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Feasible glass-melting process assisted by microwaves.

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ABSTRACT

The advantages of microwave (MW) energy processing have been verified in the sintering of a ceramic frit at a pre-industrial scale. The challenge of achieving high temperature by using MW energy at such dimensions was overcome and a mix of natural raw materials was heated until its fluxing point. Changes in dielectric properties of the raw materials mix were also measured in situ with the increase of temperature, being in accordance to thermal processes of a conventional heating process. The properties of the resulting ceramic frit were compared with the same frit obtained by the conventional sintering method. Both frits showed similar thermal behaviour regarding DTA/Tg, heating microscopy and XRD (only glassy phase was present). A Raman study confirms the existence of the mentioned glass phase. The application of the frits as glazes were performed and their properties were studied. As a result, glazes with similar properties were obtained which confirms that the MW energy processed frit is suitable for its application as a ceramic glaze.

KEYWORDS

MW energy; Ceramic Frit; Ceramic glaze; CO_2 emissions;

1. INTRODUCTION

Microwave (MW) processing is characterized by the materials interaction with electromagnetic radiation [1], which allows fast heating rates and minimization of thermal gradients in the material. Microwaves and conventional sintering greatly differ since in conventional sintering heat flows from the

surface of the material to its interior by convection, conduction and radiation [2], meanwhile in MWs sintering heat is generated within the material core, where particles are more constrained than on the surface. MW radiation heats the material through molecular interactions with the electromagnetic field [3] giving rise to a volumetric heating. By MW heating the effects of the differential sintering are minimized, which supposes an advantage over conventional sintering method [4].

When a material is exposed to MW radiation different interaction effects may occur depending on the nature of the material. The ability of the materials to be heated by MW energy is defined by the material dielectric properties. The main parameters are the dielectric constant, which represents the material's capacity to be polarized by the electromagnetic field, and the loss factor, which represents the capacity to transform this energy into heat. In general, materials with low loss factor as quartz are poor absorbers of MW energy and are not suitable for MW heating, whereas materials with high loss factor such as SiC are excellent absorbers of MW energy and hence are strong candidates for MW heating.

In general, most of mineral raw materials possess low loss factor and MW heating is very difficult. In order to solve the poor MW absorption of raw materials for ceramic, the addition of susceptors is a possible solution. Susceptors are substances with higher loss factor [5]. In addition to having a high loss factor, the susceptor material requires maintaining the final ceramic composition, either by its burning during the heating process or by its incorporation to the material by solid state chemistry. An example of materials formed using susceptors are glasses. In this sense, glasses are heated by MW with previous application of MW absorbing coatings, or by hydration [6]. In the case of fast ion conducting glass compositions, prolonged exposure to MWs produce sparking on the surface of the glass melt [7]. This fact is probably related to the mentioned above mechanism of ionic conduction which allows the MW absorption. Experiments in melting, refining, reheating for forming, thermal toughening and surface ion exchange in glasses showed that the principal advantages of MWs are fast heating and a capability to heat hot areas of the glass selectively while leaving the cooler areas unaffected. However, control of the uniformity and rate of heating are the principal difficulties.

It is described that two main mechanisms are responsible for the heating by using MWs energy: dipole rotation and ionic conduction. Electrical dipoles of the materials rotate following the alternate electromagnetic field which leads to an increase of the vibrational energy of atoms in the material. In the case of ionic conduction, the mechanism is due to ions movement with the electromagnetic field [8]. These common accepted mechanisms however are not enough to predict the heating of a specific material under MW radiation. Especially in materials formed by a mix of many different components, the interaction between charges of the different components at increasing temperatures becomes very complex, and this may hinder the prediction and control of the MW heating process. At the same time, this complexity opens the door to mechanisms in which MW energy can couple with materials. Thus, it may be possible to process materials with new or unique microstructures by selectively heating distinct phases, avoiding the use of susceptors [9]. However large changes in the loss factor of the materials due to temperature changes may involve uncontrolled heating, over firing, deformation, melting, cracking, among other processes, making it very difficult to control the sintering process [10].

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This behaviour is expected for materials that develop large amounts of glassy phase during heating, such as porcelain based ceramics or glass-ceramics. For this reason, knowledge of dielectric properties of target materials as a function of temperature becomes essential for an effective control of the MW heating process. There is a lack of MW dielectric characterization of materials as a function of temperature. These data are a key point to use MW radiation in industrial ceramics, in particular for mineral raw materials.

Regarding the MW heating, the challenge of processing glassy materials made of different raw materials by using MW energy exists. In addition, the fact of industrial processing of glassy materials in large amounts supposes an attractive challenge because of the expected reduction of energy. An example of industries that could use MW in large quantities corresponds to ceramic frits for ceramic tiles decoration. Ceramic frits are vitreous products made industrially by mixing different mineral raw materials which are melted at high temperature (~1500ºC) and then the fluxing mixture is quenched [11], so mostly glassy material is obtained [12]. Due to the high number of raw materials that are part of a frit, the microwave heating process is not obvious due to the selectivity of electromagnetic radiation. The main mineralogical raw materials in glass production are quartz, feldspars or carbonates. These materials present different molecular structure so their behaviour regarding being heated by MW energy is also distinct [13]. Frits suppose the consumption of high amounts of raw materials corresponding to ~900k Tm [14,15] only in Spain (second worldwide frit producer) and high amount of fossil fuels (mainly gas) due to the high achieved temperatures for their processing which produce high amounts of CO_2 (650Kg/Tm taking into account CO_2 elimination from the composition and burned fuel) [16]. Hence, MW assisted sintering processes would be considered as energy-efficient alternative to conventional heating procedures in ceramic manufacturing. It is described that MWs energy application leads to a considerably reduction of the processing cycle-time for rapid and uniform heating, thus resulting in substantial energy and cost savings [17]. In addition, the energy saving by using MW is assumed that also will produce a drastic decrease of the CO_2 emissions from fossil fuels.

The aim of this work is to obtain frits from raw materials by applying MW energy in a scaling-up pre-industrial process and to apply it as a ceramic glaze in order to demonstrate its applicability. To the authors´ knowledge, this is the first time that a MW energy assisted synthesis for ceramic frit at a pre-industrial scale is achieved. The first energy consumption data reported on pilot MW experiments to produce frit are compared with the conventional gas melting furnaces under use in the sector. Moreover, the changes observed in the dielectric properties of the raw mix are for the first time correlated to thermal processes measured with other conventional analysis techniques. This gives valuable information for the understanding and control of the underlying processes under MW fields..

2. EXPERIMENTAL PROCEDURE

2.1 Frit processing

A standard commercial frit composition was chosen for the development of the work (Table I). The mineralogical composition of the frit and the main characteristics (chemical formula and main reaction that occurs with temperature) of raw materials which are part of the ceramic frit are showed in Table II. The temperature values for the thermal processes are related to a conventional heating process. Nevertheless, it is described [18] that under MW heating these temperatures are eventually lower for ceramics materials due the fast heating by MW effect.

The frit composition was homogenized by wet milling in porcelain jar with alumina balls during 20 min, oven dried and sieved through a 100 µm sieving. The homogeneous mixtures of the raw materials were thermally treated in different ways for comparison purposes between conventional and MW heating sources. Hence, frit was obtained in a laboratory MW prototype [19] in batch of ~2cm^3 of sample and in a pre-industrial MW process in batch of 10Kg/h. The scale up MW oven was designed to evaluate the MW energy consumption at the pre-industrial scale step (supplementary information 1). Table III summarizes the characteristics of each process.

- In MW laboratory equipment (thereafter LAB_frit) where the MW cell is a cylindrical cavity designed to operate simultaneously in two modes, one for heating and the other one for measuring in situ the dielectric properties of the sample. The heating mode TE_{111} 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, while the measuring mode TM_{010} is fed by another probe through the bottom wall of the cavity. The source for the incident signal of the heating mode is a Vector Network Analyzer (VNA) connected to an amplifier. The VNA delivers an output of 0 dBm (1 mW) and the gain of the amplifier is around 50 dB. The maximum power delivered to the cavity in this configuration is 150 W. A second VNA is used as a source for the measuring mode, with a cross-coupling filter to avoid interferences between the heating and the measuring signals.[19]
- In pre-industrial MW equipment (thereafter MW_frit) with capacity for achieving 10Kg/h which was designed for achieving the goals of H2020 European Daphne project.[20] A cylindrical cavity with an alumina tube was designed from the results in the MWs energy laboratory equipment. The raw materials inside the tube and funnel were moved with gravity. In order to have no convective losses in the interface between the material and the funnel the velocity field in that area must be tangent to the funnel walls. The heating mode resonated at 2.45GHz of frequency. The melt was quenched by falling into water.
- In a conventional industrial gas fuel continuous furnace (thereafter ST_frit). This frit was supplied by Keraben Company (Castellon, Spain).

2.2 Frit application

In order to study the properties of the different frits, ceramic glazes were formulated from the obtained frits and kaolin. Therefore, both materials were ball milled for 20 min in a porcelain jar with alumina balls using water as media. The solid content was 40 wt% of the total mass and the relative proportions of the main components of the glazes were, in weight %: 91 frit/9 kaolin. In addition,

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0.2wt% of TFP (sodium trypoliphosphate) was added as deflocculant and 0.2wt% of CMC (caboxymethylcellulose) for facilitating the glaze adhesion to the ceramic substrate. The additives were added in excess because they burn during the sintering process and do not contribute to the final composition. The formulated glazes were sprayed onto stoneware substrate. The tiles with the green glaze layer were dried at 90 °C and fast-fired in a conventional industrial furnace (Pirometrol) in a 55 min thermal cycle, applying a soaking temperature of 1200 °C for 5 min in air atmosphere. This sintering cycle corresponds to a standard industrial fast-firing process used in stoneware tiles production.

2.3 Characterization of frits and glazes.

Thermal characterization of the raw materials mixture and frit sample were studied by differential thermal analysis and thermogravimetry in air atmosphere at 10 °C/min (DTA–Tg, Setsys Evolution 1750 °C of SETARAM Instruments, France). Hot Stage Microscope (Axel Hesse Instruments, Germany), was carried out from RT to 1200 °C in air atmosphere with a heating rate of 10 °C/min on platinum substrate.

X-Ray Difracttion (XRD) was performed with Cu Kα radiation using a Siemens D500 Diffractometer in grazing angle (0.5°), the step time being 2 s with an increase of 0.02°. The Raman studies of the frits with the use of a confocal Raman coupled with an AFM were carried out (Witec alpha300R, Witec, Ulm, Germany). Raman spectra were obtained using a 532 nm excitation laser (green laser). Raman spectral resolution of the system is ca. 0.02 cm^{-1}. The microscope base was also equipped with active vibration isolation system, which is active in the range of 0.7–1000 Hz. Collected spectra were analysed by using Witec Control Plus Software (Witec, Ulm, Germany). Gloss and color of the samples were determined by using a Konica Minolta cd500 colorimeter in the CIELab coordinates space with the mirrored component excluded configuration.

3. RESULTS

3.1 Raw materials (mixed for frit) study

The thermal behaviour study of the homogenous mixing of raw materials forming the ceramic frit is represented in Figure 1 by Heating Microscopy, Differential Thermal Analysis and Termogravimetry. The thermal processes mentioned in Table I can be observed in DTA/Tg study (Figure 1a). From 338 to 417ºC it takes place the endothermic processes of loss of structural water of different species, in particular for the Colemanite. This process occurs at 399ºC.[21] The rapid water losses cause an expansion of the Colemanite crystals that develops of uneven stresses.[22] The increase in volume of ~30% is observed by heating microscopy curve of figure 1b. At 573ºC α-quartz transforms to β-quartz signalled by an endothermic peak which is reversible during the cooling of the sample. This process supposes a variation in volume of 0.45% but it is not observed by heating microscopy because the

sample was previously expanded due to the mentioned elimination of water from Colemanite. An endothermic signal in a wide range of temperature, from 695 to 834ºC, is assigned to different processes as the decomposition and elimination of carbonates from Colemanite and Dolomite and, to a lesser extent, the elimination of oxygen from the transformation of nitrates to nitrites.[23] All the mentioned processes mean mass losses which represent ~10wt% of the sample. Finally, a change of the heating flow curve from the temperature of 1065ºC is observed due to the mass transport into the sample. The decrease of the heat flow is interrupted by a crystallization process at 1092ºC, probably due to the formation of pyroxenes, as it were previously reported.[24] At higher temperatures, a sharp decrease in heating flow curve is noticed and the same tendencies are observed in heating microscopy curve (in detail in inset of figure 1b). Hence, shrinkage behaviour of the sample occurs from ~1065°C, after the glass softening temperature, which corresponds to viscous flow of the sample.

Some of the previously studied processes are also revealed in the frit composition from the dielectric characterization by changes in the dielectric constant and the loss factor versus the temperature (figure 2a). It is noticed that the thermal events take place at similar temperatures when the sample is heated by using MW energy and by conventional heating. The Colemanite dehydration produces a change in volume that is correlated with the dielectric properties variation from 399ºC. The carbonates decomposition takes place from 695ºC and generates changes in the dielectric behaviour of the sample. From 1092ºC a marked increase of the dielectric constant and loss factor could probably be associated to the mass transport into the material and accordingly to the heating microscopy curve to the melting process. In this case, the temperature at which the processes take place is similar to the one at which the same processes take place when conventional heating is applied.

The dielectric properties of the homogeneous mixture of the raw materials for the frit composition were also calculated for comparison taking into account the accumulative response of each individual component into the frit composition (supplementary information 2). The calculated loss factor curve (supplementary information 2j) differs from the measured one (figure 2a) so the accumulative curve from the loss factor values does not explain the heating of the sample by applying MW radiation, since the interactions between components are complex. However, some trends in the heating behaviour can be partially explained from the dielectric characterization of individual components. For example, it is described that materials with loss factor values higher that 0.1 present the capacity of being efficiently heated by MW radiation.[25] In the concrete scenario of the studied frit the following raw materials show high loss factor: zinc oxide, sodium feldspar and potassium nitrate (supplementary information 2f, 2g, 2i). Thus, these components are more easily heated by using MW radiation. Zinc oxide content in the frit is 7.2wt% and it presents an exponential increase of the dielectric constant, whereas sodium feldspar is only 1.3wt% and potassium nitrate participates as low as 0.9wt% and also presents strong changes of the dielectric properties. A correct dispersion in the sample of these raw materials which are able to absorb MW radiation will enhance the heating because it will promote the activation of reactions regarding to other raw materials which form part of the frit. For instance, potassium nitrate is soluble in water salt and this fact helps to its correct dispersion in the frit sample during wet milling and homogenising processes. Therefore, during the heating process by MW

radiation, a local increase of temperature which corresponds to these raw materials is expected and, as consequence, reactions of other surrounding raw material will occur.

The temperature of the mixture of raw materials for frit shows two temperatures in which a fast heating is produced (figure 2b) after ~220ºC and ~695ºC. These temperature raises imply a higher heating rate that is coincident with chemical reactions that are related to Tg curve. At 220ºC an increase of dielectric properties is in concordance with the increasing of the loss factor for potassium nitrate in figure 2c (similar behaviour it is also observed for dielectric constant), which is probably due to the beginning of the salt melting process. The mentioned increase of dielectric losses seems to be the reason of the quick heating of the frit sample from ~220ºC. In detail, the variation of temperature from 220ºC and the increase of the heating rate are observed in figure 2d. After 220ºC, also the dehydration of Colemanite occurs at 399ºC. Thus, the modification of the dielectric constant for the frit composition from ~399ºC is attributed to the dehydration of Colemanite which supposes a variation in the volume of the whole sample. At higher temperatures, ~600ºC, the heating rate slowed down. The α-quartz to β-quartz allotropic transformation is an endothermic process that implies heat consumption. The heating rate increases again when the elimination of carbonates occurs at >695ºC observed in (DTA/Tg study in figure 1), in spite that they are endothermic processes. This can be explained by the steep increase of the loss factor from 695ºC, which allows a higher absorption of the MW energy from this temperature.

Moreover, Figure 2b demonstrates that frit is heated by MW radiation up to ~1200ºC in only 10 minutes. The average heating rate is thus 120ºC/min that it is one order of magnitude higher than standard heating rate in the ATD-Tg experiment. The presented result indicated that higher heating rates occur when the decomposition of raw materials takes place in spite of their endothermic behaviour, as it happens for other ceramic materials. [26] A possible mechanism that explains the variations of the heating rate when MW radiation is applied on materials consists of the apparition of charge carrier after the removal of OH^- or CO_2 species in the raw materials [27]. The appearance of structural defects in the crystal structure promotes a phonon-electron coupling process after the interaction of MW radiation with the sample. Available charges carries are preferentially excited by the electromagnetic field at the MW frequency. The excited charge carrier heats the crystal lattice by the small polaron hopping conduction in which the charge carrier polarizes the cations of the crystal during their movement increasing their lattice vibration. The phonon effect is related to the vibration movement of the atoms network in a periodic and elastic arrangement. [28] Hence, the quantized lattice vibration waves provoke the heating of the material. At each decomposition reaction, the structural defects promote appearance of a limited density of charge carriers in the insulating particles. Such charge carriers promote the MW absorption. In this sense, the specific raw material that presents an increasing of the dielectric loss factor in addition to a structural change with decomposition, acts as MW susceptor and therefore heats locally the sample. In this sense, the temperature locally increases where the decomposition reactions occur in spite of the endothermic consumption of heat of such processes.

3.2 Comparative study of frits.

The MW produced frits at laboratory (LAB_frit) and pre-industrial (MW_frit) equipments are compared with an industrial frit (STD_frit) produced in gas melting furnace (supplementary information 3). Differences in the physical appearance (figure S3) between the studied frits are attributed to the volume of frit and the freeze cooling in the used furnaces.

A comparative study of the physical and thermal properties of the frits was performed. Regarding the crystalline phases in frits, XRD patterns show a characteristic glassy halo and absence of crystallizations in the industrial frit (STD_frit), in figure 3a. The frit obtained by the laboratory equipment (LAB_frit) presents quartz and cristobalite as crystalline phases in addition to the halo corresponding to the glassy phase, figure 3a. The cristobalite/quartz/glassy phase ratio is ca. 0.9 / 4.4 / 94.7, according to qualitative analysis of the XRD peaks areas. The presence of quartz corresponds to raw material relics due the short residence time of the composition at high temperature. The presence of quartz or cristobalite in low amounts should not originate relevant defects during the sintering process. Anyway, frit obtained by MW in the pre-industrial demonstrator (MW_frit) only present the glassy halo free of crystalline phases, in agreement with a longer residence time of the composition in the melting state.

A Raman study was performed in order to obtain more information about the structural-microstructural nature of the frits (figure 3b). An optical micrograph of a representative frit particle is shown in addition of the Raman image of a selected region for each frit, Figure 3d. The particles of LAB_frit shows in addition of pure frit particle different small particles irregular in shaped in the surface and inside the frit particle. On the contrary, in the particles of the MW-frit and STD_frit a complex glass fracture is observe accordingly with the freeze cooling process of the glass. The presence of Wallner lines (rib shaped marks) is indicative that a surface or internal flaw is present prior to the failure event. Meanwhile twisted Hackle marks and mirror regions are indicatives of tensile stress. [29] The identified phases by Raman Spectroscopy are represented with blue color for quartz and green for the glassy phase and the obtained spectra are shown in figure 3c. The Raman active modes of quartz are $4A_1$ (single asymmetry) and 9E (double asymmetry) and correspond to the oxygen vibrations in the SiO_4 network.[30] The glassy phase is also characterized by Raman Spectroscopy having high fluorescence signal because of their non- crystalline structure. In fused silica, the Raman mode corresponding to bending vibration in the isolated SiO_4 tetrahedron presents a similar Raman shift than in the case of quartz but it is much broader.[31] Therefore, two well different areas are observed in Raman spectra for the glassy phase corresponding to the polymerization vibrations ($400cm^{-1} < \upsilon < 800cm^{-1}$) and the structural groups as silica tetrahedrons ($800cm^{-1} < \upsilon < 1200cm^{-1}$) [32] whose Raman shift depends on the number of non-bridging oxygen atoms. These phases are observed by Raman Spectroscopy in LAB_frit as XRD study shows. Cristobalite is not easily found in Raman imaging due its low presence in the sample. Similar Raman study is performed for STD_frit and MW_frit. In these cases, only the glassy phase is detected by Raman Spectroscopy, according to XRD

study. Accordingly with the structural and morphological analysis, the frit obtained in the pre-industrial MW furnace is similar to the standard frit. Thereafter the following analysis will only consider the MW_frit in comparison with the STD_frit.

Regarding the DTA/Tg study of MW_frit and STD_frit (Figure 4a), no significant mass loss or increase is registered in the studied range of temperatures for both of them. The glass transition step (675ºC), crystallization process (960-940ºC) and melting point (1098-1108ºC, which is represented by the inversion of the heat-flow curve) take place at similar temperatures for both frits, MW_frit and STD_frit. A small difference of temperature is presented at the crystallization point and slight differences in the signal shape are observed, but this effect is not significant because the amount of crystallizations in this kind of glasses is low, as it was observed by XRD. In both cases, a change in the thermogravimetric curve occurs at high temperature (1165-1175ºC) due to the volatilization of different components, mainly alkaline and alkali-earth compounds after the fluxing point.

The processes observed by heating microscopy (Figure 4b) are also in concordance with the reactions studied by differential thermal analysis. The shrinkage of the samples starts with the softening after the glass transition step, and in the case of MW_frit it needs higher temperature for the shrinkage. The melting point provokes the slowdown of the shrinkage, which means an expansion process, because the received energy is used by the sample for melting.

3.3 <u>Frit application: Glaze study</u>

The frit application as ceramic glaze is followed for MW_frit and STD_frit. The results for the different validation tests are shown in Figure 5. No differences between the mentioned glazes are observed in Figure 5a. Taking into account the relevance of the parameters as colour, luminosity and brightness of ceramic glazes, a colorimetric study is realized by using CIElab coordinates, Table IV and Supplementary Information 4. The base colour for the assay (centre of the CIELab coordinates in Supplementary Information 4) corresponds to sintered stoneware without glaze. The two points in the **Δa-Δb** diagram correspond to the glaze formulations made of STD_frit and MW_frit samples, which were deposited over stoneware substrates. It is worthy to mention that a glaze which is used as base in ceramic tiles should be as whiter as possible because it helps to improve the colour yield of the pigments which are deposited over it. Anyway, in this case the composition of the frit corresponds to a glossy frit, so gloss is also looked for because it improves the characteristics of the final bright glaze. In the case of **ΔL** coordinate (whiteness), the behaviour is similar. In the case of **a** and **b** CIElab coordinates, the difference between the values is lower than 3 units, which is the value from which a usual human eye can detect colour differences. In the case of gloss measurements, similar values are obtained for the different samples. Regarding the hardener of the glazes, both samples are scratched by Orthoclase, which means a value for Mosh hardness of 5. Water contact angle is influenced by the outer microstructure of the glaze, due to the apparition or unmelted crystallizations and the glass surface roughness. Again, the studied glazes show a difference of only 3º of this factor which does not represent a significant difference for the behaviour of the surface versus water. Therefore, the similar

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values of the characterization of the glazes demonstrate that the sintered frit in a pre-industrial MWs energy was validated for its final application.

3.4 <u>Microwave advantage: Saving energy consumption</u>

Part of the attraction of MW furnaces consists of decreasing the required processing time and therefore saving energy because of the time reduction for application of energy, as it was demonstrated for processes as drying.[33] It is reported that both, time and energy, have a relation; initially, the amount of energy for starting the thermal processes is higher in the case of MW processing, but once that the reaction is activated, the transformations that take place lead themselves to a steep increase of the temperature that reduces drastically the processing time. So the energy saving comes from the reduction of energy application for long time in a continuous way.

The total energy consumption for producing one kilogram of frit is calculated taking into account the batch preparation (weighting, dry mixing and conveying to the furnace), the melting process and the quenching step. Electricity is necessary in all stages of the process in addition to the use of gas. In a conventional gas furnace for frit the average consumption corresponds to 0.04kWh/Kg of electricity and 2.33kWh/Kg of gas fuel. Regarding frit fabrication by using MW radiation in the pre-industrial prototype, only electricity in required and the measured consumption is 0.78kWh/Kg. Thus, per kilogram of frit the required amount of energy is ~65% lower in the case of MW energy (see table V). This value is in concordance with the previously reported for drying processes by MW energy.[34] Moreover, MW pre-industrial prototype is not totally optimized in terms of thermal insulation that is supposed to contribute to the expected saving in energy consumption respecting the conventional industrial furnace for the future scale-up MW furnaces.

In the case of CO_2 emissions, European Community indicates that 1 KWh of electrical consumption generates 0.65Kg of CO_2, and for natural gas the value is 0.21Kg.[35] In addition, frit composition generates CO_2 during the heating because of carbonates (dolomite in this case) decomposition, but this amount is only 0.002 Kg per 1Kg of frit. The mayor CO_2 generation in a standard industrial glass melting furnace corresponds to burned gas. The calculation shows that the total CO_2 amount that is directly generated in the frit melting process is low in the case of MW application because there is not gas in the process, only electricity. This represents a big advantage for ceramic industry because they are subdued to strict controls of emissions and the use of MW furnaces could provide a key tool for the reduction of CO_2 emissions. Nevertheless, in the case of Spain, the total amount of CO_2 for Kg of frit would be similar in both technologies because of the high ratio of non-renewable sources that take part of the energy production system. It is expected that future progress in the incorporation of renewable sources for the production of energy will contribute greatly to the reduction of the CO_2 and thereafter the frit production from MW furnaces will contribute effectively to decrease both the energy cost and the emissions.

To sum up, the data in table V show that it is possible to achieve high temperature processes by using a green energy solution as MW. Gas fuel is a non-renewable source whereas electricity for industrial

heating processes through the use of MW can be obtained from a variety of renewable sources as sun or wind. So the fact to demonstrate the possibility of achieving high temperature process by using MW radiation opens opportunities in the field of MW application. Also, new material properties could be pursued due to the different kinetic process that takes place due to the fast increase of temperature. Additionally, MW furnaces could introduce unexpected flexibility in processing that is not available for the today gas furnaces because of their thermal inertia.

4. CONCLUSIONS

A mix of raw materials is effectively melted by using MW energy in order to obtain a ceramic frit for glazes in a pre-industrial MW furnace prototype. The resulting frits are compared with the standard industrial frit obtained from the same composition by using gas fuel for heating. The study of the evolution of the dielectric parameters of the raw materials mix during heating at the MW laboratory equipment allows determining the main contributions to the effective heating that are correlated with MW absorption after the decomposition of the raw materials. The MW laboratory equipment has a limitation in the residence of the melt at higher temperatures that impedes the complete melting of raw materials. The scale up of the MW furnace to a pre-industrial one permits to completely melt the mixture of raw materials and produces a frit similar to the conventional industrially produced material. Finally, glazes made with the frits from conventional and MW technologies present equivalent ceramic properties in terms of color, gloss and hardness, which validate the MW heating process. The MW furnace provides a relevant decreasing in energy consumption determined as ~65% of energy saved. The main contribution to the energy saving comes from the reduction of time required for the process. In this sense, the MW heating technology represents a step further in the sustainability of the mass intensive sector of the ceramic frit and opens opportunities to go forward towards the reduction of energy requirement and gas emissions.

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TABLES

Table I: Chemical frit composition expressed in terms of their equivalent oxides.

Component	Frit
SiO_2	60,00%
Al_2O_3	6,70%
B_2O_3	2,80%
Fe_2O_3	0,14%
CaO	15,40%
MgO	1,20%
Na_2O	0,47%
K_2O	3,70%
ZnO	8,9

Table II: Raw materials frit composition and the main thermal behaviour of the components.

Raw material	Formula	wt% in frit	Process T	Thermal behaviour
Colemanite	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$	4.3	350-400ºC	Dehydration
Potassium Nitrate	KNO_3	0.9	375ºC T>650ºC T>800ºC	Melting Transformation to nitrite Dissociation into NO and K_2O
Quartz	SiO_2	22.7	575ºC	Allotropic transformation
Dolomite	$MgCa(CO_3)_2$	3.2	~800 and ~930ºC	Decarbonation
Calcium Carbonate	$CaCO_3$	20.6	~840ºC	Decarbonation
Feldspar Sand	$SiO_2 \cdot Al_2O_3 \cdot K_2O$	22.1	-	-
Potassium Feldspar	$KAlSi_3O_8$	15.7	-	-
Zinc Oxide	ZnO	7.2	-	-
Calcined Alumina	Al_2O_3	2.0	-	-
Sodium Feldspar	$NaAlSi_3O_8$	1.3	-	-

*Table III: Characteristics of the three different processes for achieving frits (*MWs at frequency=2.45GHz).*

Process	Capacity	Time	Heating energy	Reaction cavity
MW laboratory equipment (LAB_frit)	1.0 g/assay	>10 min	MW from electricity	Quartz tube
Designed MW pre-industrial equipment (MW_frit)	10 Kg/h	~40 s	MW from electricity	Alumina tube
Conventional industrial gas furnace (STD_frit)	1250 Kg/h	~3600 s	Gas	$Al_2O_3 – ZrO_2$ refractory

Table IV: Comparative characterization values for glazes made of STD_frit and MW_frit.

Characterization		STD_frit	MW_frit
Colorimetry	Δa	-0.33	-0.41
	Δb	0.39	0.31
	ΔL	5.2	5.1
Gloss units		99	102
Mosh Hardness		5	5
Water contact angle		32º	35º

Table V. Comparison of energy consumption and gas emission between the conventional gas furnace and MWs pre-industrial furnace energy for the production of frit.

Frit	Process scale	Process Time	Energy consumption (KWh/Kg frit)			CO_2 emission (Kg/Kg grit)	
			Electricity	Gas fuel	Total energy	Directly generated	Total generated
STD_frit	Industrial fluxing furnace	~60 minutes	0.04	2.33	2.37	0.52 + 0.002*	0.52
MW_frit	Pre-industrial prototype	40 seconds	0.04 + 0.78	0	0.82	0.002*	0.53

*CO_2 generated by the decomposition of dolomite**

FIGURE CAPTIONS

Figure 1: Thermal behaviour of the frit composition sample. a) DTA/Tg study. b) Heating Microscopy study.

Figure 2: a) Dielectric properties of the homogenous mixture of raw materials with frit composition when is heated by using MW energy. b) Temperature behaviour of frit composition sample with applied time under MW energy (heating time) and their heating rate. c) Detail of the dielectric losses in the range 170-280ºC. d) Detail region of the heating curve in which higher heating rate are observed 100>T>600ºC.

Figure 3: a) XRD of the obtained frits. b) Optical micrograph of a representative frit particle and the Raman image of a corresponding marked square in which green color signalled the glassy phase and blue color signalled the quartz phase. Raman image shows color intensity accordingly with intensity of the main Raman peak. c) Average Raman Spectra of the main components found in the Raman Spectrocopy analysis.

Figure 4: STD_frit and MW_frit characterization.   a) DTA/Tg study. b) Heating Microscopy study.

Figure 5. Glazes made of STD_frit and MW_frit and applied as spry-drying.