SYNTHESIS OF $Ni_{(x)}$ $Zn_{(1-X)}$ Fe_2O_4 TYPE FERRITES BY MICROWAVE DECOMPOSITION OF HYDROTALCITES FOR THE FUNCTIONALISATION OF PORCELAIN SUBSTRATES

A. Lahlahi Attalhaoui, I. Nebot-Diaz, M. Oset, J.G. Paulo

Escuela Superior de Cerámica de l'Alcora – ISEACV (Castellón) Spain
(Group of ceramic materials for new technologies)

ABSTRACT

This project describes the development of a ceramic substrate for use in electromagnetic induction plates, which are traditionally made of glass-ceramic material. The glass-ceramic materials used for this type of application are mainly characterised by their high resistance to thermal shock and their high magnetic permeability indexes, which prevent or minimise shielding of the magnetic field.

In order to develop such a ceramic material with the magnetic, thermal and mechanical properties required for induction heating technology, a porcelain stoneware composition was doped with mixed ferrites of Ni-Zn. These ferrites are characterised by their low coercivity coefficients, which encourages flow of a high-frequency magnetic field. The ferrites were prepared by different synthesis routes and even ferrite nanoparticles were produced without the need to resort to highly energy-intensive milling processes.

Including ferrites in a porcelain stoneware composition generates magnetisation, creating eddy currents that heat the entire mass of the substrate very uniformly by the Joule effect. This leads to a reduced temperature gradient inside the workpiece, unlike compositions with no ferrites, in which heating is by direct conduction.

By reducing the temperature gradient in the workpiece, it is possible to reduce the difference in internal stresses between the top and bottom of the plate, which is the main cause of thermal shock fracture.

In addition to thermal shock, other essential properties in this type of materials, such as magnetic permeability and mechanical strength, were also improved. The last section of the project was dedicated to studying the potential variables that affect viability in industrial production (dilatometric, thermal and mechanical studies, etc.).

1. AIM

The aim of this project was to research the functionalisation of porcelain stoneware substrates. Such research revolves around the objective of synthesising ferrites suitable for high induction frequencies. These ferrites will provide porcelain stoneware compositions with the properties required for them to be used as induction heating plates (resistance to thermal shock, high magnetic permeability, mechanical strength, etc.).

2. STATE OF THE ART AND JUSTIFICATION

Heating plates are made of a glass-ceramic material, usually lithium aluminium silicates (LAS). This is mainly because LAS have high resistance to thermal shock, as thermal expansion is close to zero given the arrangement of their crystals.

The problem of conventional vitrified materials such as porcelain is found in the stresses that are created in the ceramic body when temperature gradients exist in the workpiece. These stresses generate micro-cracks that eventually lead to fractures [(1)] [(2)].

Over the last decade, numerous attempts have been made to solve this problem of thermal shock in ceramic induction hobs. For example, a number of the patents registered on this subject are ES 2 455 442 A1 (2014), [(1)] US 20170006668A1 (2017) [(2)], or ES 1 228 326 U (2019) [(3)], which all focus on mechanical treatment of the ceramic piece (holes, different thicknesses, vessel insulation, etc.)

3. THEORETICAL BASIS

An induction heating system operates by connecting a coil to an electrical net supplying an alternating current of 50-60 Hz, which is then amplified to between 20 and 60 kHz, thus generating a magnetic field.

This magnetic field must pass through the ceramic plate and reach the base of the ferromagnetic vessel, in which the alternating, high-frequency electric field is induced.

If a secondary winding, instead of a vessel, is fitted, the artefact would then be basically an electrical transformer. However, in induction plates, the secondary coil is replaced by a vessel made of a ferromagnetic material with low electrical conductivity. In the absence of a flowing current, eddy currents are created in the vessel, which are responsible for heating the vessel due to the Joule effect. Heating is also produced by other sources, namely the film effect and the magnetic hysteresis cycle (4).

Magnetising the ceramic plate is intended to improve thermal shock by inducing eddy currents in the actual ceramic. That way, the thermal gradient is reduced and with it the stresses in the workpiece.

The ferrimagnetic material used to dope a porcelain composition is a mixed ferrite of Ni-Zn. Ferrites of this type are soft with a spinel-like cubic structure $(M)[B_2]X_4$. These crystals are characterised by their low coercivity coefficient and high magnetic susceptibility, i.e., they have narrow hysteresis cycles. This means that they can be easily magnetised and demagnetised, making them very suitable for high working frequencies (20-70 kHz), as is the case with induction hobs. That is why this type of material, which prevents magnetic field shielding, was chosen. Such shielding would occur if hard hexagonal ferrites of the magnetoplumbite type (7) were used.

The zinc ferrite $(Zn)[Fe_2]O_4$ has a normal spinel-like structure where the Zn^{2+} ions are located in the tetrahedral cavities, while the Fe^{3+} ions are located in the octahedral areas.

Such a structure means, on the one hand, that the spines of the Fe^{3+} ions have an anti-parallel orientation, thus overriding the magnetic moments.

On the other hand, the nickel ferrite $(Ni)[Fe_2]O_4$ has a (partially) inverted spinel structure. The Fe^{3+} ions are distributed between the octahedral and tetrahedral cavities, which generates a charge compensation in the Fe^{3+} ions. The resulting magnetism originates in the Ni^{2+} ions, which have 2 unpaired electrons in their d layer, to produce $[t_2g^6\ eg^2]$ as their electronic field configuration (8).

The inversion of the ferrite structure leads to stronger magnetism, switching from paramagnetic behaviour in normal spinel-type ferrites to ferrimagnetic behaviour in inverse spinel ferrites.

To further reinforce the ferrite's magnetism, the $(Ni)[Fe_2]O_4$ structure is doped with other ions. Ni^{2+} ions could be replaced with Zn^{2+} ions in order to force an inverse spinel with the formula $Zn_{(8-x)}\ Ni_{(x)}Fe_{16}\ O_{32}$. When x=8, the ferrite is nickel-exclusive and if x=0, it is zinc-exclusive, and all values in between are mixed spinels (9).

4. EXPERIMENTAL PROCESS

The first decision was to undertake research to ascertain the ferrite with the best magnetic permeabilities.

Mixed Ni-Zn ferrites were synthesised according to the following equation:

$$Zn_{(1-x)}\,Ni_{(x)}Fe_2\,O_4$$

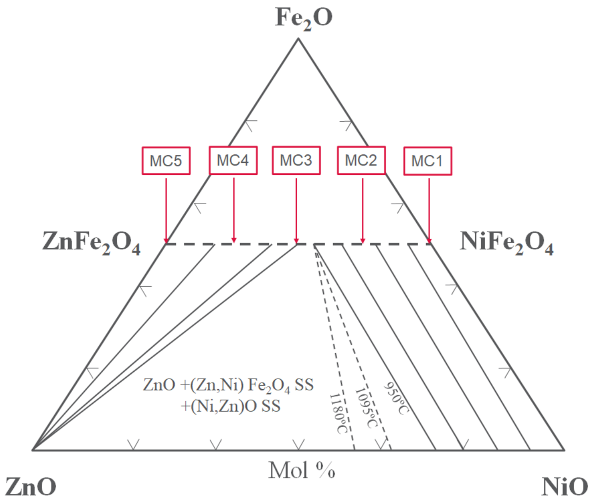


Figure 1*Ternary diagram of Fe-Ni-Zn. (Nickel spinel ferrites: A review, 2020)*

The research involved implementing what are known as solid-state solubility studies. On the one hand, it aims to synthesise exclusive Ni and Zn ferrites (respectively, MC1 and MC5) separately, and on the other hand, to include three variations, with x set at 0.625, 0.5 and 0.375 (MC2, MC3 and MC4 respectively).

This first stage - synthesis – was performed by employing a ceramic method, since earlier magnetic permeability studies show that considerable amounts of material are required to form different workpieces.

To perform magnetic permeability measurements, a test directly proportional to magnetic permeability was carried out. The temperature that 900 mL of water reach in 140 seconds was measured.

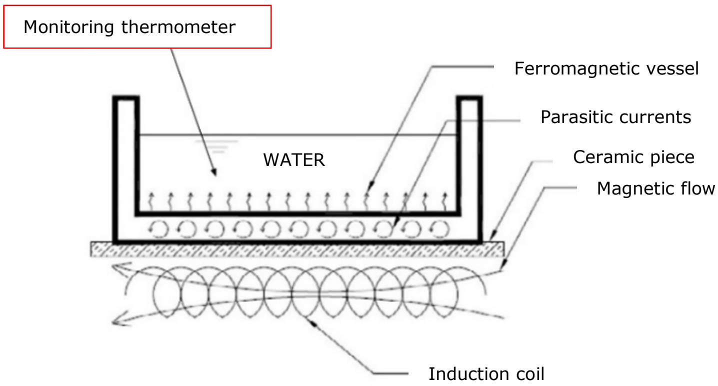


***Figure 2**. Magnetic permeability measurement diagram*

Heating speed is conditioned by the ceramic material's resistance to the passage of the magnetic field, so that the greater the slope on the heating curve, the greater the magnetic permeability.

As mentioned earlier, there exist a multitude of tests to assess resistance to thermal shock, but none of them reproduces the stress to which a ceramic piece is subjected in induction plates. Consequently, a test was designed to reproduce as reliably as possible such sudden and localised heating on a single face.

The test was made by placing a magnetic porcelain piece and an empty vessel, whose temperatures are around 350 ºC, on an induction coil.

The temperature reached by a magnetic vessel causes high thermal gradients in the ceramic piece. To quantify the piece's resistance to thermal shock, it was inspected for breaks or cracks. In addition, to demonstrate the thermal gradient, a type-K thermocouple was fitted on the upper face of the piece in contact with the vessel, and at the same time another one was fitted underneath.

Once the magnetic permeability and thermal shock results were available, the next step was to optimise synthesis of the resulting magnetic materials. A phase forming study was carried out to see how the phases develop in view of different process variables: calcination equipment (kiln or microwave), calcination temperature and duration, and synthesis route (ceramic method or hydrotalcite co-precipitation).

Synthesising hydrotalcites is based on the controlled precipitation of metals within a given structure, which in this case is shown in the following formula, whose molecular weight is 111.63 g/mol:

$$[Ni_{0.208}\,Zn_{0.125}\,Fe_{0.667}\,(OH)_2]\ (CO_3)_{0.335}$$

The pH range to achieve simultaneous precipitation of all three metals at concentrations of 0.5M is given by Zn, which has the narrowest range, namely between pH 7 and 12; nevertheless, our work was performed at pH 8-9, to avoid partial precipitation due to possible fluctuations in pH.

5. ANALYSIS OF RESULTS

5.1. MAGNETIC PERMEABILITY

Clear differences were found when measuring the heating rate of 900 mL of water. The porcelain pieces were 15% doped with the various synthesised ferrites.

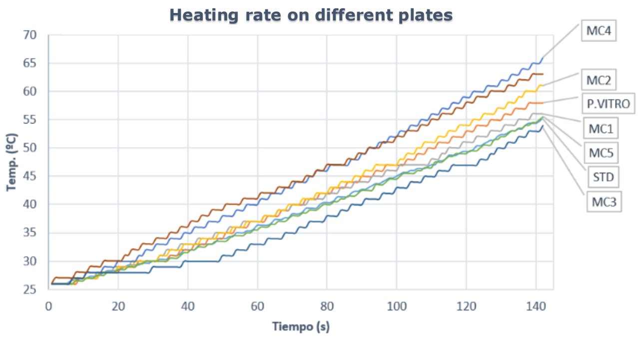
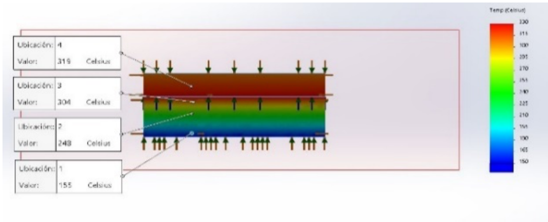
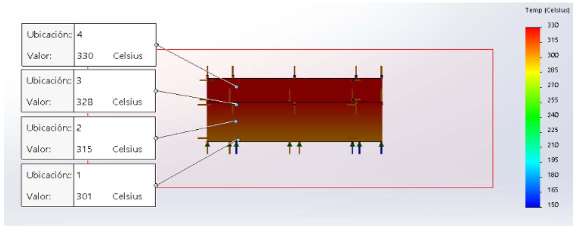
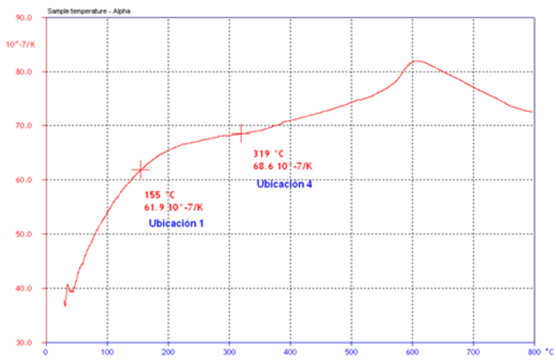
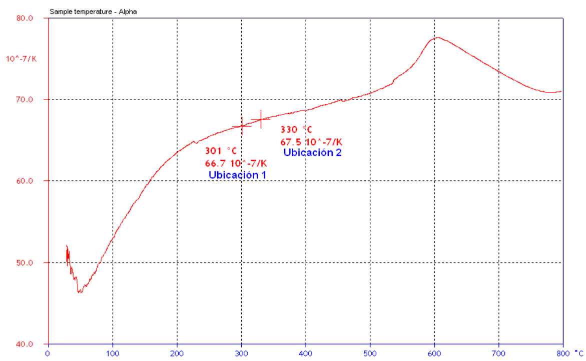


Figure 3. *Heating rate with different materials as substrate.*

The best results were obtained when the porcelain plate was doped with $Ni_{0.625}Zn_{0.375}Fe_2O_4$ (MC4) ferrite, as was to be expected, given the magnetic strengthening that occurs. The results with the glass-ceramic plate and the conventional porcelain were lower than with magnetic porcelain.

5.2. THERMAL SHOCK

The thermal difference between the upper face in contact with the vessel and the lower face was measured. The thermal gradient created in the conventional porcelain body was observed together with the significant difference in the coefficient of thermal expansion (CTE) that exists at the same point in the sample piece. In the case of non-conventional porcelain, such thermal gradients are minimised, and it is possible to prevent the piece from fracturing.

Conventional porcelain	Non-onventional porcelain
	
 Δ**CDE** = 7 $\cdot 10^{-7}$ ºC^{-1}	 Δ**CDE** = 0,8 $\cdot 10^{-7}$ ºC^{-1}

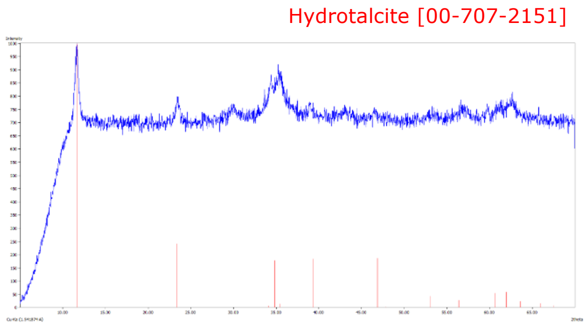
	Cycles									
% MC4	1	2	3	4	5	6	7	8	9	10
15	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
10	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
5	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
2	OK	OK	OK	OK	OK	---	---	---	---	---
1	OK	OK	---	---	---	---	---	---	---	---
0	OK	OK	---	---	---	---	---	---	---	---

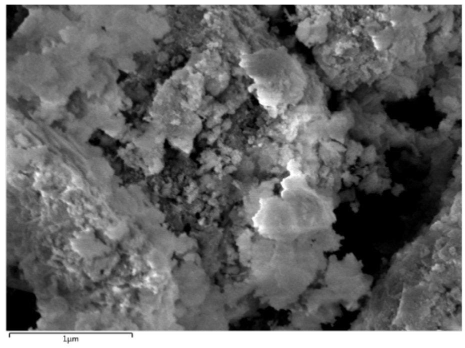
The table below shows data of stress cycles subjected on the porcelain by varying the percentage of MC4 ferrite. One can see that greater resistance to thermal shock is already perceived from 5% onwards.

5.3. PHASE FORMATION STUDIES

a. HYDROTALCITE PHASE

Using X-ray diffraction (XRD) tests, we were able to confirm that a hydrotalcite of Ni, Zn and Fe was indeed synthesised as expected. The peaks obtained matched those in the theoretical hydrotalcite, although it is true that there was a lot of background noise, possibly caused by the nanometre size of the particles.





b. FERRITE PHASE

In the diffractograms of the calcined samples, a single-phase formation of mixed nickel-zinc ferrite was observed in all samples. As for the peaks, it should be noted that they were narrow with high intensities. That means that the crystals are well-defined, as was to be seen in subsequent scanning electron microscopies (SEMs).

In the samples synthesised by the ceramic method, a further corundum (Al_2O_3) phase, in addition to ferrite, was seen to appear. This corundum phase was due to contaminations from the grinding media used to reduce particle size. No secondary phases appeared in the non-conventional synthesis, as there was no need to reduce particle size.

The following diffractograms show calcining at 1000ºC for 30 minutes in a muffle kiln. The ceramic route is on the right and hydrotalcite synthesis on the left.

Peak intensities are higher in the case of non-conventional synthesis. This is mainly due to the use of particles of nanometric sizes, as was observed in hydrotalcite microscopy.

The best results in non-conventional synthesis (hydrotalcites) were achieved by calcination in a muffle kiln at a temperature of 1200ºC (maximum temperature) for 30 minutes. In regard to crystal morphology, the best results were not those with the greatest intensity, as was to be seen using electron microscopy.

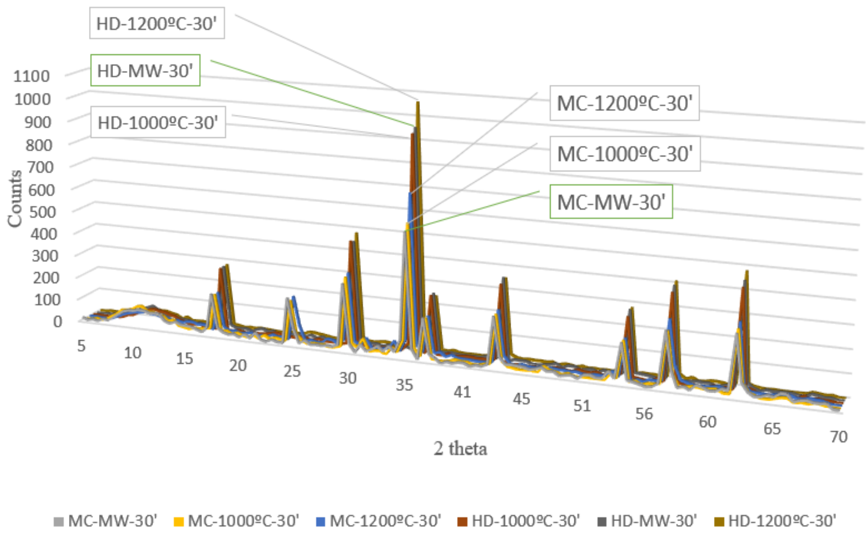


Figure 4*. Diffractograms of the samples calcined in a muffle kiln (30 min), in a kiln (1000 and 1200ºC), and in MW (microwave). Samples synthesised by the ceramic method (MC) and by hydrotalcites (HDTC). Source: authors*

The formation of large and compact crystalline aggregates was seen in the ceramic route. The size of each crystal was greater than 200 nm and the aggregate was also much larger.

In synthesis using the non-conventional method, the size of the crystals was nanometric – less than 200 nm. The findings showed very narrow particle size distributions as well as great morphological homogeneity among the particles. Also significant was the absence of crystalline aggregates, unlike in the ceramic route.

When calcination temperature was increased to 1200ºC for 30 minutes, the grains were seen to be bigger compared to calcination at 1000ºC. This larger size implies higher intensities in the diffractograms, since the crystal is bigger and, therefore, so is the diffraction.

As far as particle size is concerned, although grain growth occurred, it was still lower in the sample synthesised by the non-conventional route.

In the non-conventionally synthesised sample, it was significant that the aggregates formed were easy to disintegrate, because a compact vitreous phase had not been formed. That did not occur with the ferrite samples synthesised by conventional means. Although particle sizes of less than 1 µm were found, the crystalline aggregates that formed were larger and also extremely compact and difficult to break up, as was later confirmed during the grinding process.

Undoubtedly, the best results in terms of crystal morphology and particle size were those obtained by microwave-calcined hydrotalcites. Particle size distribution was seen to be very narrow. Particle sizes were less than 100 nm, a far cry from the results obtained by the ceramic method, where crystal size was much larger, as can be seen in the photos below, taken at 31,000x magnification.

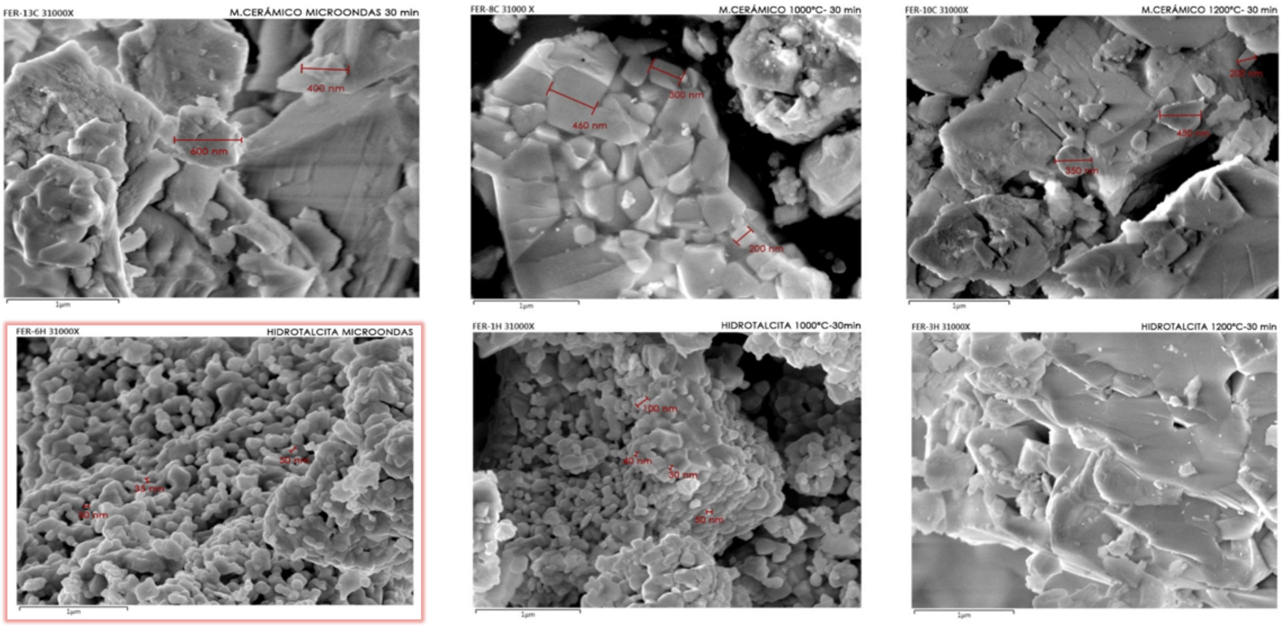


***Figure 5**. SEM image collection*

6. CONCLUSIONS

In conclusion to this paper, it should be remembered that the main objective was to undertake research to synthesise ferrites suitable for high-induction frequencies that would give porcelain stoneware compositions the properties required for induction applications. This objective has been met, as the previous section on Results proves.

Having completed the experimental process, a series of conclusions can be drawn from the results obtained:

- The functionalisation of an already well-known product, as is porcelain stoneware, has been achieved.
- Ceramic destined for kitchen worktops has gained value, as it now becomes an element to use in a common household appliance, as is the induction hob.
- Resistance to thermal shock and permeability of the magnetic field have been improved, which are the two major issues of concern in the literature dealing with ceramic induction plates that we reviewed.
- This research also confirms that the magnetic field is strengthened or shielded depending on the type of ferrite, and for that reason, the second goal of this work was to focus on a specific ferrite that reinforces it.
- In ferrite synthesis using the ceramic route, energy costs to adapt particle size are seen to be excessive compared to non-conventional synthesis that does not call for particle grinding.
- With non-conventional ferrite synthesis based on the decomposition of hydrotalcites, nanometric particle sizes can be achieved without any need for grinding.
- Our crystallographic characterisation of the synthesised ferrites showed that better defined crystallization is obtained using the non-conventional route.
- The use of microwaves for the calcination of hydrotalcites produces a narrow distribution range of sizes, an absence of crystal aggregates, and high and narrow diffraction peaks, which suggest better and greater crystal formation. This is largely thanks to the high heating speeds used.
- The viability and properties of this material have been demonstrated in theory, at the laboratory scale.

7. REFERENCES

[1] Universitat de Barcelona. Materials . Vitrocerámica. [En línea] Grup d'Innovació per la Millora de la Docència en Estructura, Propietats i Processat de Materials (GIMDEPPM). http://www.ub.edu/cmematerials/es/content/vitrocer%C3%A1mica.

[2] Álvarez Paucar, Carlos Guillermo. Vitrocerámicos con bajo coeficiente de expansión térmica. Madrid : UNIVERSIDAD AUTÓNOMA DE MADRID, 2016.

[3] Barbero González, Alberto Eugenio. Sistema de cocinado que permite cocinar directamente sobre la encimera. ES 2 455 442 A1 España (Madrid), 15 de Abril de 2014.

[4] Sergey Nikolenko, Denver,. Cooking appliance. US20170006668A1 USA, 5 de Enero de 2017.

[5] Aztiria Goenaga, Aiser. Encimera cerámica de cocción. ES 1 228 326 U España - AZPEITIA, 22 de Marzo de 2019.

[6] Álvarez García, Jose Antonio. Así funciona. Así funciona la cocina de inducción. [En línea] Febrero de 2016. [Citado el: 21 de 02 de 2021.] http://www.asifunciona.com/electrotecnia/af_cocina/af_cocina_induccion_2.htm.

[7] Gutiérrez, Verónica Balnco. Propiedades magnéticas de nanopartículas de ferritas MFe2O4. Madrid : Tesis doctoral Universidad Complutense de Madrid, 2011.

[8] Nikel spinel ferrites: A review. Journal of Magnetism and Magnetic Materials (MMM). s.l. : Elserver, 2020.

[9] Nebot Diaz, Isaac. Estudio y caracterización de compuestos tipo espinela mediante rutas de síntesis no convencionales. Castellón : s.n., 2001.

[10] Van der Zaag, PJ. Ferrites. Philips Research Laboratories. Eindhoven : Elsevier, 2016.