We are IntechOpen, the world's leading publisher of Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Advanced Ceramic Materials Sintered by Microwave Technology

Amparo Borrell and Maria Dolores Salvador

Additional information is available at the end of the chapter

Abstract

Processing of ceramic materials has also a strong impact in the quality of the consolidated body, as it plays a key role in the resulting microstructure and, as a consequence, in its final properties. Advanced ceramic materials are commonly processed as powders and densified via a high-temperature process. Traditional processing techniques include hot isostatic pressing, mold casting, and sintering in conventional ovens. As ceramics require very high processing temperatures compared to metals and polymers, these processes tend to be very energy intensive and result in higher production costs to the manufacturers. Therefore, new technologies known as nonconventional sintering techniques, such as microwave technology, are being developed in order to reduce energy consumption, while maintaining or even improving the characteristics of the resulting ceramic material. This novel and innovative technology aims at helping industrial sectors lower their production costs and, at the same time, lessen their environmental impact. On the other hand, it is interesting and necessary to know and explore the basic principles of microwaves to advance in the development of materials that demand, every day more, the different industrial sectors. This chapter presents the most recent advances of two materials with a great industrial future: zirconia and lithium aluminosilicate.

Keywords: ceramic materials, microwave technology, microstructure, mechanical properties, advanced applications

1. Introduction

High-temperature processes are required to consolidate ceramic powders, such as zirconia (Y-TZP), alumina, silicon carbide, and so on, in order to obtain full densification of the material. Sintering is a common material processing technique aimed at fulfilling this task.

The fundamental principle behind sintering consists in the thermal activation of mass transfer mechanisms when exposing a powder compact, known as a "green" body, to a high-temperature process, at a dwell temperature below the melting point of the material. The main purpose of sintering is to obtain a dense and resistant body with properties as close as possible to those of a theoretical, fully dense solid. However, in some cases, sintering can also be employed to adjust some of the properties based on the performance requirements of the material by not reaching full consolidation, such as in porous materials.

Two main types of sintering can be identified based on the nature of the process: liquid phase and solid phase. Even though the term liquid phase may suggest exceeding the melting point of the material, it is used to describe the addition of compounds with significantly lower melting points that aid in the consolidation of the main powder, which is regarded as the matrix phase and provides the main properties of the consolidated body. In this chapter, however, only solid phase sintering is considered.

Currently, innovative sintering methods are being explored and studied in order to modify densification mechanisms that may improve the microstructure and mechanical properties of sintered materials and also is very important to reduce time fabrication of these materials. Two main stages have been recognized during the sintering process: densification and grain growth [1]. The main purpose for modifying sintering mechanisms is to obtain relative densities close to theoretical values, while maintaining a controlled, but limited, grain growth [2]. Also, the optimization of the process by reducing the sintering time to decrease energy consumption and/or increasing heating rates is an important aspect that is being considered [3]. As a consequence, in order to improve the sintering process, novel non-conventional sintering methods have been investigated and developed.

Particularly, microwave sintering represents an interesting opportunity at consolidating advanced ceramic materials with a reduced processing time and energy consumption by utilizing electromagnetic radiation to provide high-enough temperatures that allow full densification of the material. The most important advantages of microwave sintering against conventional sintering methods are listed as follows [4, 5]:

- shorter sintering time and lower energy consumption;
- higher heating rates can be used;
- materials with a finer (nanometric) microstructure with a high degree of densification and enhanced mechanical properties may be obtained due to the densification mechanisms involved;
- flexible due to the possibility of processing *near-net-shape* materials.

This chapter reports on microwave material interaction, the basics of microwave processing, heating mechanisms, theoretical aspects in dielectric heating, and microwave systems for heating. The challenges in the field of microwave processing of advanced materials, such as zirconia and lithium aluminosilicate, have been discussed and studied from the point of view of different authors.

2. Microwave sintering technology

2.1. Microwave sintering

Microwaves have been used since the 1960s for heating purposes, particularly for food- and water-based products. Industrially, the use of microwave energy has become increasingly important because it represents an alternative to traditional with high-temperature processes. For example, so far, it has been employed in wood drying, resin curing, and polymer synthesis. The growing interest in industrial microwave heating is due mostly to the reduction of production costs resulting from lower energy consumption and shorter processing times [6–8]. However, several aspects need to still be investigated as each material behaves differently in the presence of microwaves.

The application of microwave heating has now expanded to material science and technology, beginning with process control and moving onto ceramic drying, powder calcination, and decomposition of gases with microwave plasma, in addition to powder synthesis [5]. Scientific interest on this powerful tool has been recorded in the study as there has been an increase of bibliographical entries for the term "microwaves" in the last decades because the applications of this technology have diversified enormously. In the last 25 years, research and development on the dielectric heating attributed to microwaves began with topics in chemical synthesis and material processing, such as reactive sintering of superconductors, magneto-resistors, nanomaterials production, vitreous phase formation, hydrothermal generation of zeolites, among others [9]. In this sense, one of the major areas for research and development of microwave heating involves sintering of ceramic powders [10, 11].

Microwave sintering is considered a relatively new ceramic material processing technique that differs significantly from conventional sintering methods due to the nature of the heat transfer mechanisms involved. Hence, microwave sintering is classified as a non-conventional sintering technique. This method presents itself as a fast, economical, and flexible processing tool. Some of the most important advantages against conventional sintering systems include lower energy consumption and production costs, reduction of processing times, higher heating rates, and, in some cases, even an improvement in the physical properties of the consolidated material [6, 12]. As a consequence, scientific interest in this novel technique has been developed progressively.

In a general sense, microwave sintering increases the densification of the material at lower dwell temperatures when compared to conventional sintering [13, 14], employing shorter times and less energy [15, 16], and resulting in an improvement of the microstructure and mechanical properties [17, 18].

The first sinterability studies of ceramics by exposure to microwave energy were carried out on the so-called black ceramics, which are the compounds based on tungsten carbide (WC). Two of the main issues regarding sintering of these materials by conventional means are the high temperatures (>1500°C) and long dwell times that result in grain coarsening. For the first time, in 1991, J. P. Cheng showed that the WC/Co system could be sintered by microwave heating technology [19]. In his work, a commercial WC powder with a 6–12 mol% Co content was investigated, and an improvement in the mechanical properties was achieved when

compared to conventional methods by utilizing sintering temperature between 1250 and 1320°C and dwell times of only 10–30 min. The relative density values were close to theoretical and a fine and homogeneous microstructure was observed, without the use of grain growth inhibitors. Also, the materials exhibited a higher resistance to corrosion and erosion [20].

The next step involved the processing of more traditional ceramic materials such as alumina and zirconia. Even though alumina behaves as a transparent material in the presence of microwaves, susceptors, which are materials with a high microwave absorbance, or dopants can be employed. Tian et al. were able to obtain 99.9% relative density values with an average grain size of 1.9 μm for MgO-doped Al_2O_3 sintered at 1700°C in a microwave oven [21]. Additionally, Katz and Blake were able to reach a densification of 99% for α-alumina with grain sizes between 5 and 50 μm after microwave sintering, where the total processing time was 100 min at a dwell temperature of 1400°C [22]. Transparent alumina materials have also been obtained via microwave processing at lower sintering temperature and shorter times [23].

In the case of nanometric yttria-stabilized zirconia (YSZ), microstructure and mechanical properties can be enhanced when processed via microwave sintering [24]. By application of hybrid heating with the aid of a susceptor, sintered materials with densities close to theoretical values can be obtained at temperatures 200°C below those employed in conventional sintering [25, 26]. Moreover, the grain size decreases considerably and hardness values are almost 2 GPa higher [18].

In the last 5 years, research on microwave sintering has also focused in the processing of ceramic composites to improve their functional as well as structural properties and extend its applications to several industrial sectors. Also, the design and optimization of current microwave ovens has also been an important research topic. These systems need to be adjusted to the characteristics of the material that is to be processed, since the behavior under a microwave field varies from one to another. Therefore, studying the fundamental principles and involved mechanisms in microwave energy conversion may allow the production of more energy-efficient ovens.

2.2. Microwave heating fundamentals

Microwaves are a form of electromagnetic radiation that correspond to frequencies between 300 MHz (λ = 1 m) and 300 GHz (λ = 1 mm), as shown in **Figure 1**. Among their most important industrial applications are telecommunications and heating. The possibility to use microwave energy for heat generation was first discovered in the late 1940s, while tests were being carried out with magnetrons [8]. Consequently, the first microwave systems for food heating were developed. As research in microwave energy and its applications continued, uses expanded to industrial processes such as drying and curing. In the last few decades, sintering of materials with microwave radiation has also become an active field of investigation.

2.2.1. Interaction of microwaves with matter

Microwaves, as any other type of electromagnetic radiation, have electrical and magnetic field components, amplitude, phase angle, and the ability to propagate, that is, to transfer
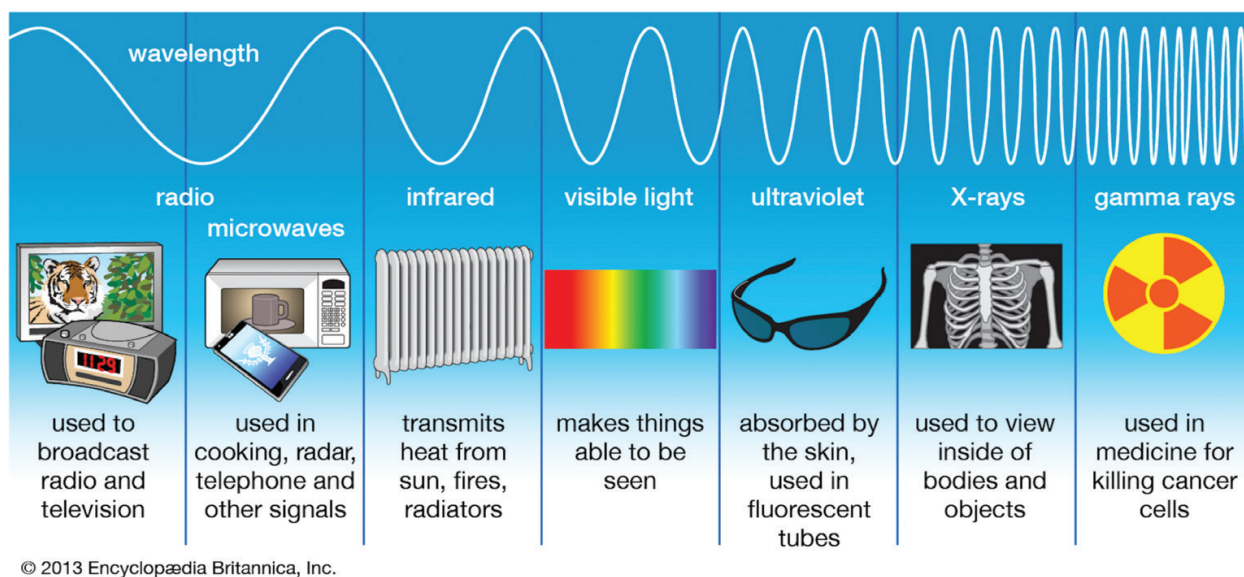
Figure 1. Electromagnetic spectrum diagram.

energy from one point to another. These properties govern the interaction of microwaves with materials and produce heating in some of them. Depending on the electrical and magnetic properties of the material, their interaction with microwaves can be classified as one of three types [5]:

- **Transparent**: Microwaves penetrate and are transmitted through the material completely with no energy transfer occurring (**Figure 2a**). These materials are known as low-loss insulators.

- **Opaque**: Microwaves are reflected with no penetration into the material and no energy transfer. These are known as conductors (**Figure 2b**). Metals are mostly considered to be opaque to microwave energy.

- **Absorbent**: Microwaves are absorbed by the material, and an exchange of electromagnetic energy occurs (**Figure 2c**). The amount of absorption depends on the dielectric properties of the material.

A fourth type of interaction known as mixed absorption has also been proposed. In this particular case, mixed or multi-phase materials with different degrees of microwave absorption are sought after. Most electrically insulating ceramics such as alumina, MgO, silica, and glasses are transparent to microwaves at room temperature, but, when heated above a certain critical temperature T_c, they begin to absorb and couple more effectively with microwave radiation. Other ceramics, such as SiC, are able to absorb microwave energy more efficiently at room temperature. Therefore, the addition of a microwave-absorbing second phase to ceramics that behave transparent at room temperature can greatly enhance the interaction of the system with microwaves allowing a hybrid heating of the material. In Section 5, a more in-depth description of hybrid heating is given.
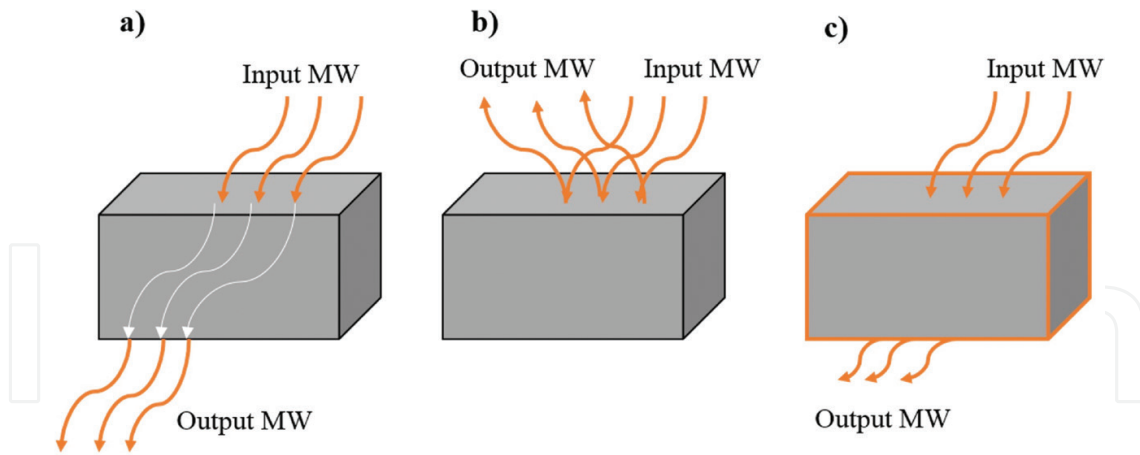
Figure 2. Material/microwave interaction representation classified according to their behavior: (a) transparent, (b) opaque, and (c) absorbent.

2.2.2. Microwave heating mechanisms

In order to explain the interaction of absorbing materials with microwave radiation and the energy transfer that occurs during this interaction, several physical mechanisms have been proposed. These mechanisms include bipolar rotation, resistive heating, electromagnetic heating, and dielectric heating. Depending on the material, the response to incoming radiation can be attributed to one mechanism or a combination of several of them:

- **Bipolar rotation** occurs when electrically neutral polar molecules with positive and negatives charges are separated. Within a microwave field, these dipoles rotate in the direction of increasing amplitude. As a consequence of this rotation, friction among the molecules arises generating heat uniformly throughout the material.

- **Resistive heating** occurs in conductors or semiconductors with relatively high electrical resistivity. These materials possess free electrons or a high ionic content where the ions receive enough freedom so current can be generated.

- **Electromagnetic heating** takes place in materials with magnetic properties that are highly susceptible to external electromagnetic fields, such as those induced by microwave radiation. This type of heating can be described as magnetic pole rotation of the material analogous to the rotation of polar molecules in oscillating electrical fields.

- Finally, the fourth mechanism, **dielectric heating**, is a mix of bipolar rotations and resistive heating. In microwave sintering of ceramics, this is the predominant mechanism. In the next section, the principles of dielectric heating in microwave-absorbent materials are described.

2.3. Theoretical aspects in dielectric heating

The degree of interaction between the microwave electric and magnetic field components with the dielectric or magnetic material determines the rate at which energy is dissipated in the

material by the various mechanisms. The properties of the material that are most important for the interaction are the permittivity ε for a dielectric material and the permeability μ for a magnetic material [27]. Considering that dielectric heating is the most relevant mechanism for ceramics, this description will only focus in aspects related to permittivity and properties that arise from it.

When microwaves penetrate the material, the electromagnetic field induces motion in the free and bound charges (electrons and ions) and in dipoles. The induced motion is resisted because it causes a departure from the natural equilibrium of the system, and this resistance due to frictional, elastic, and inertial forces leads to the dissipation of energy. As a result, the electric field associated with microwave radiation is attenuated, and heating of the material occurs.

The dielectric interaction between materials and microwave radiation can be described by two main parameters [6, 28–30]:

- absorbed power, P

- depth of microwave penetration, D

Both parameters play a critical role in the uniform heating of the material. The absorbed power is the volumetric absorption of microwave energy (in W/m³) and is expressed according to the following equation:

$$P = \sigma |E|^2 = 2\pi f \varepsilon_0 \varepsilon'' |E|^2 = 2\pi f \varepsilon_0 \varepsilon' \tan\theta |E|^2 \qquad (1)$$

where f = frequency of the electric field and E = amplitude of the electric field.

The loss tangent, $tan\theta$, is a term associated with the capacity of the material to be polarized and heat itself. In other words, these terms describe the microwave energy conversion into heat. The relationship describing the loss tangent is given by

$$\tan\theta = \varepsilon''/\varepsilon' \qquad (2)$$

where ε'' = loss factor; ε' = dielectric constant, inherent to the material.

The loss factor, ε'', measures the ability of the material to convert the incoming microwave energy into heat, and the dielectric constant, ε', measures the polarizability of the material. In microwave material processing, maximum values for ε'' in combination with mild values of ε' are desired (**Figure 3**).

Both, ε' and ε'', depend on temperature and the frequency of the field. At low frequencies, all microwave energy is absorbed by the rotating movement of the dipoles and ε' reaches a maximum; however, there are no collisions because the displacement is very slow. At high frequencies, the material does not have enough time to respond to the oscillating electric field, and therefore, ε' reaches a minimum. The loss of energy caused by the collisions is represented by ε''. The key relies on finding a frequency for each material at which the absorption of energy (ε') as well as the loss of energy (ε'') is high.
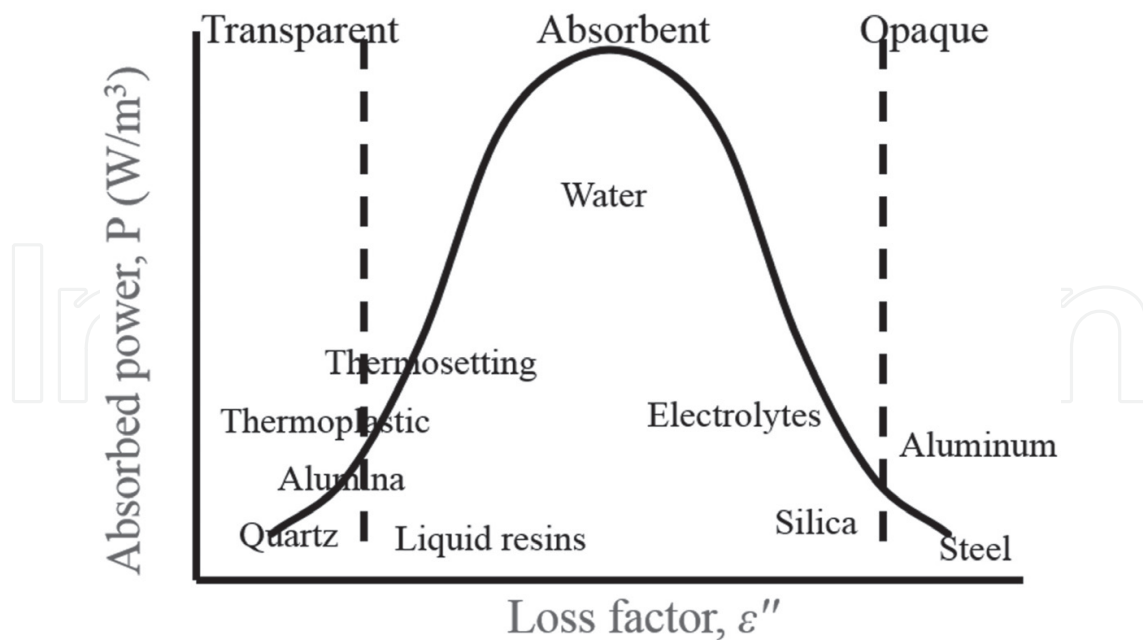
Figure 3. Relationship between factor loss and absorbed power at a frequency of 2.45 GHz and room temperature for some common materials.

A general explanation is based on a fundamental body, such as a grain particle, in its neutral state containing polarized molecules distributed in random positions. These molecules can easily be reoriented by the effect of an external electric field, as shown in **Figure 4**.

If the polarity of the electric field is changing constantly, molecules will modify their orientation accordingly in a very fast manner so as to align with the field (**Figure 5**) and, as a consequence, heat will be generated due to the friction among them and electrical resistive effects from unbound charges. The material heats up as a function of the absorbed energy during this process.

The main difference with respect to conventional sintering is the direction of heat flow [31], because in conventional sintering, heat is transferred from the surface of the material toward the inside due to the heating mechanisms involved. In contrast, in microwave sintering, in the presence of a strong electric field, molecules vibrate with the same intensity and at the same
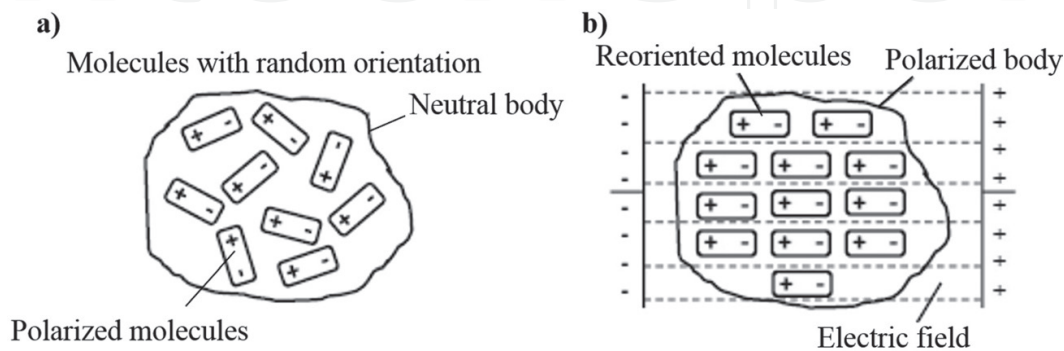

Figure 4. Position of the molecules (a) in its natural state, and (b) with the application of an external electric field.

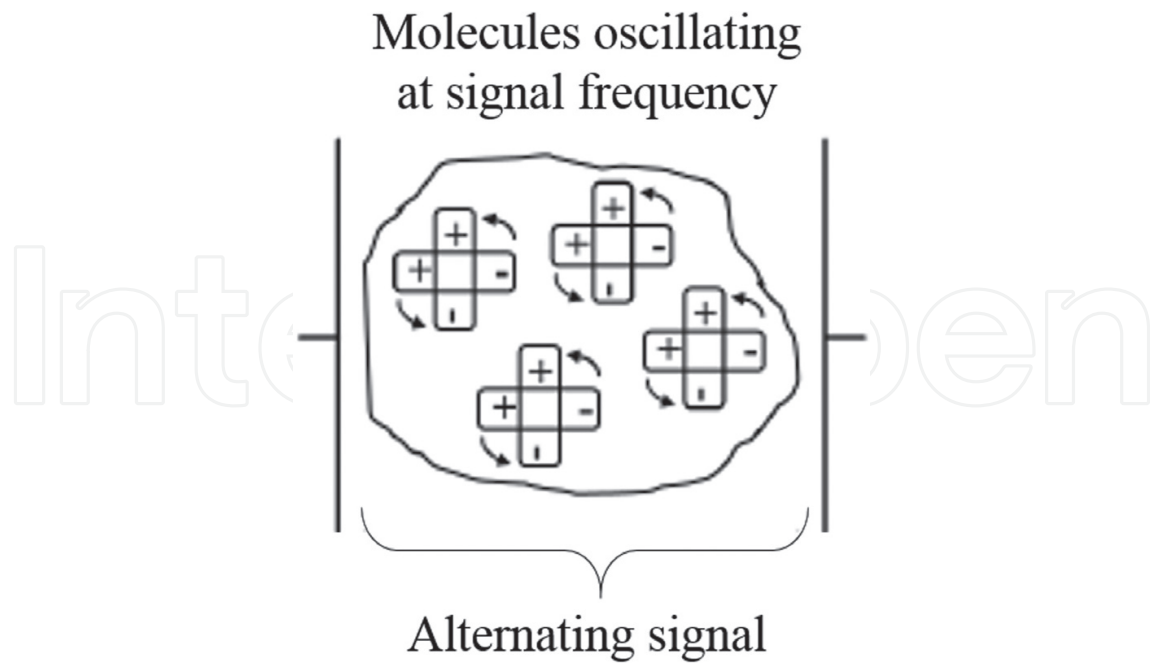## Molecules oscillating at signal frequency

Figure 5. Representation of the reorientation of the molecules in the presence of an alternating electric field, such as that induced by microwaves.

time generate heat throughout the whole material as a consequence of the characteristics of dielectric heating.

The second main parameter in microwave/material interaction is microwave penetration depth, D. This parameter determines the penetration depth at which the power is reduced by half and is expressed in the following manner:

$$D = \frac{3\,\pi_0}{8.686\pi \tan\theta \left(\frac{\varepsilon'}{\varepsilon_0}\right)^{\frac{1}{2}}} = \frac{C}{2\pi f \sqrt{2\,\varepsilon'} \left(\sqrt{1+\tan^2\theta}-1\right)^{\frac{1}{2}}} \tag{3}$$

High frequencies in combination with high dielectric property values translate into superficial heating of the material, while low frequencies with small dielectric property values give place to volumetric heating.

Based on the properties of materials, it is well known that those with a high conductivity and permeability present a lower penetration depth for a given frequency. The penetration depth of many materials oscillates around 1 μm, which means that heating tends to stay at the surface. If powders with a particle size of approximately that of D are employed, there is the possibility to heat the whole surface directly and homogeneously.

2.4. Microwave systems for heating

A microwave oven is composed of three main elements: (1) microwave source, which is in charge of generating the electromagnetic radiation, (2) transmission lines, which transmit the microwaves, and (3) a resonant cavity, which is where the interaction with matter takes place [28].

The theoretical principle that governs each of the components is based on Maxwell Equations [30, 32]:

$$\nabla \times \mathbf{E} = \frac{\partial \mathbf{B}}{\partial t}, \ \nabla \cdot \mathbf{B} = 0. \tag{4}$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}, \ \nabla \cdot \mathbf{D} = \rho \tag{5}$$

where $\mathbf{E}$ = electric field vector; $\mathbf{B}$ = magnetic flux density vector; $\mathbf{H}$ = magnetic field vector; $\mathbf{J}$ = current density vector; $\mathbf{D}$ = electric flux density vector; ρ = charge density.

Maxwell equations are the physical laws that describe an electromagnetic field and its variations with time. The design of an efficient microwave system to process materials requires understanding of electromagnetic theory.

In the following paragraphs, a description of the different components that are part of a microwave system is given.

Magnetron: This is the most important part of a microwave source. This device transforms the electrical energy from the low-frequency electric grid into a high-frequency electromagnetic energy (microwaves). It consists of a metallic cylinder where a series of resonant cavities are disposed radially and communicated to a major central cavity, which has a titanium filament in its axis (**Figure 6**). The cylinder acts as an anode and the central filament as a cathode. The filament, which is connected to the negative pole of a continuous current source, becomes
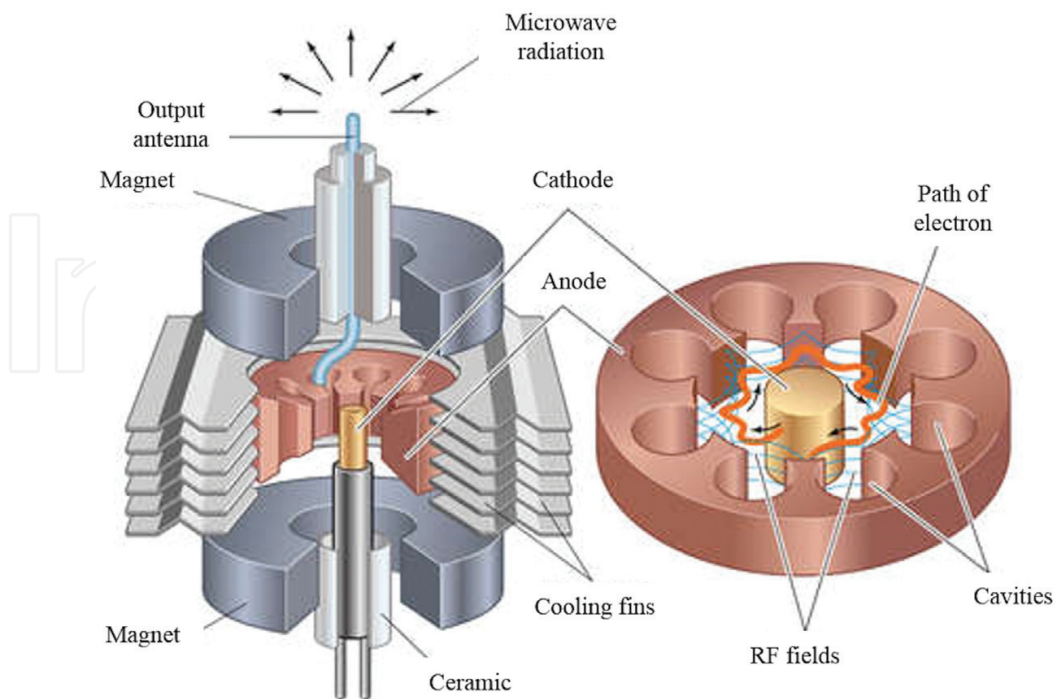

Figure 6. Magnetron schematic showing all the elements required for generation of microwave radiation.

incandescent and emits electrons by thermionic effect. The cylinder, connected to the positive pole, attracts the electrons. The whole setup is located between the poles of a powerful electromagnet.

The open space between the plate and the cathode is referred to as interaction space. In this space, electric and magnetic fields interact to exert a force on the electrons. Given that an electric charge creates an electromagnetic field around it, all the electrons, moving in circles in the cavities, produce electromagnetic waves, in this case microwaves, perpendicular to their own displacement and with a frequency that depends on the size of the cavities.

Usually, for microwave heating applications, the frequency of the generated electromagnetic radiation is 2.45 GHz. This frequency corresponds to one of the so-called Industrial, Scientific and Medical (ISM) frequencies, which are free of utilization for these types of applications. The insertion of magnetrons in commercial microwave ovens for home use has translated in more economical sources of this frequency by allowing the fabrication of magnetrons in a large scale. Moreover, other ISM frequencies are also employed for heating applications, such as Bluetooth and WiFi [33]. The power generated by the magnetron can be controlled by changing the amplitude of the cathode's current or the intensity of the magnetic field.

Transmission lines: This element is responsible for transmitting the generated microwave radiation by the source to the main cavity. In low-power systems, transmission lines are usually coaxial cables. However, for high-frequency systems, the loss occurring in the coaxial cables is quite substantial. Therefore, circular or rectangular waveguides are necessary for proper wave transmission.

Circulator: This component provides protection to the source against possible unwanted load reflections. The circulator is capable of redirecting the microwave power that was not consumed by the material to be sintered toward a water load. This water load heats up avoiding that the reflected power gets back causing damages to the source.

Reflectometer: This element measures the effective consumed power by the material sample to be heated. This information provides reliable information about the power consumed during the sintering of the sample.

Tuning system: This element is fixed to the microwave oven and is employed to couple the microwave incident radiation to the cavity. Different types of tuners can be utilized. For example, the simplest one consists of an iris that couples the incident power directly to the cavity. More complex tuners are the three-stub adapter that allows a dynamic adaptation of the coupling process to the cavity.

Resonant cavity: This is the microwave system nucleus, where the incident electromagnetic radiation heats and sinters the material. Cavity design is one of the most critical parts of microwave equipment for material processing. The temperature distribution within the material, which is heated by microwave radiation, is inherently linked to the distribution of the electric field inside the cavity. In material processing, resonant cavities with different mode configurations, including single-mode, multi-mode, and multi-mode with variable frequency, are employed [32, 34].

The size of a single-mode resonant cavity must be in the order of one wavelength. Additionally, in order to maintain a resonant mode, these systems require a microwave source that allows frequency variations or that the cavity dynamically changes its size to couple the frequency of the microwaves. Generally, the distribution of the electromagnetic field in this type of cavity is well known. With an adequate cavity design, the microwave field may be focalized to a particular zone where the material sample can be sintered. An additional advantage for this type of cavity is the fact that the dielectric properties of the material can be monitored during sintering.

Multi-mode cavities are able to maintain several modes simultaneously. The design of home microwave ovens is based on this type of cavity. The greater the size of the cavity, the higher the number of possible resonant modes. Hence, multi-mode cavities are larger than a wavelength, which contrast with the size of single-mode systems.

The presence of different resonant modes results in the existence of multiple hotspots inside the cavity. Local fluctuations in the electromagnetic field can result in overheating of certain areas. In order to minimize these hotspots, the electromagnetic field must be uniform. Field uniformity can be achieved by increasing the size of the cavity and varying the sample position dynamically, for example, with a rotating plate or stirrers. By increasing cavity size, the number of modes increases and, as a consequence, the heating patterns of each mode begin to superimpose and the stirrers or the plates change the distribution of the field inside the cavity.

2.5. Microwave hybrid heating: bidirectional heating

One of the main issues associated with microwave sintering of materials is their initial microwave radiation absorption and heating. Most of the processing is carried out at a relatively low frequency of 2.45 GHz, which makes the initial heating of the material very difficult to control. Another important problem that may arise consists in the thermal instability that materials are prone to due to the changes in their properties, such as their dielectric constant, ε'. Variations in dielectric properties as a function of temperature may translate into poor temperature control and overheating of the specimen. Such behavior is present in several materials such as alumina and zirconia.

Temperature gradients that arise during heating can produce microcracking and an unequal distribution of resulting physical properties, such as density and hardness. Therefore, thermal insulators or coatings may be necessary to avoid the presence of these gradients. Nonetheless, these insulators can provoke the control loss of the temperature.

Ceramics tend to exhibit an abrupt increase in ε'' as a function of increasing temperature. The temperature at which dielectric properties change is known as the critical temperature, T_c. Below T_c at a given frequency, most ceramics are poor absorbers behaving as transparent materials and need to be heated by an external source. No mathematical relationship has been found that relates temperature to fundamental material properties, hence T_c values must be measured experimentally [35, 36]. This T_c can pose some problems when processing complex and large samples. Unless heated uniformly by an external source, localized hotspots can develop in the material. These spots begin to absorb microwave radiation before the rest of the material in phenomenon known as thermal runaway. As a consequence, this can lead to the fracture and/or warping of specimens. Thermal runaway can be limited by using uniform external heating and a homogeneous microwave field.

A plausible solution that materials scientists and engineers have developed consists on a hybrid method that combines direct microwave heating coupled with heat transfer coming from another material that surrounds the specimen to be sintered [37]. This system is an example of mixed absorption heating, with a high dielectric loss at both low and high temperatures.

In this scenario, microwaves are absorbed by the material with highest dielectric losses at room temperature while microwaves propagate through the material with lower losses at room temperature. Heat and energy are transferred from the absorbing material to the transparent material. This type of heating makes use of a specific component known as a susceptor. This heating-aid element is the absorbent material and possesses a very high dielectric loss at room temperature, transmitting heat to the material to be sintered via conventional heat transfer mechanisms. Once the material has heated sufficiently surpassing its T_c, changing its dielectric properties, and inducing high dielectric losses, it is able to absorb microwave energy and heat itself.

This combined action, known as microwave hybrid heating, can be employed for fast sintering of compacted powders. In this particular case, the direction of heat flow in the specimen to be sintered occurs in two directions: from the surface to the nucleus due to the effect of the susceptor and from the nucleus to the surface once it is able to absorb microwave radiation [37]. A representation of a bidirectional hybrid heating can be seen in **Figure 7**.
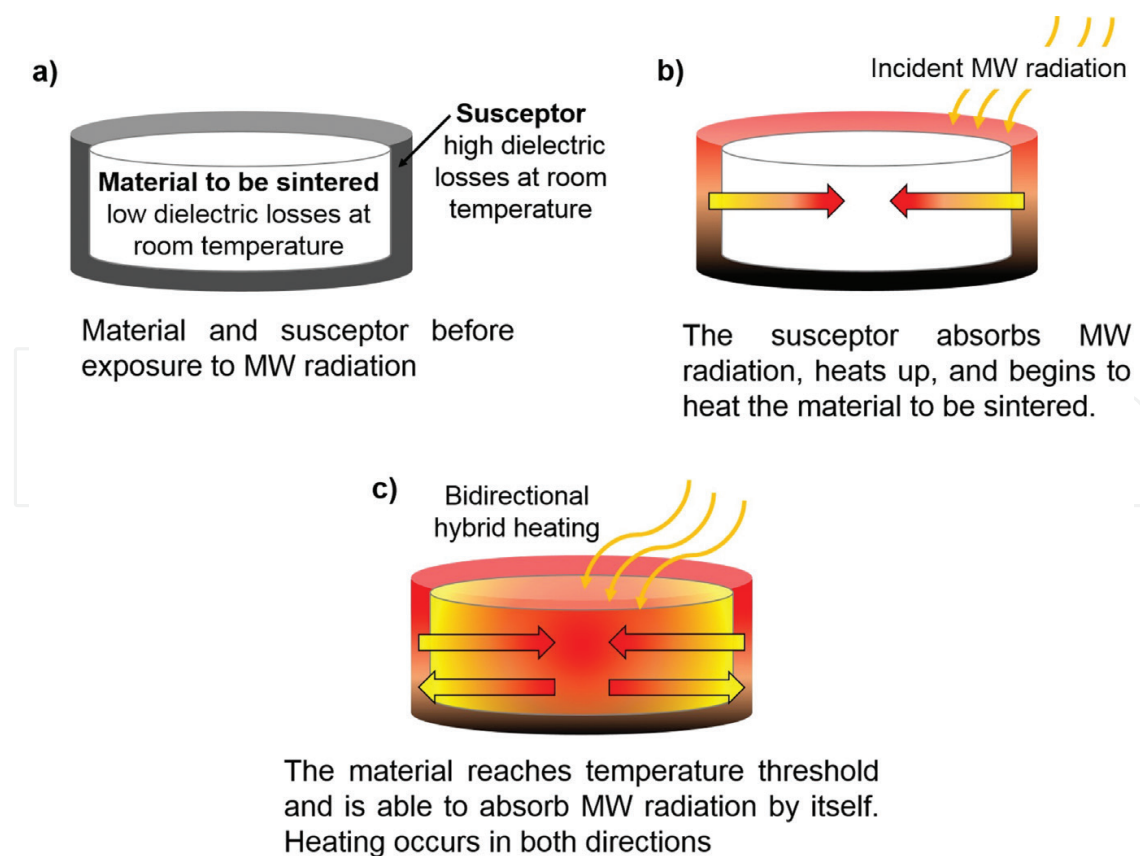

Figure 7. Sequence diagram of microwave hybrid heating for material sintering: (a) before exposure to microwave radiation, (b) susceptor heating under MW radiation, and (c) specimen to be sintered able to absorb MW energy giving place to bidirectional hybrid heating.

2.6. Microwave sintering of zirconia

Mechanical properties and microstructure of Y-TZP-sintered materials are strongly influenced by the degree of densification and grain nucleation that result due to the sintering process. This is, in turn, determined by the heating mechanisms that take place within the material. Current commercial sintering of ceramic materials is based on conventional heat transfer mechanisms: conduction, convection, and radiation. In this case, heat is generated from heating elements and a temperature gradient arises, as heat is transferred from the surface to the material's core. This method, however, requires long processing times. As a consequence, grain broadening occurs [38], which leads to a decrease in the final mechanical properties of the material [39]. It also requires a high-energy consumption to reach such high temperatures, which must also be maintained for long periods of time (around 2–4 h or more) if fully dense materials are desired.

One advantageous and useful non-conventional method that can modify the densification mechanisms and results in faster processing of Y-TZP ceramics is microwave sintering [40]. The energy conversion of electromagnetic radiation into heat by the material itself due to the material's dielectric properties is the driving force for densification [41]. The rise in temperature is determined by the amount of energy absorbed in the process. The acceleration of diffusion mechanisms during sintering by the oscillating electric field has also been proposed by some authors to explain enhancement of the sintering process, in what is called a "microwave effect" [42]. Because it is a non-contact technique, the effects of differential sintering are minimized [43], which is another advantage over conventional sintering methods, where differential densification is an important problem that arises from the slow heating rates.

The dielectric loss factor of zirconia is quite different from those of other oxide and non-oxide ceramics. At a frequency of 2.45 GHz, zirconia does not couple adequately with microwaves at room temperature. The loss factor, ε'', of Y-TZP at room temperature is similar to microwave-transparent materials, with a value of approximately 0.04 [25]. However, the dielectric loss increases tremendously with temperature, reaching a value of almost 100 at 1000°C. Therefore, zirconia can become a very absorptive material by raising its temperature. In order to achieve this, two different approaches can be found:

- With the aid of a susceptor, generally (SiC), as it has been described in the previous section. This method is the most commonly found in the study [25, 44, 45].

- Employing conventional resistive elements to initially heat the zirconia until its Tc is reached, and zirconia is able to interact with the microwave field by itself [46].

Previous reports [4, 18, 47] have demonstrated that with microwave sintering, highly dense materials can be obtained without a substantial grain coarsening because dwell time is considerably shorter and heating rates are quite high in comparison with conventional sintering [48]. Energy consumption is also significantly reduced as a consequence of the mechanisms involved in microwave heating and the abovementioned shortening of processing times. As a result, several advantages arise including improved mechanical properties and reduced environmental impact [5, 49]. This method may provide lower costs for professionals and customers maintaining or even improving the quality of the final product.

In general, the study suggests that microwave sintering of zirconia can result in comparable mechanical properties and high degrees of densification comparable to those achieved with conventional sintering systems at lower dwell temperatures and significantly shorter sintering times [50–54]. Moreover, some studies have demonstrated that microwave-sintered specimens exhibit enhanced crystallinity [55] and improved mechanical properties [18, 49, 56].

2.7. Microwave sintering of lithium aluminosilicate

Over the past few decades, the lithium aluminosilicate (LAS) compositions have been extensively studied because it is very low or even negative thermal expansion compounds have found a wide application field including cookware, bakeware, electronic devices, telescope mirror blanks, ring-laser gyroscopes, and optically stable platforms [57]. Sintered negative thermal expansion materials have usually low mechanical strength because the expansion anisotropy causes microcracking. This is due to different extents of thermal expansion in different crystallographic orientations, which induces internal stress with temperature change. On the other hand, it has been reported by Pelletant et al. [58] that the microcracking depends on the grain size; therefore, an increase in the β-eucryptite grain size causes a progressive microcracking and consequently a more negative bulk of thermal expansion coefficient. Nevertheless, the usefulness of these thermal properties in the production of materials with null expansion has a wide range of potential engineering, photonic, electronic, and structural applications [59].

β-Eucryptite is the most negative thermal expansion phase in the lithium aluminosilicate system, and therefore β-eucryptite has been thoroughly studied [60]. Compared with the number of studies of glass–ceramic materials, there are few studies in the literature, which deal with this system as a ceramic material in the solid state [61]. This is important because as far as possible, obtaining 100% theoretically dense materials in this system in solid state would improve the mechanical properties as such modulus of elasticity compared with glass-ceramic materials with similar thermal shock characteristics. In LAS system, the high temperatures required to fully densify ceramic powders result in large grain sizes due to Ostwald ripening when traditional sintering techniques are used [38]. This makes obtaining dense materials with nanometric and submicrometric grain sizes extremely difficult, and, as a consequence, the sintered materials do not achieve high mechanical properties. To overcome the problem of grain growth, non-conventional sintering methods have emerged as promising techniques [62–65].

Spark plasma sintering (SPS) was reported in [62] as a non-conventional sintering technique for LAS materials that can lead to high relative dense ceramics with no or with very low amounts of a glassy phase. This technique is restricted to materials with disk forms of different diameters, whereas materials with a near-net-shape approach have still not been possible to obtain. Moreover, Vanmeensel et al. [66] reported that the temperature distribution inside the tool and specimen is not homogeneous during the spark plasma sintering technique, especially, for electrical insulating samples (such as LAS ceramics), due to temperature gradient existing between the border and the center of the sample in the intermediate and final stage of sintering. Other important factor to consider is the high-energy consumption of SPS technique.

Microwave heating is a non-conventional sintering technique to solve the difficulties found with previous techniques such as SPS. The microwave technique was specially designed to fabricate ceramic LAS bodies with a high density, a very low glass proportion, and high mechanical properties (hardness and Young's modulus) [63]. An important characteristic associated to microwave process, it is possible to directly obtain materials with complex parts (*near-net-shape* components) directly in the microwave furnace without the application of pressure and without any carbon contamination. This supposes other significant advantage compared with the spark plasma sintering [64]. This point is essential in order to use this sintering technology where the final dimension of the sintered component has to be almost constant in order to reduce the final machining cost of nanocomposites.

Previous reports [63–65] confirmed the possibility of successfully obtaining well-densified β-eucryptite ceramics by using microwave sintering technology with glass-free at relatively low temperatures (1200°C) and very low energy consumed (<80 W). **Figure 8** shows the temperature profile and microwave-absorbed power during the sintering process of an LAS specimen [63]. The figure shows a microwave experiment with a resident time of the ceramic sample of 10 min around 1200°C. The LAS material is a good absorber of microwave radiation at 2.45 GHz, and this implies that the heating is homogeneously distributed throughout the material. The dilatometric data presented for the cryogenic temperature interval are essential in order to design these kinds of materials for space applications in which controlled and very low thermal expansion behavior are needed at very low temperatures. This is the case of mirror blanks in satellites, where exceptional thermal properties are demanded together with exceptional mechanical properties, that is, the β-eucryptite sample sintered at 1200°C shows Young's modulus of 110 MPa and a hardness of 7.1 GPa values [63]. Compared with other heating modes, conventional, and spark plasma sintering [64], the most important characteristics associated to microwave process are the rapid and volumetric heating, which improves the final properties of the materials.
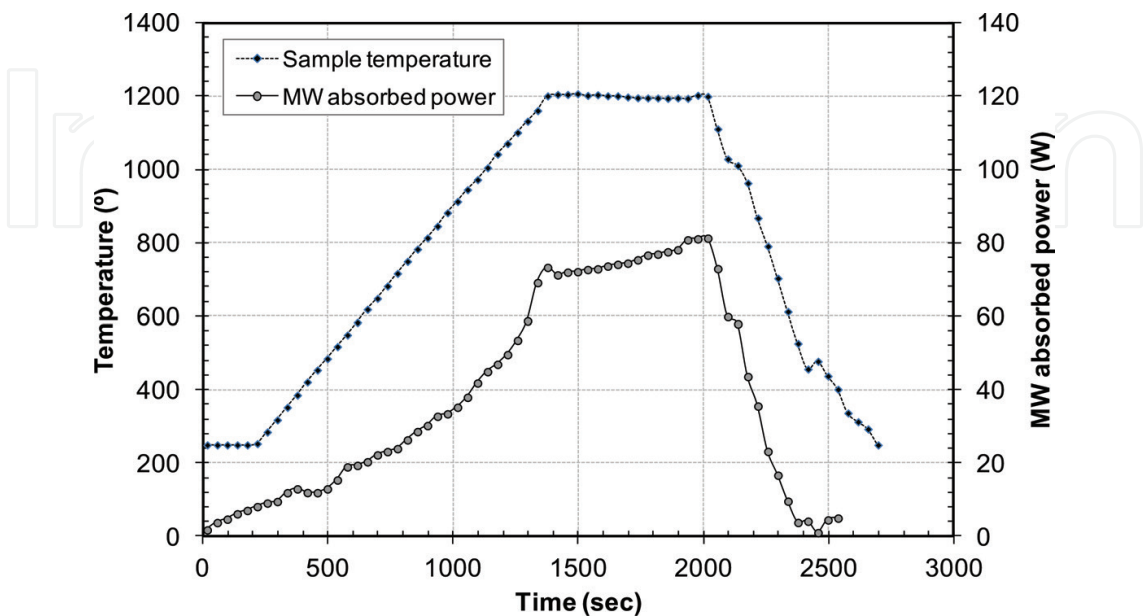

Figure 8. Temperature profile and microwave absorbed power during the sintering process of the LAS specimen.

2.8. Advantages and disadvantages of microwave sintering technology

During sintering process, the heating occurs by the three conventional heat transfer mechanisms: conduction, convection, and radiation. Conduction results by heat diffusion between surfaces in contact, for example, in walls inside the furnace that are in contact with the compact. Convective heat transfer occurs from the bulk flow of the gas in the furnace to the compact surface. Thermal radiation is emitted by high-temperature furnace elements and converted into electromagnetic energy that is transferred to the surroundings. The compact receives this electromagnetic energy causing it to heat up. Heat from radiation is, however, quite low, and most of the heating of the compact occurs by means of conduction and convection. Due to the nature of heat transfer mechanisms involved in this method, the surface of the material always heats first, and a temperature gradient between the compact surface and the interior of the material arises, resulting in heat flow from the surface to the bulk. As a consequence, considerably long dwell times (>2 h) are required in order to obtain a complete temperature homogenization and uniform heat distribution.

Another important sintering approach is pressure-assisted sintering, which consists in the external application of pressure during the heating process. Four main ways can be employed to apply pressure. The first one is hot pressing (HP), resulting from uniaxially applying pressure to the powder in a die. The second one is sinter forging, which is similar to hot pressing but without confining the sample in a die. The third one is called hot isostatic pressing (HIP), which consists in the isostatic application of pressure by means of a gas. The fourth one is spark plasma sintering (SPS) and flash sintering which is similar to HP but using a high heating rate. Pressure-assisted sintering enhances the rate of densification significantly relative to the coarsening rate [27]. However, an important disadvantage of pressure-assisted sintering is the high cost of production being only available for specific industrial applications that require specialized, high-cost components. Another limitation is that only simple shapes can be processed due to the use of dyes.

Currently, most commercial materials are processed by conventional sintering and SPS. One of the major drawbacks of these systems, particularly for ceramics, is the high-energy consumption required to reach such high temperatures and dwell times in order to obtain an adequate densification and mechanical properties. Therefore, new approaches on sintering of these materials need to be explored. For example, employing furnaces for heating components with small dimensions would not be energetically efficient. Hence, sintering systems with a focalized energy delivery to the material, such as microwave sintering, can decrease energy use significantly. Moreover, techniques must be flexible and allow for the processing of near-net-shape materials because complex and unique pieces are needed since shapes vary completely from one application to the next. Therefore, microwave sintering confirms as an interesting alternative for the processing of advance ceramics.

3. Conclusions

Currently, innovative sintering methods are being explored and studied in order to reduce energy consumption and production costs, as well as processing tools that allow modification of the densification mechanisms that may improve the microstructure and mechanical

properties of sintered materials. The main purpose for modifying sintering mechanisms is to obtain relative densities close to theoretical values, while maintaining a controlled, but limited, grain growth. Potential of microwaves in material processing has been identified several decades ago. However, owing to limited understanding of the phenomena, their use remained largely confined to only a few materials. Moreover, the overwhelming success of microwave in communication overshadowed its application in other areas. However, discrete attempts in material processing yielded many breakthroughs. In the last 65 years, the microwave processing of materials has become popular due to its potential advantages over the conventional techniques. Overall, microwave sintering is a very good alternative for sintering and consolidating commercial materials for structural applications due to the resulting finer microstructure, enhanced mechanical properties, and reduction in processing times and energy consumption.

Acknowledgements

Author details

Amparo Borrell* and Maria Dolores Salvador

*Address all correspondence to: aborrell@upv.es

Institute of Materials Technology, Polytechnic University of Valencia, Valencia, Spain

References

[1] Barba A, Clausell C, Felíu C, Monzó M. Sintering of $(Cu_{0.25}Ni_{0.25}Zn_{0.50})Fe_2O_4$ ferrite. Journal of the American Ceramic Society. 2004;**87**:571-577

[2] Nightingale SS, Dunne DP, Worner HK. Sintering and grain growth of 3 mol% yttria zirconia in a microwave field. Journal of Materials Science. 1996;**31**:5039-5043

[3] Carter CB, Norton MG. Ceramic Materials Science and Engineering. 1st ed. New York: Springer; 2007

[4] Oghbaei M, Mirzaee O. Microwave versus conventional sintering: A review of fundamentals, advantages and applications. Journal of Alloys and Compounds. 2010;**494**:175-189

[5] Clark DE, Sutton WH. Microwave processing of materials. Annual Review of Materials Science. 1996;**26**:299-331

[6] Presenda A, Salvador MD, Penaranda-Foix FL, Moreno R, Borrell A. Effect of microwave sintering on microstructure and mechanical properties in Y-TZP materials used for dental applications. Ceramics International. 2015;**41**:7125-7132

[7] Rybakov KI, Olevsky EA, Krikun EV. Microwave sintering: Fundamentals and modeling. Journal of the American Ceramic Society. 2013;**96**:1003-1020

[8] Osepchuk JM. History of microwave heating applications. IEEE Transactions on Microwave Theory and Techniques. 1984;**32**:1200-1224

[9] Whittaker AG. Diffusion in microwave-heated ceramics. Chemistry of Materials. 2005;**17**:3426-3432

[10] Boch P, Lequeux N. Do microwaves increase the sinterability of ceramics? Solid State Ionics. 1997;**101-103**:1229-1233

[11] Agrawal DK. Microwave processing of ceramics. Current Opinion in Solid State & Materials Science. 1998;**3**:480-485

[12] Gupta M, Wong WLE. Enhancing overall mechanical performance of metallic materials using two-directional microwave assisted rapid sintering. Scripta Materialia. 2005;**52**:479-483

[13] Wang J, Binner J, Vaidhyanathan B, Joomun N, Kilner J, Dimitrakis G, et al. Evidence for the microwave effect during hybrid sintering. Journal of the American Ceramic Society. 2006;**89**:1977-1984

[14] Charmond S, Carry CP, Bouvard D. Densification and microstructure evolution of Y-tetragonal zirconia polycrystal powder during direct and hybrid microwave sintering in a single-mode cavity. Journal of the European Ceramic Society. 2010;**30**:1211-1221

[15] Xie Z, Yang J, Huang Y. Densification and grain growth of alumina by microwave processing. Materials Letters. 1998;**37**:215-220

[16] Peelamedu RD, Roy R, Agrawal D. Anisothermal reaction synthesis of garnets, ferrites, and spinels in microwave field. Materials Research Bulletin. 2001;**36**:2723-2739

[17] Chatterjee A, Basak T, Ayappa KG. Analysis of microwave sintering of ceramics. AIChE Journal. 1998;**44**:2302-2311

[18] Borrell A, Salvador MD, Peñaranda-Foix FL, Cátala-Civera JM. Microwave sintering of zirconia materials: Mechanical and microstructural properties. International Journal of Applied Ceramic Technology. 2013;**10**:313-320

[19] Cheng J. Study on microwave sintering technique of ceramics materials [thesis]. Wuhan University of Technology; 1991

[20] Breval E, Cheng JP, Agrawal DK, Gigl P, Dennis M, Roy R, et al. Comparison between microwave and conventional sintering of WC/Co composites. Materials Science and Engineering A. 2005;**391**:285-295

[21] Tian YL, Johnson DL, Brodwin ME. Ultrafine microstructure of Al_2O_3 produced by microwave sintering. In Ceramic Transactions Vol. I, Ceramic Powder Science 2, Part B. Westerville, Ohio: American Ceramic Society; 1988. pp. 925-932

[22] Katz JD, Blake RD. Microwave sintering of multiple alumina and composite components. American Ceramic Society Bulletin. 1991;**70**:1304-1308

[23] Cheng J, Agrawal D, Zhang Y, Roy R. Microwave sintering of transparent alumina. Materials Letters. 2002;**56**:587-592

[24] Binner J, Annapoorani K, Paul A, Santacruz I, Vaidhyanathan B. Dense nanostructured zirconia by two stage conventional/hybrid microwave sintering. Journal of the European Ceramic Society. 2008;**28**:973-977

[25] Goldstein A, Travitzky N, Singurindy A, Kravchik M. Direct microwave sintering of yttria-stabilized zirconia at 2.45 GHz. Journal of the European Ceramic Society. 1999;**19**: 2067-2072

[26] Upadhyaya DD, Ghosh A, Gurumurthy KR, Prasad R. Microwave sintering of cubic zirconia. Ceramics International. 2001;**27**:415-418

[27] Rahaman MN. Sintering of Ceramics. New York: Taylor & Francis Group, CRC Press; 2007

[28] Thostenson ET, Chou T-W. Microwave processing: Fundamentals and applications. Composites. Part A, Applied Science and Manufacturing. 1999;**30**:1055-1071

[29] Acierno D, Barba AA, D'Amore M. Heat transfer phenomena during processing materials with microwave energy. Heat and Mass Transfer. 2004;**40**:413-420

[30] Kitchen HJ, Vallance SR, Kennedy JL, Tapia-Ruiz N, Carassiti L, Harrison A, et al. Modern microwave methods in solid-state inorganic materials chemistry: From fundamentals to manufacturing. Chemical Reviews. 2013;**114**:1170-1206

[31] Link G, Miksch S, Thumm M, Takayama S. Microwave sintering techniques—More than just a different way of heating? Ceramic Engineering and Science Proceedings. 2008;**28**:55-66

[32] Chandrasekaran S, Ramanathan S, Basak T. Microwave material processing—A review. AIChE Journal. 2012;**58**:330-363

[33] Astigarraga-Urquiza J, Astigarraga-Aguirre J. Hornos de Alta Frecuencia Y Microondas. Teoría, cálculo Y Aplicaciones. McGraw-Hill; 1995

[34] Bykov YV, Rybakov KI, Semenov VE. High-temperature microwave processing of materials. Journal of Physics D: Applied Physics. 2001;**34**:R55-R75

[35] Katz JD. Microwave sintering of ceramics. Annual Review of Materials Science. 1992;**22**: 153-170

[36] Clark DE. Microwave Solutions for Ceramic Engineers. Westerville, Ohio: American Ceramic Society; 2005

[37] Lasri J, Ramesh PD, Schächter L. Energy conversion during microwave sintering of a multiphase ceramic surrounded by a susceptor. Journal of the American Ceramic Society. 2000; **83**:1465-1468

[38] Anselmi-Tamburini U, Garay JE, Munir ZA. Fast low-temperature consolidation of bulk nanometric ceramic materials. Scripta Materialia. 2006;**54**:823-828

[39] Hall EO. The deformation and ageing of mild steel: III discussion of results. Proceedings of the Physical Society Section B. 1951;**64**:747-753

[40] Borrell A, Salvador MD, Miranda M, Penaranda-Foix FL, Catala-Civera JM. Microwave technique: A powerful tool for sintering ceramic materials. Current Nanoscience. 2014;**10**:32-35

[41] Goldstein A, Travitzky N, Singurindy A, Kravchik M. Direct microwave sintering of yttria-stabilized zirconia at 2.45 GHz. Journal of the European Ceramic Society. 1999;**19**:2067-2072

[42] Semenov VE, Rybakov KI. What type of transport phenomena can be induced by microwave field in solids and how these phenomena contribute to materials processing. In: Miyake S, editor. Novel Materials Processing by Advanced Electromagnetic Energy Sources: Proceedings of the International Symposium, MAPEES'04, 2004, Osaka, Japan. Oxford: Elsevier; 2005. p. 111-117

[43] Menezes RR, Kiminami RHGA. Microwave sintering of alumina–zirconia nanocomposites. Journal of Materials Processing Technology. 2008;**203**:513-517

[44] Benavente R, Salvador MD, Penaranda-Foix FL, Pallone E, Borrell A. Mechanical properties and microstructural evolution of alumina-zirconia nanocomposites by microwave sintering. Ceramics International. 2014;**40**:11291-11297

[45] Nightingale SA, Worner HK, Dunne DP. Microstructural development during the microwave sintering of yttria—zirconia ceramics. Journal of the American Ceramic Society. 1997;**80**:394-400

[46] Zhang R, Fu SL, Lu HX, Xu HL, Han DF, Zheng LL. Processes affecting microwave sintering of ZTA ceramics. Journal of Inorganic Materials. 2001;**16**:178-182

[47] Park SS, Meek TT. Characterization of ZrO_2-Al_2O_3 composites sintered in a 2.45 GHz electromagnetic field. Journal of Materials Science. 1991;**26**:6309-6313

[48] Tsakaloudi V, Papazoglou E, Zaspalis VT. Microwave firing of MnZn-ferrites. Materials Science and Engineering B. 2004;**106**:289-294

[49] Borrell A, Salvador MD, Rayón E, Peñaranda-Foix FL. Improvement of microstructural properties of 3Y-TZP materials by conventional and non-conventional sintering techniques. Ceramics International. 2012;**38**:39-43

[50] García-Gañán C, Meléndez-Martínez JJ, Gómez-García D, Domínguez-Rodríguez A. Microwave sintering of nanocrystalline YTZP (3 mol%). Journal of Materials Science. 2006;**41**:5231-5234

[51] Presenda A, Salvador MD, Penaranda-Foix FL, Catala-Civera JM, Pallone E, Ferreira J, Borrell A. Effects of microwave sintering in aging resistance of zirconia-based ceramics. Chemical Engineering and Processing—Process Intensification. 2017;**122**:404-412

[52] Ai Y, Xie X, He W, Liang B, Chen W. Microstructure and properties of Al_2O_3-ZrO_2 ceramics prepared by microwave sintering. Key Engineering Materials. 2014;**633**:193-197

[53] Presenda A, Salvador MD, Vleugels J, Moreno R, Borrell A. Fretting fatigue wear behavior of Y-TZP dental ceramics processed by non-conventional microwave sintering. Journal of the American Ceramic Society. 2017;**100**:1842-1852

[54] Borrell A, Salvador MD, Peñaranda-Foix FL, Plaza-Gonzalez PJ, Garcia-Baños B, Garcia-Nieto S. Adaptive microwave system for optimum new material sintering. In: 2013 IEEE MTT-S International Microwave Symposium Digest (IMS); 2013. pp. 1-4

[55] Vasudevan R, Karthik T, Ganesan S, Jayavel R. Effect of microwave sintering on the structural and densification behavior of sol–gel derived zirconia toughened alumina (ZTA) nanocomposites. Ceramics International. 2013;**39**:3195-3204

[56] Monaco C, Prete F, Leonelli C, Esposito L, Tucci A. Microstructural study of microwave sintered zirconia for dental applications. Ceramics International. 2015;**41**:1255-1261

[57] Beall GH, Pinckney LR. Nanophase glass-ceramics. Journal of the American Ceramic Society. 1999;**82**:5-16

[58] Pelletant A, Reveron H, Chêvalier J, Fantozzi G, Blanchard L, Guinot F, Falzon F. Grain size dependence of pure β-eucryptite thermal expansion coefficient. Materials Letters. 2012;**66**:68-71

[59] Chen JC, Huang GC, Hu C, Weng JP. Synthesis of negative-thermal expansion ZrW_2O_8 substrates. Scripta Materialia. 2003;**49**:261-266

[60] Sheu GJ, Chen JC, Shiu JY, Hu C. Synthesis of negative thermal expansion TiO_2-doped LAS substrates. Scripta Materialia. 2005;**53**:577-580

[61] García-Moreno O, Fernández A, Khainakov S, Torrecillas R. Negative thermal expansion of lithium aluminosilicate ceramics at cryogenic temperatures. Scripta Materialia. 2010;**63**:170-173

[62] García-Moreno O, Fernández A, Torrecillas R. Solid state sintering of very low and negative thermal expansion ceramics by spark plasma sintering. Ceramic International. 2011;**37**:1079-1083

[63] Benavente R, Borrell A, Salvador MD, García-Moreno O, Peñaranda-Foix FL, Catala-Civera JM. Fabrication of near-zero thermal expansion of fully dense β-eucryptite ceramics by microwave sintering. Ceramic International. 2014;**40**:935-941

[64] Benavente R, Salvador MD, García-Moreno O, Peñaranda-Foix FL, Catalá-Civera JM, Borrell A. Microwave, spark plasma and conventional sintering to obtain controlled thermal expansion β-eucryptite materials. International Journal of Applied Ceramic Technology. 2015;**12**(S2):E187-E193

[65] Benavente R, Salvador MD, Martínez-Amesti A, Fernández A, Borrell A. Effect of sintering technology in β-eucryptite ceramics: Influence on fatigue life and effect of microcracks. Materials Science and Engineering. 2016;**651**:668-674

[66] Vanmeensel K, Laptev A, Hennicke J, Vleugels J, Van der Biest O. Modelling of the temperature distribution during field assisted sintering. Acta Materialia. 2005;**53**:4379-4388