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Additional Information

A step ahead on efficient microwave heating: relevance of electron-phonon coupling in kaolin.

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ABSTRACT

The thermal evolution of kaolin clay under microwave radiation shows an unexpected large heating rate up to 500ºC/min for temperatures >650ºC. Such heating rate is associated with a resistivity drop of >10^3 Ω.m observed after the dehydroxylation process. The high efficiency of the microwave heating effect is correlated with the presence of surface carriers that absorbs microwaves electromagnetic field and produces crystal heating by electron-phonon coupling or small polaron. The layered structure of the clay-based materials allows the appearance of charge carriers at the surface of the crystal lattice that is electromagnetically activated. This effect represents a breakthrough in the efficient use of microwaves energy in order to produce efficient thermal treatments in large volume of non-metallic minerals with a drastic reduction of the greenhouse gasses for mass production industries.

KEYWORDS

Kaolin clay; Dielectric properties; Microwaves; Electron-phonon coupling

1. INTRODUCTION

One of the most critical issues in today's society is the large amount of greenhouse gasses generated annually in thermal processes. The growing energy consumption coupled with the demand for materials is in part at the origin of this excessive increase in resources. Today, the society challenge is increasing the energy production from renewable and non-polluting sources. Moreover, green energy production also seeks to use energy in an efficient way, as an example, by electric vehicles with batteries. However, industrial production of bulk materials still requires high temperature treatments associated to further bearing gas emissions by decomposition of raw materials. Thus, the main sectors of infrastructure and building topped the list of industrialized materials of mass production as cements, ceramics or glasses. A common aspect of these materials is the use of large quantity of mineral raw materials that require heat treatments at high temperatures, above 1000°C. In most cases, fossil fuels or gas are used for thermal processing. Generally speaking, the electric furnaces are inefficient and incompatible with the processing rates of tons per hour that most of these materials require. The relevant question to be answered is whether there is any possibility to use electricity in an efficient way for the heat treatment of materials.

In this regard, the use of microwave energy is extensively proposed as an efficient thermal process of materials which are capable of absorbing electromagnetic radiation (Thostenson and Chou, 1999). In this case, sintering times decrease, in general the processes need lower temperatures (Roy et al., 1999), and in mostly of cases “in situ” CO_2 emissions are reduced in comparison with combustion processes. The lack of knowledge related to the materials behaviour under microwave radiation is limiting up today the heating applications to the laboratory scale. So, it is required a breakthrough to open the way to use microwave technology in the mass production processing of materials at high temperature.

In conventional heating methods the heat is transferred between objects through the mechanisms of conduction, radiation and convection. In this case, the surface of the material is firstly heated and then, there is a temperature gradient from the surface to bulk of the material. By comparison, in microwaves heating processes, the electromagnetic energy is absorbed volumetrically by the material and transforms into heat. Thus, the energy could directly transfer to the material within an inner uniform temperature distribution (Oghbaei and Mirzaee, 2010). Microwaves can interact with materials through either polarization or conduction processes (Sun et al., 2016). Both processes give rise to dielectric losses at certain frequency ranges. The dielectric losses are due to ion conduction at lower frequencies and to rotation of permanent dipoles at higher frequencies. Thus the dielectric properties ultimately determine the effect of the electromagnetic field on the material. Overall, there are three types of materials according to the response to the microwave radiation: reflector, receptive, and transparent. Materials with high conductance and low capacitance, such as metals, have high dielectric loss factors. As the dielectric loss factor gets very large values, the penetration depth of microwaves approaches zero and the materials are considered as microwave reflectors or mirrors. Conversely, in materials with low dielectric loss factors very little amount of electromagnetic energy interacts with the material and it is considered as transparent material against microwave energy (Mandal and Sen, 2017). Microwave radiation transfers energy most effectively to materials that have semiconductor behaviour and medium dielectric loss factors. In contrast, conventional heating transfers heat in a most efficiently way to materials with high thermal conductivity (Oghbaei and Mirzaee, 2010).

The potential use of heating by microwave energy inspires to the materials towards the efficient use of energy. The reason is that there are challenging demands from the industry for new and improved thermal processes in order to obtain finer microstructures and to enhance physical and chemical properties, apart from the mentioned advantages of the use of microwaves energy (Leonelli et al., 2008). In this

sense, many experiments were performed applying microwaves energy at laboratory scale (García-Baños et al., 2016) by using 2.45GHz as frequency band because it is the standard magnetron frequency for domestic microwaves. But in general, at room temperature oxide materials do not absorb microwaves appreciably at 2.45 GHz. In order to improve microwave absorption by the oxides, several attempts were pursuit as: conventional preheating; by adding absorbents (e.g., SiC, carbon, binders) (Bhattacharya and Basak, 2017); by altering the materials microstructure and the defects structure as Agrawal (1998); by changing their form (e.g., bulk vs. powder); or by tuning the frequency (Clark and Sutton, 1996). In this way, the behavior of some ceramic oxides which are widely used in different application fields as Al_2O_3, TiO_2, ZnO and Bi_2O_3 were studied versus microwaves interaction (Bindra and S. Bahel, 2010). Also advanced materials as PZT, $BaTiO_3$, ceramic perovskites or ZnO varistors were thermally processed by using microwaves energy. (Clark et al., 2005; Fang et al., 2009] In these experiments the “microwave effect” is claimed to be behind a faster thermal treatment. The “microwaves effect” is described as a non-thermal phenomenon that consists of accelerated kinetics (Vaidhyanathan et al., 2001; Roy et al., 2002). In a sintering process, the microwave effect is quantified by the difference between the required temperatures by microwave heating versus conventional heating, typically electrical heating, that leads similar microstructures. In this sense, saving in energy consumptions is argued thanks to microwaves energy application.

Nowadays a large volume of non-metallic mineral products in industry is manufactured by thermal processes. Non-metallic mineral industry is dominated by cement, glass and ceramic industries. Large amounts of energy are used in heating processes at high temperatures of non-metallic minerals which inevitably produce large quantities of greenhouse gasses, mainly CO_2. A clear example is the cement industries which are responsible for ca. 10% of CO_2 world production from carbonate oxidation and fuel combustion (Olivier et al., 2014). But non-metallic minerals are transparent to the

113 microwave radiation. However, the challenge to use microwave energy in the heating
114 processes could make possible to drastically reduce the amount of CO_2 from fossil
115 fuels. Moreover, the lack of knowledge related to the behavior of non-metallic minerals
116 under microwave radiation versus temperature impedes to realize the transformation of
117 these industries. One clay mineral that is present in most of the cement, glass and
118 ceramic production processes are kaolinite. Kaolinite is part of the group of industrial
119 minerals, with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered clay mineral, as
120 for such, the individual layers consist of tetrahedral layers of silica (SiO_4) linked through
121 oxygen atoms to octahedral layers of alumina (AlO_6). Rocks rich in kaolinite are known
122 as well as fire kaolin clay or ball clay. Brindley and Nakahira, 1959 reported the
123 reaction series from Kaolinite-mullite during the thermal treatment in a conventional
124 heating.

125 In this sense, this work shows an in situ study of the dielectric properties of kaolin clay
126 under microwaves radiation. The thermal behaviour of kaolin is compared with the
127 observed by conventional heating. Therefore, dielectric properties are studied and
128 microwave effect for large heating rates at temperatures >650ºC is correlated with the
129 drastic drop of resistivity in the kaolinite after the dehydroxylation process. A
130 mechanism for effective heating under microwaves radiation is proposed based on the
131 electron-phonon-coupling. The study is a first step in the knowledge of the application
132 of microwaves with the purpose of heating large amounts of materials that generate
133 high CO_2 emissions during heating, such as kaolinite-based materials as kaolin clay.

134 ## 2. EXPERIMENTAL PROCEDURE

135 Pure industrial-type kaolin clay (from Keraben Group, reference MK_KE01) having
136 96% of kaolinite was chosen for the study. The kaolin clay raw material in form of
137 powder was sieved using a mesh of 100µm and die pressed at 25MPa to obtain
138 cylindrical samples with dimensions of 1mm (for electrical resistance and impedance

measures) or 10 mm (for dielectric assays by applying microwaves energy) in thickness and 10 mm in diameter. Samples were thermally treated at different heating rates (from 5 to 40ºC/min) up to 1100ºC by using two different heating methodologies:

- Conventional: electrical furnace Nabertherm Model L9 from Germany with a program controller S27.
- Microwaves: microvawes laboratory equipment where the microwave cell is a cylindrical resonance cavity designed to operate simultaneously in two modes, one for heating and the other one for measuring, as Catalá-Civera et al. 2015 designed. The heating mode (TE111), designed to resonate near the ISM standard frequency of 2.45 GHz, is fed into the cavity by a probe inserted through the side wall (Figure S1). Once tube and sample are positioned inside the cavity, control software implemented in Labview allows setting the desired heating rate, monitoring the sample temperature, recording the video image of the sample and the response of the cavity, both for the measuring and heating modes. A PID algorithm adjusts the source bandwidth to follow the changes in the cavity response and obtain the desired heating rate throughout the process.

The samples were characterized chemically by X-ray fluorescence using a XRF Philips MagiX spectrometer, structurally by X-ray diffraction using a Bruker AXS D8 – Advance diffractometer (Madison, WI, USA.), granulometrically by laser diffraction using a Malvern Mastersize equipment, and microstructurally by using a Field Emission Scanning Electronic Microscope FESEM Hitachi S-4700, Hitachi. The thermal transformations in the range 30–1200 ºC with a heating rate of 10ºC/min were studied by means of differential thermal, DTA, and thermogravimetric, TG, analysis using a Thermo-Analizer Netzch STA 409 with a temperature controller Netzch TASC 414/2 being the reference α-Al_2O_3 and a Hot-stage microscopy by a Leica Leitz microscope.

The dielectric properties during the heating under microwave radiation were evaluated in the microwaves energy laboratory equipment. The dielectric measure mode (TM010)

is fed by a probe (a different one from the heating mode) through the bottom wall of the cavity. A Vector Network Analyzer is used as a source for the measuring mode, with a cross-coupling filter to avoid interferences between the heating and the measuring signals.

Impedance spectroscopy allowed calculating the electrical resistance and capacitance against the frequency by adequate electrical circuit's analysis. The measurements were obtained by using an impedance analyzer (HP4294A, Agilent Technologies Inc., Santa Clara, CA). The frequency range was from 100Hz to 10MHz for dielectric constant measurements. The temperature range is up to 700ºC using a 2ºC/min heating-cooling rate, for both impedance measurements and for electric modulus. Impedance arcs were obtained by Nyquist plot from 630ºC to 700ºC due to the resolution of the measurements and for this reason only impedance arcs in this range appear plotted. Capacitance was calculated from the value $\omega_{max} \cdot R \cdot C=1$, where $\omega_{max}=2\pi f_{max}$ and f_{max} is the frequency at the maximum value of the impedance arc for different temperatures. DC electrical resistance was measured by the same impedance analyzer from 30ºC to 700ºC and it was recorder during heating and cooling of fresh and thermally treated kaolin clay pressed discs previously electroded by using silver paste.

3. RESULTS AND DISCUSSION

The behaviour of kaolin clay cylinders when they are heated by using microwave energy at different constant heating rates (5 - 40ºC/min) was studied (Figure 1a). In all cases, at low temperatures, <650ºC, kaolin clay samples heat accordingly to the selected heating rate, denoted as region **1.** Unexpectedly, there is a sudden increase of the heating rate at ≈650ºC independently of the initial selected heating rate, region **2**.

At slower heating rates the anomalous increase of temperature is more visible in Figure 1a. At higher temperatures the samples regulate the heating rate up to the initial heating ratio, region **3**, which is more clearly observed for the lower heating rates. The heating rates obtained for the different sintering cycles by using microwaves energy were studied (figure 1b). The previously mentioned regions are delimited also for shake of clarity. The heating rates in region 1 are in concordance with the initially selected heating rates for the thermal treatments (inset in Figure 1b). Nevertheless, as it was mentioned before, a change of heating ratios takes place from ≈650ºC. This variation is more pronounced for lower initial heating rates, it means, the anomalous experimental heating rates in region 2 are inversely proportional to the ones that were programmed in microwave laboratory equipment.

In fact, in order to keep the heating ratio constant during the initial stage of the heating processes (below 200ºC) by using microwaves energy, a relevant change of the microwave bandwidth is required (figure 1c). At room temperature the material shows low selectivity to microwave radiation and the low absorption is signalled by a higher bandwidth as an indication of the low efficient heating process. At temperatures higher than ~160ºC the bandwidth decreased and this fact signalled an increase of energy transferred from the microwave field to the sample. From ~280ºC, a nearly constant frequency keeps the heating rate relatively constant until ~650ºC. Above 650ºC the bandwidth is maintained with a small increasing and a further decreasing in the region **3** denotes higher absorption of microwave radiation by the sample, figure 1c. The enhancement of heating rates for microwave heating could be associated to the usually named “microwave effect”. The microwave effect thus is observed in kaolin clay samples in a temperature range where the heating rate increases one order of magnitude. This increase is observed for low selected heating rates. It is worth to remark that, during the whole experiment, the heating source is always the microwaves radiation. In this sense, region 2 shows higher efficiency in the conversion process of

electromagnetic radiation into heat. However, the effective heating rate could be ascribing to well-known thermochemical structural changes from kaolinite to metakaolin as a consequence of the temperature.

The main temperature points at which changes take place are correlated from Differential Thermal Analysis, DTA, and Termogravimetry, TG, studies of kaolin clay when it is heated conventionally (Figure 2a). At ~535ºC an endothermic process that corresponds to the dehydroxylation of kaolinite and then metakaolin occurs (reactions are described in S2). This endothermic transformation requires energy absorption in order to remove the chemically bonded hydroxyl groups. TG curve shows that nearly 10 wt% of water is eliminated from the structure during this reaction and therefore the total mass of the kaolin clay sample decreased accordingly. The kaolinite dehydroxylation is accomplished with a slight shrinkage of the sample and therefore porosity usually rises in this process. Regarding the loss of water, it is worthy to mention that it is a non-reversible process that provokes appearance of new defects into the kaolinite structure and the material transform to metakaolin. In order to understand the structural modifications, Kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) is composed by a SiO_4 tetrahedrons layer and a Al_2O_3 octahedrons layer that confreres the characteristic laminar type morphology of clays having typically 1.24 nm in thickness and more than 200 nm in equivalent diameter (Hu and Liu, 2003). The hydroxyl groups are responsible for the appearance of defects on the material structure. Moreover kaolinite layers are linked by hydrogen bridges between OH^-. This morphology is the responsible for the high specific surface of the kaolinite clays (Varga, 2007). The structural dehydroxylation of kaolinite is produced by a combination of two different processes that occur in the heating step (Sperinck et al., 2011): the continuous loss of water at the inter-layer and the discontinuous loss of structural (inner-layer) water. The dehydroxylation of structural water might result in the disturbance of the $Al(O,OH)_6$ octahedral layers by the outer hydroxyls, but it does not have much effect on the SiO_4

245 tetrahedral layers due to the more stable inner hydroxyls groups. The outer hydroxyls
246 of octahedral layers correspond nearly to 87% of the water in the material, and may be
247 more easily removed by heating than inner ones, that will maintain a more ordered
248 SiO_4 tetrahedral group in structure during dehydroxylation (Giesse and Datta, 1973). All
249 these processes explain the reason because the dehydroxylation process occurs in a
250 wide temperature range, from ~475 to ~583ºC.

251 A further heating produces an exothermic peak at ~980ºC indicating the structural re-
252 crystallization from layered units of metakaolin to aluminium-silicon spinel or pre-mullite
253 type crystals (reactions are described in figure S2) (Sahnoune et al., 2007). During this
254 process, the excess of SiO_4 tetrahedral units become amorphous silica that assists a
255 mass diffusion process and improves the densification. It is described that the
256 formation mechanism of mullite starts with two pre-reactions which consist of the
257 formation of pseudo-tetragonal mullite (at ~700ºC) in a solid-liquid phase and its
258 posterior transformation to orthorhombic mullite at ~800ºC as a solid state reaction.
259 (Zhang et al., 2014) These processes could explain the increase of the heating ratio
260 from 700ºC in Figure 1b and the existence of variations in the band width curve of
261 Figure 1c at the mentioned temperatures.

262 It was studied the dielectric losses of kaolin as a function of the temperature under the
263 presence of microwaves radiation during heating and without microwaves radiation
264 during cooling (Figure 2b). The dielectric losses are linked to the microwaves power
265 adsorption. During heating from room temperature to ≥150ºC a small decrease of the
266 dielectric losses occurs. The dielectric losses during heating remained after this
267 temperature quite below the 0.1, value that indicates low microwaves energy
268 absorption and therefore low effectiveness during heating step (Fernandez et al.,
269 2015). This fact correlates with the high values of the band width which were observed
270 for those temperatures in Figure 1c. Into the range from 475ºC to 583ºC, a sudden
271 increase of dielectric losses indicates a drastic change of the dielectric behaviour

where the loss factor exceeds the value of 1.5. This increase is un-coincident with any changes in the previous microwaves heating curves, Figure 1, but it is coincident with the dehydroxylation process of kaolin, Figure 2a. After the dielectric loss enhancement, several variations of dielectric losses appear. The more intense peaks are located at the temperature ranges between 800-900ºC and 1090-1210ºC (signalled in figure 2b). This time, the effective increase of the measured heating rate is coincident with the pre-reactions of the formation of pseudo-tetragonal mullite at ~700ºC, its posterior transformation to orthorhombic mullite at ~800ºC. During cooling, none of these process should occurs and, accordingly, the value of dielectric losses decreased but it kept a value higher than 0.2 indicating the structural and microstructural evolution of the sample. Hence, the increase of power absorption with the temperature from 650 - 700ºC is in principle supported by the increasing of dielectric loss factor which is related to the existence of amorphous silica and alumina that contributes to the mass transport for the reordering of the structure after the dehydroxylation.

The thermal conductivity of kaolinite and metakaolin keeps nearly constant in the range of temperature in which both materials do not suffer changes (Michot et al., 2008). It means that the changes in the dielectric behaviour of the sample during the heating step have not relation to the thermal conductivity of the material. Nevertheless, the densification at higher temperatures could affect the dielectric response of the sample inside the resonant microwave cavity as the one used in the present work. The presence of structural hydroxyl groups produces low microwave adsorption by dipole rotation (as it occurs in the temperature range of 160-473ºC, before the beginning of the dehydroxylation process). In addition their elimination initially seems to be related with the sudden improve of the heating by microwaves energy adsorption. Nevertheless, a correlation between the defects originated during the dehydroxylation and the sudden increase of microwaves energy absorption could be in principle established. A subsequent second thermal heating on the previous sample shows a

similar behaviour in dielectric losses vs temperature (see Figure S3), but this time to a lesser extent. During the second thermal heating the material is not able to suffer dehydroxylation and thus the microwave effect that assists the higher heating rate should be attributed to a different mechanism than the dipole rotation and could not be related to the water elimination from the kaolin structure.

In order to understand the unusual behaviour of the kaolin during the dehydroxylation step, an in situ measurement of the electrical resistivity was attempted in a conventional furnace. The static or DC resistance of the sample was measured during both the heating and the cooling steps. A drastic change in the DC resistance with the increase of the temperature is found for kaolin samples (Figure 3a). The value of the initial DC resistivity at room temperature, $>10^8\Omega$.cm (not shown), is not a real value because initially kaolin is an insulator compound and its resistance overflows the equipment of measure (Equipment measure range: from 300Ω.m to $3x10^8\Omega$.m). An abrupt decreasing of the DC resistivity takes place at ~555ºC up to ~$3x10^6\Omega$.cm, that it is more than 2 orders of magnitude of lower resistances than the initial values. The resistivity drop suffers an exponential decay. This resistance decay fits the mass losses in the range of temperatures where the dehydroxylation of the kaolin takes place. It is described that the mentioned decrease might arise partly for an increase in the cations mobility during the dehydroxylation process (Tari et al., 1999). In this way, if the cations mobility enhances, it will contribute to the total conductivity and so the resistance of the entire system will decrease. It is surprisingly that the DC resistivity value recovers up to ~$3x10^8\Omega$.cm during the cooling of the sample. Moreover, DC resistivity is recovered at low temperature and the abrupt drop experiences an hysteresis, ca. -5ºC (see inset in Figure 3a). In a second heating process (at this time metakaolin is the initial compound because the dehydroxylation process already took place during the first heating cycle), the electrical resistivity vs temperature follows a similar trend than during the first cycle, nevertheless a difference of ~5ºC is also observed. This fact indicates a lack of

relationships between the dehydroxylation and the change of resistivity because the dehydroxylation process in kaolin is not reversible. Hence, the strong drop of the resistance with the temperature cannot be attributed to the water elimination. Taking into account that both kaolinite and metakaolin are intrinsically resistive materials for nature, the unusual changes in resistivity should be attributed to thermally activated surface phenomena (Lorite et al., 2012). The presence of surface carriers are originated when the OH^- are eliminated during heating. To remove an H_2O molecule it is required two hydrogen atoms located in neighbouring hydroxyl groups, as well as one of the bonded oxygen atoms from hydroxyl groups (Ondruška et al., 2015). So, the remaining oxygen from hydroxyl is then converted to structural oxygen after swiping the free electron located on terminal oxygen to particle edges resulting in large oscillating dipoles. In other words, the vacancies which are produced by the loss of hydroxyls groups from the structure create large distortion in the layers. These structural changes are responsible for the appearance of surface dipoles that are thermally activated in order to increase conductivity in a reversible way.

In order to discriminate whether a conduction mechanism takes place in the samples an impedance spectroscopy analysis is attempted (Figure 3b-c). For all the heating and cooling cycles the formation of a single impedance semicircle is observed at temperatures >650ºC (Figure S4), in the range of temperatures where the decreasing of the resistivity shows an exponential decay behaviour. The impedance arcs are adjusted taking into account the RC circuit described in Figure 3b inset. Typical values of relaxation frequency (fr) of the impedance arc might give a good indication of the nature of the main contribution to conductivity, e.g. from the intrinsic contribution as crystal lattice or extrinsic contribution as grain boundaries/intergranular phases (Ribeiro et al., 2004). In general, high values of relaxation frequency are ascribed to the intrinsic contribution. Moreover, the values of capacity are in the order of 10^{-12} Farads (see Figure 3b) for the different temperatures and heating cycles. This aspect confirms that

353 the resistivity corresponds to the same electro-active region. The conductivity slightly
354 increases with the increasing of temperature indicating semiconductor behaviour. This
355 fact points the differences of temperature in the process of changes of resistivity
356 between the heating and the cooling step of the sample. The excitation keeps
357 remaining when temperature decreases. Due to the layered morphology of the kaolinite
358 based materials, the structural defects are present at the interfaces between the former
359 layers. Thus, the surface carriers are responsible for the increase of conductivity in
360 metakaolin and thereof behind the high heating rate observed. Zemanova et al. 2006
361 applied microwaves energy in smectite clay minerals and observed MW heating
362 efficiency thanks to an ionic conduction contribution for neutralization of layer charges.
363 In concrete, smectite presents alkali and alkali earth cations apart from electrons after
364 dehydration processes, and both charges with different polarity tray to join for
365 neutralization of the system. Nevertheless, kaolinite has not alkali and earth alkaline
366 ions in the structure so the mechanism may be different. In Kaolinite, the phase change
367 at 980ºC promotes the accommodation of the structure and charges so the heating
368 ration decreases after the transformation.

369 An electron-phonon-coupling mechanism could explain the microwave absorption of
370 the surface carriers to an excited state and their interaction with cations in the crystal
371 lattice, which provokes their displacement from the equilibrium positions. Electron-
372 phonon coupling is a major coherent mechanism, which often causes scattering and
373 energy dissipation in semiconductor electronic (Chen et al., 2015). In such a way the
374 microwave effect which is responsible to the observed high heating rates could be
375 ascribed to such mechanism.

376 The behaviours according to the thermal evolution of the kaolin under the presence of
377 microwaves energy and the heating mechanism of the material when is irradiated by
378 microwaves are summarized in Figure 4. At low temperature when microwaves interact
379 with kaolinite, the excitation of dipoles takes place, mostly from terminal OH. During the

dehydroxylation process it occurs the mechanism which consists of swiping the free electron located on terminal oxygen to particle edges, resulting in large oscillating dipoles induced by oscillating MW E-field. In the obtained metakaolin, the charges displace along the structure because of the insulator character of the material. The movement of charges along the surface causes an electron phonon-coupling, so that the cations displacement in the crystal lattice from the equilibrium position is carried out depending on their charge and the charge carriers. The displacements of the cations promote an increase of the kinetic energy of the crystalline network since they generate a quantized lattice vibration wave or phonon. The charge carriers on the surface of the layered particles efficiently absorb microwave radiation. However, the sample has a high resistivity, which leads to a limited density of charge carriers in it. Thus, the lack of charge carriers produces inefficiency in the microwave absorption process at high doses of applied energy. The same situation occurs when large heating rates are programmed in the laboratory equipment. At the time that the amount of microwaves energy is reduced, an increase of the efficiency occurs and thus very large efficiency is obtained when the heating rate exceeds 500ºC/min. In such conditions, the charge carriers are excited by the microwave radiation and the electron-phonon-coupling mechanism occurs. Hence, the microwaves energy is transferred into heat on the oxide material. Lower heating curves than the selected ones are not attempted because of the regulation instability of the laboratory equipment.

At higher temperatures, the presence of phonons in the crystal lattice scatters the charge carrier and therefore the mobility of the charge carriers reduces considerably in spite of the increase of conductivity in the material. The chemical reactions would contribute also to limit the amount of charge carriers. As consequence, the electron-phonon-coupling is efficient only in the range of temperature in which the surface carriers are available and, in spite of the large dielectric losses, the solid reduce their heating rate.

The implication of the above findings is quite relevant for both the academia and the industry. In a first approach, the heating of minerals in mass production industries could be benefited from this mechanism by combining adequate materials in order to produce advanced industrial heating microwave furnaces. The authors of this publication are also reporting the use of an adequate mixing of minerals to produce glass melting process of frits used in the tile industry (Daphne Project, 2012; García-Baños et al., 2015). In this case, an adequate combination of minerals allows the efficient heating at different temperatures. Temperatures higher than 1500ºC are obtained and the process is scaled to pilot plant production with >65% saving in terms of energy.

In a second approach, the selective heating of semiconductor materials, in particular oxide materials having surface defects as nanomaterials, also could be benefited from this effect. In this manner, higher chemical potential regions could increase rapidly their temperature and surface diffusion mechanism is promoted. Additionally, electron excitation between nanostructures, as quantum dots, could modulate not only the electrical conductivity states in silicon quantum dots (Ferrus et al., 2014), but also the thermal conductivity or local heating of the particles.

In summary, the presence of surface charges in semiconductors improves the heating of the material by an electron-phonon coupling mechanism when microwaves energy is applied. The high efficiency of the process is higher than the standard dipole rotation. In this sense, the mechanism of electron-phonon-coupling could be behind the so called “microwave effect” in more materials than expected because the hopping mechanism appears in poor conductive materials or in high disorder materials with low carrier density. The present study stimulates to find new solutions for industrial heating that runs in the sense to save energy and to obtain drastic reductions of CO_2 emissions when microwaves are used.

4. CONCLUSIONS

A step ahead to the effective use of microwave radiation for mass production materials based on oxide minerals is shown. The dielectric properties of the kaolin samples versus temperature are evaluated under microwave radiation. The thermal evolution of kaolin under microwaves energy exposition shows an unexpected large heating rate up to 500ºC/min for temperatures >650ºC. Such heating rate is associated with a resistivity drop of $>10^3$ Ω.m observed after the kaolin dehydroxylation process and a relevant increasing of the dielectric losses. While the processes of dehydroxylation of the kaolin structure are not reversible, the drastic decrease in resistivity is reversible with a small hysteresis and thereafter the high rate of heating which is showed under microwave radiation is correlated with the charge carriers responsible for the decreasing of the resistivity. The layered structure of the clay-based materials allows the appearance of charge carriers at the surface after dehydroxylation and thus these surface defects of the crystal lattice are electromagnetically activated. The high efficient of the microwave heating effect is correlated with the presence of surface carriers that absorbs microwave electromagnetic field and produces crystal heating by electron-phonon-coupling or small polaron. This effect represents a breakthrough in the efficient use of microwave energy in order to produce efficient thermal treatments in large volume of non-metallic minerals with a drastic reduction of the greenhouse gasses for mass production industries.

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SUPPLEMENTARY INFORMATION

Supplementary Information 1.- Microwaves energy laboratory equipment.

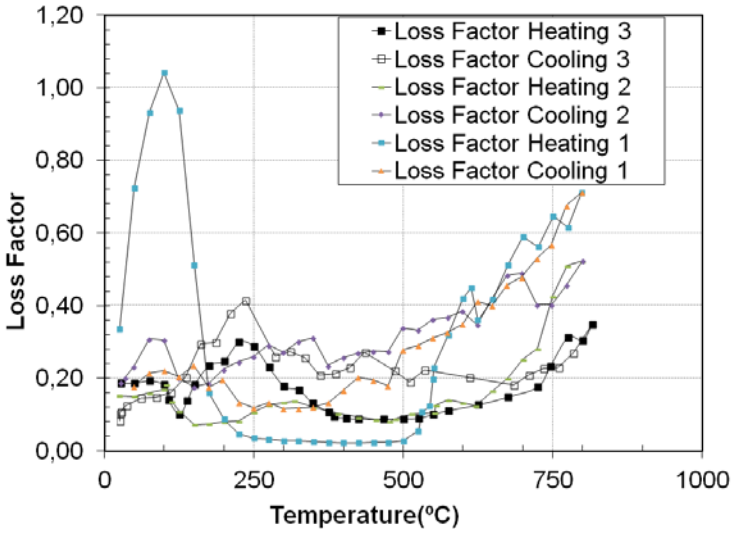
$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ [Kaolinite] $\rightarrow$ $Al_2O_3 \cdot 2SiO_2 + 2H_2O$ [Metakaolin] 475ºC - 583ºC

$2(Al_2O_3 \cdot 2SiO_2)$ [Metakaolin] $\rightarrow$ $2Al_2O_3 \cdot 3SiO_2$ [Pre-Mullite = Al-Si Spinel] $+ SiO_2$ [Amorphous] 985ºC

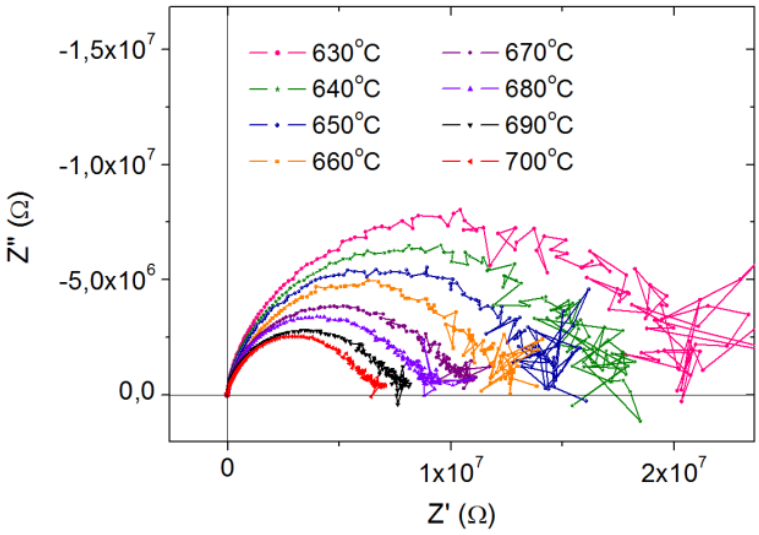
$3(2Al_2O_3 \cdot 3SiO_2)$ [Pre-Mullite = Al-Si Spinel] $\rightarrow$ $2(3Al_2O_3 \cdot 2SiO_2)$ [Mullite] $+ 5SiO_2$ [Amorphous] 1250ºC

$2(3Al_2O_3 \cdot 2SiO_2)$ [Mullite] $+ 5SiO_2$ [Amorphous] $\rightarrow$ $2(3Al_2O_3 \cdot 2SiO_2)$ [Mullite] $+ 5SiO_2$ [Cristobalite] 1330ºC

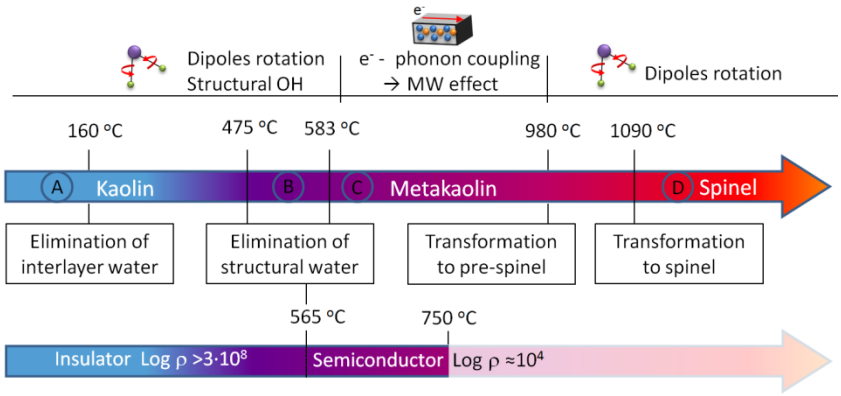
Supplementary Information 2.- Processes with temperature form kaolin.



Supplementary Information 3.- Dielectric properties (loss factor) of metakaolin during several heating-cooling cycles. This time, temperature achieves only 800ºC in order to not to crystallize mullite phase.



Supplementary Information 4.- Impedance arcs of metakaolin sample (from kaolin clay heated at T>550ºC) at the temperature range 630ºC<T<700ºC, during heating process.



Supplementary information 5.- Summary of processes in kaolin and later phases with temperature, dielectric behavior and causes of the heating.

(A) At the region A, from RT up to ~475ºC, the dipole rotation is in the origin of the microwave heating of the kaolin. As the absorption of microwave is low, higher bandwidth and low heating rate are produced. In this region A, the presence of hydroxyl groups and the ionization of water occur on the crystal surfaces.

(B) At the range of temperature 475ºC-583ºC, the dehydroxylation of structural water into kaolinite takes place as it was observed by Tg study and the accommodation of the structure occurs up to ~650ºC as it was demonstrated by DTA. During the process (at ~565ºC), electrical measurements showed that DC resistivity of the sample decreases.

(C) From ~650ºC and up to T~980ºC, a high heating rate is observed when microwaves energy is applied to the sample. The high heating rate may be related to a Microwaves effect and it occurs as a consequence of the appearance of surface carriers originated from the uncompensated removal of hydroxyl groups from the crystal lattice. Carriers are activated by microwave absorption and the excess of energy is transmitted to the crystal lattice in term of electron-phonon coupling.

(D) Finally the charges as the mass transport occurs, the surface of the metakaolin reduces and at region D, from 980ºC the heating curve decreases. At high temperature, the pre-spinel

687 phase is achieved and the atoms network is relaxed and dilated, the systems has higher amount

688 of vibration energy and the dipoles rotation is favored.