decreases the electric field norm by about 600 V/m. Moreover, electric field difference is more important between the neck region and the outer particles about 3500 V/m than between the neck region and the central particle. The figure 5.20 shows that the variation along z axis has the same behaviour as along x axis, except the E-field norm gradient which it is about 800 V/m between the centre and the surfaces of the central particle instead of 300 V/m along x axis.

Now, we present in the figures 5.21 and 5.22 the variation of the electric field norm in the cross section containing neck plane (xz). The variations in this plane seem to be weak in both axes.



z axis neck region

Figure 5.21: The variation of electric field norm in the neck plane along z axis (0, -radius, z) for three different neck sizes (0, 0.1 and 0.2).

Along z axis (figure 5.21), the electric field norm at the centre of the neck increases from 6200 up to 6450 V/m when the neck size increases and it is in general higher without neck. It is important to mention that due to the mesh size limits at very small scale, the meshing is not sufficient in the plane of the neck region, which makes the obtained results less reliable.



Figure 5.22: The variation of electric field norm in the neck plane along x axis (x, -radius, 0) for three different neck sizes (0, 0.1 and 0.2).

Along x axis, the electric field norm has the same trend as along z axis but it varies at the centre from 6000 up to 6400 V/m. In addition, in case of no neck between particles, the electric field norm is lower than the previous case.

Finally, the presence of the neck is the major parameter which controls the decrease of the electric field norm in the material bulk and the neck size has a secondary effect on it.

5.3.2 The effect of packing configuration

As previously, a model of three particles (a radius of 0.1 mm) having no neck placed in a new configuration is presented in this section. The figure 5.23 shows a schematic presentation of the packing in z axis which is parallel to E-field direction (see figures 5.2 and 5.3).

It is important to mention that the central particle of this packing has the same position as in the configuration along y axis (figure 5.16) which is perpendicular to the E-field direction.



Figure 5.23: Schematic presentation showing the position of the system of three spheres (0.1 mm of radius) and the axes in Z configuration.

The figures 5.24 and 5.25 present the variation of electric field magnitude and the temperature respectively for the two packing along their corresponding configuration axes (y axis for Y configuration and z axis for Z configuration).



Figure 5.24: The variation of electric field norm for Z and Y configurations.



Figure 5.25: The variation of temperature for Z and Y configurations.

The electric field (figure 5.24) is in general higher for Z configuration because this configuration is parallel to the E field direction. The value of the electric field in the centre of the central particle of the Z configuration is 17000 V/m instead of 8000 V/m for Y configuration. Moreover, the electric field magnitude in Z configuration close to the neck region is much more important (about 170000 V/m) than the Y configuration which is equal to 6000 V/m and the variation has a reverse behaviour when it passes from the centre of the system to the neck region. Moreover, comparing to the maximum E-field magnitude in the empty cavity (see figure 5.2), the electric field norm close to the neck region in Z configuration is three times greater.

Concerning the temperature, Z configuration shows a higher value compared to Y configuration which agrees with the fact that the electric field is higher in Z configuration. But due to low size of the particles the temperature can attend not more than 30 °C whereas for the same configurations of particles with a radius of 1 mm and in the presence of the crucible the temperature difference between the two configurations in the central particle is more than 400 °C (figure 5.26).



Figure 5.26: the variation of temperature within a cross section (in yz) of the three particles: (a) in Y configuration and (b) in Z configuration.

The centre of the central particle has 220 °C in case of Y configuration and 629 °C in case of Z configuration.

As this system doesn't take into account the radiative and the convective losses, this drop in temperature results from the material weight which is 1000 times lower for 0.2 mm of particle size compared to 2 mm of particle size.

5.4 The electric field interaction and the heating of full ceria particles packing

In this section, we present the results concerning the effect of **the radiative losses** for 27 ceria particles in a cavity with crucible. Then, the equivalent volume of one ceria sphere will be presented to be compared to the packing. It is important to mention that both internal and external sample surfaces are exposed to the same radiation coming from the crucible.

5.4.1 The full packing in crucible

Here, in the packing of 27 particles of ceria with 1 mm of radius, the central particle has the same position as the two previous configurations with three particles and with one particle. The figure 5.26 presents the electric field norm among the 27 particles. It has a highest magnitude at the poles of the particles in z direction and especially close to the contact between them.



Figure 5.26: The variation of electric field norm among the 27 particles, radius=1 mm.

The figure 5.27 presents the variation of the electric field norm along x and y axes then the figure 5.28 present its variation along z axis. The variation in x and y axes shows that the electric field norm has an inverse behaviour through the neck compared to the variation in z axis. A variation of electric field magnitude about -4000 V/m (x and y axes) is shown from the centre of each particle to the neck region, whereas this variation becomes very high about 65000 V/m along E-field axis (z-axis).



Figure 5.27: The variation of electric field norm in x and y axes.



Figure 5.28: The variation of electric field norm in z axis.

The figure 5.29 presents the variation of the temperature along the three axes. The maximum temperature reached in the centre of the packing after 2000 s was 520 °C, this temperature decreases by about 10 °C in the neck region and again by about 20 °C from the neck region to the external surfaces of outer particles. By taking into account the thermal losses and the thermal diffusion in solid state, the thermal gradient in the packing appears.



Figure 5.29: The variation of temperature in x, y and z axis after 2000 s.

5.4.2 The effect of surface area and the compacting on the heating

In this part, we will try to quantify the effect on the heating of:

- Surface area (particle size and particles number)

- Compacting of several particles (one or 27 particles).

The table 5.4 presents both configurations and their corresponding volume, surface area and volume over surface area ratio (V/S).

System (radius)	Volume (mm ³)	Surface area (mm ²)	V/S (mm)
1 sphere (r mm)	$\frac{4}{3}\pi r^3$	$4\pi r^2$	$\frac{r}{3}$
27 spheres (r mm)	$\frac{27}{3}\pi r^3$	$27\pi r^2$	$\frac{r}{3}$

Table 5.4: Values of volume and surface area for both configurations.

The figure 5.30 presents the variation of temperature in two different configurations (one and 27 spheres) at the centre of the central sphere of the system during the first 400 seconds.



Figure 5.30: The variation of temperature in the centre in case of one and 27 spheres.

The heating of one ceria sphere with 3 mm of radius, which corresponds to the same volume of 27 spheres with 1 mm of radius presented in the previous part. For one sphere, as expected and seen in section 5.2.1, when the particle size increases the temperature increases from $120^{\circ}C$ (1 mm radius) up to $750^{\circ}C$ (5 mm radius). The same behavior is observed for the 27 particles configuration in which the maximum temperature increases from $77^{\circ}C$ (0.2 mm radius) up to $515^{\circ}C$ (1 mm radius). This trend is related to the reduction of V/S ratio which corresponds to the global reduction the radiative losses at the surface.

For an equivalent surface area in both configurations, the configuration of one spherical particle has higher temperature due its higher volume of matter compared to the second configuration. For example, the maximum temperature for one sphere of 1 mm is about 120° C, whereas for the same surface are in case of 27 spheres with 0.2 mm the temperature is about 77° C.

Comparing the two configurations with the same weight of material, 1 sphere with 3 mm radius and 27 spheres with 1mm radius, we can see that the heating rate during the first 100 seconds is higher in the packing configuration and the maximum temperature reached is also higher in the packing configuration (515°C) compared to one particle (485°C). Despite the higher surface area in packing configuration which could lead to greater thermal losses, the central particle of the packing keeps high temperature due to the containment of this configuration.

Comparing the two configurations with the same V/S ratio, 1 sphere with 1 mm radius and 27 spheres with 1mm radius, the temperature of the central particle in the packing is higher than the second configuration, respectively 515°C and 120°C.
In general, the heating rate for the packing configuration is higher during the first 100 seconds than the second configuration. Moreover, the configuration of packing with 1 mm of radius has the highest heating rate due the containment between the particles which make the heating faster.

5.5 Discussions

The results presented within this chapter provide us some elements to be tested and used in the experimental sintering process. Firstly, the size of the particle increases the electric field magnitude and its gradient in this particle which lead to increase the heating. Secondly, the loss tangent is the factor in which the heating mainly depends despite the effect of ε ' and ε '' on the electric field magnitude. Third, the different results concerning the neck size show that the neck size affects to the gradient of the electric field. In Y configuration, the electric field becomes lower; the difference seen in the electric field norm during the increase of the neck size/particle size ratio by only 20% corresponds to a decrease of of the dissipated power by 13%. The Z configuration leads to an intensification of the electric field and consequently a higher heating. The electric field is significantly modified due to the presence of particles packing in the cavity; it is not homogenous and leads to different temperatures depending on the orientations of the electric field and the neck. We could expect a differential sintering according to this inhomogeneous situation, like Whittaker who supports the idea that the mass transport mechanism during the sintering of a ceramic evolves preferentially along the electric field vector [8]. Finally, in a packing system of multi-particles of ceria which corresponds to a realistic configuration of a fine powdered green sample, seems to be more suitable for heating process by microwave technique and therefore could drive to the densification.

On the other hand, we showed that the electric field was modified close to the neck and in the volume of a particle which could affect the grain boundary diffusion and the lattice diffusion, which are the two mechanisms responsible for the densification.

5.6 Conclusion

The simulation study presented in this chapter shows several effects which can be faced during the direct microwave sintering of ceria particles, despite it didn't include the mechanical physics of the sintering due to its unavailability in our software license. Therefore, the different parts of this chapter aim to predict the influence of microwave heating of ceria particles in microwave cavity fed by realistic conditions. It shows that the microwave heating is possible for ceria particles and it can be improved by changing the configuration to the respect of the E-field direction.

Moreover, the effect of the dielectric properties on the heating has been quantified and it is clear that they present an important influence on the heating by the loss tangent ($tan \delta$) which includes the real and the imaginary parts of the dielectric permittivity. The radiative and

convective losses and the effect of packing have been identified by the two configurations presented. The results show the packing configuration has a better heating despite its losses, due to the containment. If it was possible to model a packing with much more particles, this configuration could provide a high heating rate and high temperature.

Finally, the presence of neck whatever its size modifies the electric field magnitude with complex way depending on the orientation of the electric field with interfaces.

Résumé en français : Effet du champ micro-ondes sur des particules modèles et des particules de Cérine: une simulation multi-physique.

Dans ce chapitre, une étude basée sur la simulation multi-physique du champ de électromagnétique et du champ de température dans et autour d'un empilement granulaire modèle est présenté. Ces travaux montrent l'effet de la taille d'une particule sphérique modèle sur le champ électrique (E) dans la particule et autour d'elle. Dans le cadre d'empilements modèles de Cérine, nous avons montré que la présence d'un cou entre ces particules, son orientation par rapport au champ E et le nombre de particules constitutives de cet empilement jouent un rôle déterminant sur l'intensité du champ E. Il en résulte certes un chauffage hétérogène de cet ensemble de particule, mais avec des gradients de température qui sont surtout liés aux pertes thermiques.

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Conclusions

In this part, the main outlines of our research work and the general conclusion in first will be presented and, then the recommended further work will be discussed in the second section.

1 General Conclusion

Firstly, the literature shows a need to understand the electromagnetic effect on ceria sintering due a lack of studies on it. Secondly, a method for the determination of the dielectric properties of ceria has been developed after taking into account the limits due to the temperature measurement and the sample dimensions and examined by different approaches such as experimental and simulation studies. Thirdly, the results obtained concerning the dielectric properties by the developed system and the thermal parameters showed the dependency of (ε) and (ε) of ceria on the temperature and the porosity of the samples. It provided also an idea about microwave heating especially above 750°C whereby the ionic conduction of ceria became important. Fourthly, the comparison between the sintering by microwave heating and by conventional heating by dilatometry has been carried out. Experimentally, it shows the effect of grain size particles and the heating rate by both techniques. The microwave heating acts on the grain coarsening of ceria based materials more than the conventional heating. On the other hand, the conventional heating improves the final densification more than the microwave heating. The heating rates have low effect on the final density and remarkable effect on the grain size. Finally, the simulation study confirmed that the microwave heating is possible for ceria particles packing and it has a different interaction according to the orientation of interfaces with respect to the E-field direction. Moreover, the effect of the dielectric properties on the heating has been quantified. The packing configuration had higher heating despite its losses, due to the heat containment. In addition, the presence of a neck modified the electric field magnitude which would have an influence on the densification mechanism.

In this work, we developed a system for the determination of the dielectric properties of ceria samples up to 1000°C. The sintering by microwave heating of ceria was investigated and has shown its operating ability. The sintering by microwave was more suitable for the nanometric powder than the micro-metric powder; it provided therefore an advantage for sintering of the xerogel spheres of ceria which is the main task of the project. Despite the low loss tangent of ceria, we have shown that the heating by microwave of ceria is possible experimentally and by simulation approach. Hence, in order to model the sintering, we need to determine the physical properties up to higher temperature, about 1500°C which is the sintering temperature of ceria materials.

Finally, this work proves the feasibility of using microwave technology for the purpose of sintering ceria based materials, which leads to achieve the last task of the new nuclear wastes recycling technique. Thus, the success in this new technology can drive to significant and promised reduction in the radioactive nuclear wastes overall the world today and across future generations.

2 Future work

Some suggestions and open guidelines concerning this thesis would help to improve and continue this work, are listed below:

- 1- The system developed for the dielectric properties must be tested for a large range of materials which have known properties in order to quantify its applicability and improve the method if needed.
- 2- Ceria based materials interact differently with microwave heating depending on its grain size (for example in this study Micro-metric and Nano-metric samples), so a further work could focus to identify which parameters are responsible for the dielectric properties.
- 3- The sintering of small amount of ceria was possible by a single mode applicator but the use of multimode applicator has to be tested once the process will be applied in industrial field.
- 4- The simulation study has to be continued especially by including the solid mechanics and coupling with thermal and electromagnetic physics in order to have a more realistic approach.
- 5- Moreover, to confirm the results obtained in the simulation concerning the Y and Z configurations for three particles case, an experimental study with ceria spheres supplied by PSI laboratory would be very interesting.

Appendix: QuickWave simulator

The modelling by finite difference time domain (FDTD) is a well-known as an efficient method in numerical analysis for solving partial differential equations such as Maxwell equations in electromagnetic waves field. The solver used is called QuickWave and it is commercial software made by QWED, Poland.

1 The principle: FDTD

This is a research approach approximate solutions of partial differential equations. It is based on the standard formulation of the first order Maxwell equations in matter. In other words, this is a temporal and spatial resolution of the electromagnetic field in a dielectric structure with optical response. The discretization of derivative operators used a diagram centred finite difference, with a formulation in which the error is the second order for each discretization. This discretization is achieved by the formulation of Taylor-Young [1]. The temporal pattern type Leap-Frog [2] is based on the calculation of the electric field E at the time n.dt and the magnetic field H at the time (n + 1/2).dt.

The figures 1 and 2 show the temporal and the spatial discretization for the numerical solution of Maxwell's equations in FDTD:



Figure.1: Time discretization type Leap-Frog [2].



Figure.2: FDTD mesh in spatial 3D with the position of the components of the electric and magnetic field (the unknown) in the hexahedral cell according to Yee scheme [1].

In order to get a numerical convergence, the velocity of the electromagnetic wave in the mesh should be confined. Hence, the principle convergence constraint consists to ensure that the ratio of the field at two successive instants is less than 1. The relationship between the time discretization and the space discretization is given in 3D scheme by:

$$c_{\max} . dt \le \frac{1}{\left(\frac{1}{dx^2} + \frac{1}{dy^2} + \frac{1}{dz^2}\right)^{0.5}}$$

where c_{max} is the physical velocity of the electromagnetic wave in the medium dt is the time step

dx, dy, dz are the space steps

In practically, each mesh cell has a size which equals to the tenth of the wavelength.

2 QuickWave tools

QuickWave is software provided for the design and development of the electromagnetic simulation. It is based on the finite difference time domain FDTD and contains three main modules:

-QW-Editor:

It is the interface for building and editing the geometry of the applicator and the sample and for defining the excitement of the ports, the type of the treatment and the desired conditions (resonant mode, pulse, sine, frequency...).

-QW-Simulator:

It is the interface of resolution of the FDTD equations. It includes also the different configurations to present the results (output data) such as multimode, multiport, S-matrix, pattern of field, dissipated power, etc....

-QW-BHM (Basic Heating Module):

It is used for the applications concerning the heating. It operates the FDTD solver, with the modification of the enthalpy depending on the medium parameters. In addition, a module called **QW-Optimiser Plus** is integrated with QW-Simulator and it is used as optimizer for the multiobjective problem.

References

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École Nationale Supérieure des Mines de Saint-Étienne

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Hussein HAMMOUD

SINTERING OF CERIUM OXIDE BASED MATERIALS BY MICROWAVE HEATING

Speciality: Materials Science and Engineering

Keywords: Ceramic materials, cerium dioxide, sintering, microwave heating, multi-physics simulation, electric field, cavity perturbation theory

Abstract:

The main objective of this thesis is the evaluation of the heating by microwave technology and its applicability in the densification step, as a part of nuclear long life wastes recycling process and then the following up of the sintering of cerium oxide, a non-radioactive simulant of plutonium oxide. In this work, we developed a system for determining the dielectric properties of cerium oxide and made a comparative study between the sintering by microwave heating in a single-mode cavity and the conventional sintering in a dilatometer for two different powders of ceria: the first one has a micrometric particle size and the second has a nanometric one. In addition, we performed several numerical simulations on the basis of a model coupling electromagnetics and heat transfer. In these works, we have shown the effect of the size of a spherical model particle on the electric field (E) inside and around the particle. In the framework of a packing model of particles, the presence of a neck between these particles, their orientation relative to E field, and the number of these particles showed a decisive role in the intensity of the E field which has a direct impact on the heating of the particles.

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Hussein HAMMOUD

FRITTAGE DES MATERIAUX A BASE DE L'OXYDE DE CERIUM PAR CHAUFFAGE MICRO-ONDES

Spécialité: Science et Génie des Matériaux

Mots clefs : Matériaux céramiques, dioxyde de cérium, frittage, chauffage micro-ondes, simulation multi-physique, champ électrique, théorie de la perturbation de la cavité

Résumé :

L'objectif principal de cette thèse est l'évaluation de la technologie de chauffage par micro-ondes et son applicabilité dans l'étape de densification, dans le cadre d'un procédé de recyclage des déchets nucléaires à très longue vie et ensuite le suivi du procédé de frittage de l'oxyde de cérium, simulant de l'oxyde de plutonium. Dans ce travail, nous avons développé un système permettant de déterminer les propriétés diélectriques de l'oxyde de cérium et avons fait une étude comparative entre le frittage par chauffage micro-ondes dans une cavité monomode et le frittage conventionnel dans un dilatomètre classique pour deux poudres de cérine: l'une de taille micrométrique, la seconde de taille nanométrique. En outre, nous avons effectué des simulations numériques sur la base d'un modèle couplant électromagnétisme et transfert de chaleur. Ces travaux ont montré l'effet de la taille d'une particule sphérique modèle sur le champ électrique (E) dans la particule et autour d'elle. Dans le cadre d'empilements modèles, nous avons montré que la présence d'un cou entre ces particules, leur orientation par rapport au champ E et le nombre de particules constitutives de cet empilement jouent un rôle déterminant sur l'intensité du champ E, ce qui a des conséquences sur le chauffage des particules.