THE DIELECTRIC MEASUREMENTS OF CERAMIC MATERIALS TO THE OPTIMIZATION AND CONTROL OF THE MICROWAVE PROCESSING

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Abstract. *Microwave processing of materials is a promising technology that offers advantages over conventional processing methods. A suitable control over the temperature developed within the materials is required to avoid problems of heterogeneity and thermal runaways in the microwave processing. Understanding the microwave absorption by the material is the key for this solution. The temperature dependence of the dielectric properties of ceramics and inorganic materials measured by the resonant cavity technique shows that the structure, which determines the electromagnetic properties of the material, is complex and normally presents disorder and non-stoichiometric defects which influences the electromagnetic properties and the mechanism of microwave absorption in the solid state, where ionic and electronic conduction play important roles.*

Keywords*. Microwave processing, Ceramic Materials, Dielectric Measurements*

1. Introduction

The use of microwaves for the inorganic solid-state preparations and ceramics processing has been reported extensively in the literature (Sutton, Snyder et all, Roy et all, Agrawal, Thakur et all, Gasnier et all). Microwave processing of materials is a promising technology which offers numerous advantages over conventional methods (Metaxas et all, Mingos, Roussy et all). The inverse temperature profile due to volumetric heating in particular provides improved or unique microstructure and properties. By using the microwave processing method, however, a greater degree of control over the temperature distribution developed within the material is required in order to avoid heterogeneity and thermal runaways (Roussy et all).

Improvements can be done by better understanding of the microwave absorption by the material to be processed. The structure determines the basic electromagnetic properties of the material. The structure of solid state materials such as ceramics, inorganic compounds and composites, crystalline or not, is complex and normally present disorder and non-stoichiometric defects. Non-stoichiometric and disorder materials have important properties and behaviour which are intimately associated with their atomic ordering patterns. Contrarily to the gas and liquid phases, the dipolar orientation is not a preponderant mechanism of microwave absorption in the solid state, where ionic and electronic conduction play important roles (Von Hippel, Bottcher).

At high frequency electromagnetic field, the permittivity of a material becomes complex

$$\varepsilon = \varepsilon' - j\,\varepsilon'' \qquad (1)$$

The microwave power dissipation per unit of volume in a material is dependent upon the total conductivity and the square of the internal electric field E in the sample:

$$P = \sigma\,(E)^2 = \omega\,\varepsilon_o\,\varepsilon''\,(E)^2 \qquad (2)$$

where σ is the total electric conductivity at this frequency, ω the angular frequency, ε_o the vacuum permittivity, ε'' the loss factor. The relationship between the conductivity and the loss factor is established by

$$\varepsilon'' = \sigma / \omega\,\varepsilon_o \qquad (3)$$

Modelling the interaction of ceramic and inorganic materials with the electromagnetic fields present in the microwave applicator is desired to anticipated such problems of heterogeneity. However, theoretical modelling of the process is hindered by the fact that the thermal profile in the sample during microwave heating is dependent on the dielectric and thermal properties of the samples (Freeman et all). These properties, such as the complex permittivity and the thermal conductivity, are largely dependent on the density, the structure and the temperature of the materials (Metaxas et all, Von Hippel).

This work presents the use of the resonant cavity technique to measure the temperature dependency of the dielectric properties of ceramics and inorganic materials, and improve understanding the behaviour of the material to be processed by microwaves.

2. Experimental Procedure

The dielectric properties at microwave frequency were measured by the relative cavity perturbation method in the TE102 dielectric resonator mode. In the resonant cavity method, a small volume ($0.5cm^3$) of the sample is placed into the cavity tangential to the electrical field. The Q-factor value is obtained for empty cavity by the equation $Q = fo/\Delta f$. The same principle is used to obtain a calibration curve with different patterns, where Q represent loaded or unloaded Q-factor, fo is the centre of frequency of resonance response and Δf the half width of resonance peak measured by a vector network analyser (Nyfors et all).

The Q measurements allows the calculation of the dielectric loss ($Q \propto 1/\tan\delta$), and fo permits to calculate the permittivity ($fo \propto \varepsilon'$). The samples were heated in a microwave chamber with controlled temperature, and transferred rapidly to the cavity. This procedure cause 5% of errors on the temperature values, but it is necessary once thermocouples or thermometers cannot be used during the microwave measurements due to their interference. The sample placed into the cavity cause a relative resonant frequency shift smaller than 0.005. The permittivities measurement errors in the present method were estimated as <3%.

3. Results and Discussion

The results obtained from the permittivity measurements as function of the temperature for the kaolin (9% H_2O) show the existence of complex phenomenons of absorption of microwaves due to various mechanisms of dissipation (Figure 1 and 2). At the lower temperatures, the water presence plays a particular role in the dielectric properties of materials. The water can be present under three form: a fraction known as "structural or composition water", other fraction known as "bonded or crystallisation water" and a last fraction call "free water". This seems to be confirmed by the measurement of the dielectric properties as function of the temperature to the clay (21% H_2O), illustrated in figures 1 and 2.

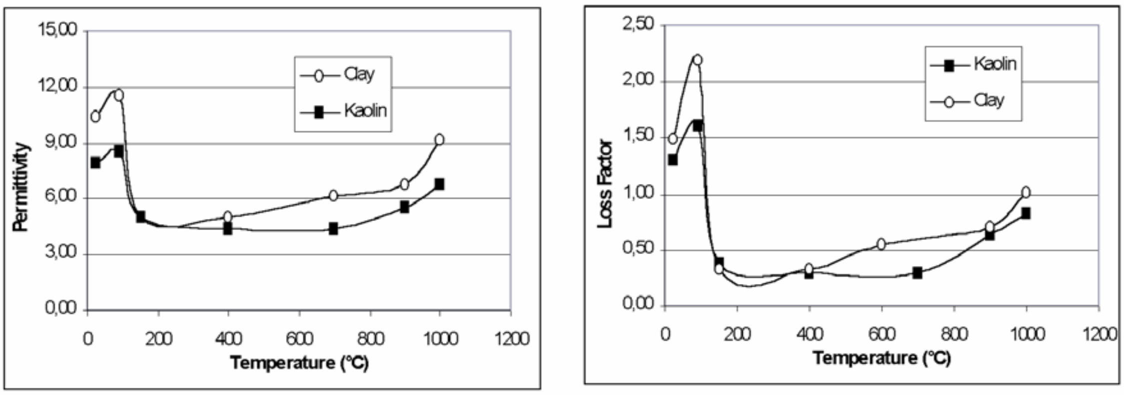


Figure 1 and 2: Dielectric properties of clay and kaolin as function of temperature.

It can be observed on these curves that between 25 and 100°C, the absorbing capacity of microwaves increases. This absorption arises from the Maxwell-Wagner effect between the different phases, and also from the increase of the "free water" freedom from the electrostatic positions to take dipolar orientation. This behaviour is observed in other kinds of substances like biological materials and saturated ionic solutions (Metaxas et all). Between 100 and 200°C, the "free water" and "bounded water" contents are eliminated and absorption decreases. The water desorption is a drying process that depends on the particle size (surface area) and crystallinity of the clay. The kaolin group mineral derivatives are poorly crystallised, amorphous clay characterised by substantial reduction in particle size and high specific surface.

Above 400°C, the dehydratation of the structural water (dehydroxylation of the aluminosilicate lattices) and the decomposition of the clay take place. The dehydroxylation temperature depends on the degree of arrangement of the structure. The increase on absorption is due to the ionic migration inside the solid structure, which increases with the temperature, specially in clays where carbonates and other salt decompositions occurs above 700°C.

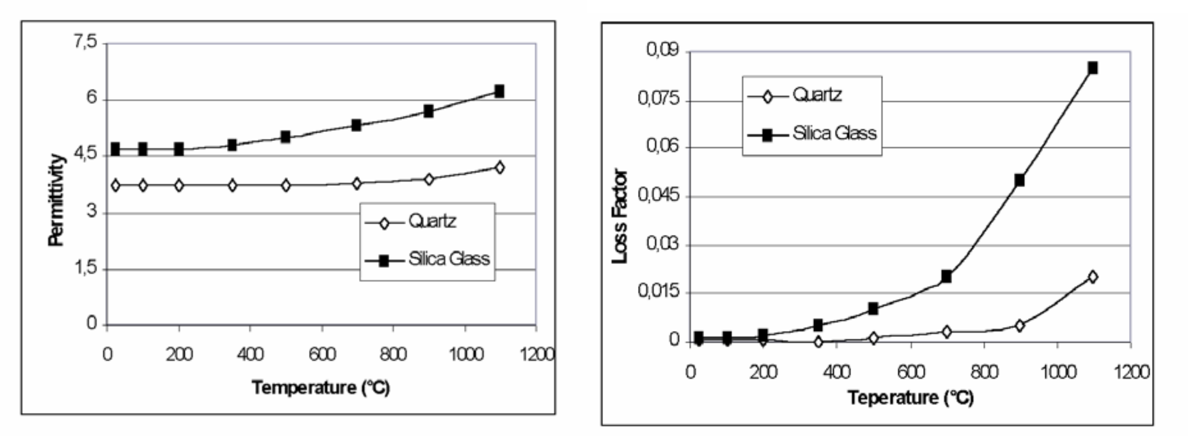


Figure 3 and 4: Dielectric properties of quartz and soda-silica based glass as function of temperature.

The dielectric properties measurements for the quartz and soda-silica based glass show weak absorption effects due probably to vibrational-deformation losses which are related to defects in the basic silicon-oxygen network (strongly polar covalent bonds), and the ionic conduction caused by migration of mobile ions, mainly sodium in soda-silica based glass. The presence of sodium, a modifier network, justifies the different losses observed between quartz and soda-silica glass measurements at higher temperatures as illustrated in figures 3 and 4.

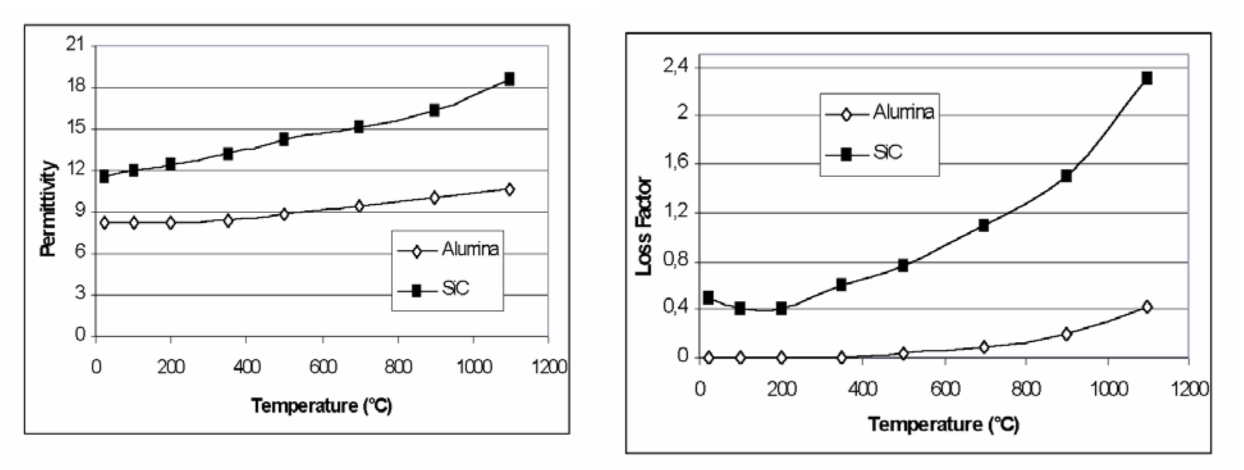


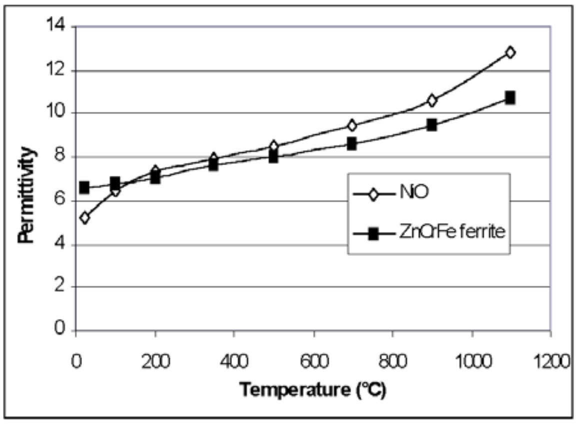
Figure 5 and 6: Dielectric properties of alumina and SiC as function of temperature.

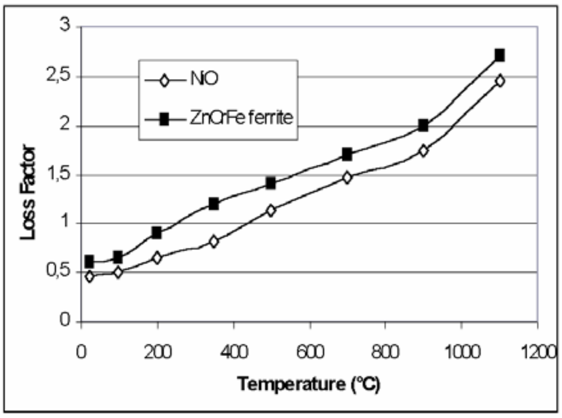
Alumina (Al_2O_3) is a well known dielectric material (insulator) characterised by weak ionic and electronic conductivity due to the ionic bonds. It is confirmed by the measurements of permittivity and loss factor (figures 5 and 6). The increase of the dielectric losses with the temperature is associated with the thermal activation of the valence band electrons (oxygen orbital) that migrate to the conduction band level (aluminium orbital). It is important to keep in mind that the dielectric properties of the α and γ-alumina are normally different from β-alumina, this is caused by the different structures (Von Hippel). In β-alumina, the structure has empty spaces that can be occupied by impurities as contaminant ions with high mobility such as H, Li, Na, and divalent cation as Mg in low concentration (within the solubility limit) that alter significantly the conductivity when associated a disorder and non-stoichiometric defects.

The disordered charge distribution and substitutional impurities associated with oxygen vacancies in a random distribution of defects in the crystal structure increase the dielectric losses even when electronic and ionic conduction are completely suppressed.

SiC is a material that also presents a polymorphism, where the covalent network structures of SiC and β-SiC are wurtzite and zinc blende respectively. The covalent bonding in these materials presents band gap magnitudes in order of 3.1 and 2.2eV conferring semiconductor characteristics as observed by the dielectric measurements, where the loss factor increase with the temperature due to the electronic conductivity.

Sulphides, nitrides and others materials that contain anions less electronegative than oxygen, the substitution tends to stabilize lower oxidation states of metals and makes the bonding characteristics more covalent, delocalising the valence electrons and producing band-gaps narrower than by analogous oxides.





Transition metal oxides can present semiconductor behaviour. The conductivity of *d* electrons in transition metal compounds is often increased when the element is available in more than one oxidation state. NiO normally has a very low conductivity, but when in a non-stoichiometric proportions it can present semiconductor properties (Von Hippel). This fact can justify its dielectric behaviour presented during the measurements (figures 7 and 8).

The ZnCrFe ferrite (spinel group) has different metal ions occupying specific sites in the crystal structure, two different ions in two specific sites (a metal M^{+2} and a metal M^{+3}). This arrangement causes a transfer of *d* electrons between the different metals in a structured path or vector. This electric vector result in specific electromagnetic properties that gear strong interacts with the electric and magnetic microwave fields as demonstrated by the dielectric measurements in TE102 cavity using the electric mode (figures 7 and 8).

4. Conclusions

The dielectric measurements by the resonant cavity method demonstrated very useful to determine the electrical behavior of ceramic materials during microwave processing. By this method is possible to observe absorption mechanism such as dipolar orientation, ion conduction and electronic conduction when the electric mode is applied.

This approach is essential to understand the electronic properties of the materials and its process suitability, correlating them with the structure and the different mechanisms of charge transport such as electron/hole conduction, oxygen ion conduction, proton (sodium) conduction, ionic conduction in solid electrolytes, and others.

The solid-state materials have historically been prepared through high temperature solid-state reactions, generally affording the most thermodynamically stable phases, a variety of techniques such as well controlled microwave processing and others that have been developed and can improve the limitations inherent in this traditional approach.

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