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Study of magnetic properties of NiZnCu ferrite synthesized by Pechini method and solid-state reactions

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Ni-Zn-Cu ferrites are exhibiting excellent magnetic properties at large frequencies and are consequently produced as low-loss magnetic materials used for magnetic components in power electronics. Here we present an experimental study of $(\text{Ni}_{0.31}\text{Zn}_{0.49}\text{Cu}_{0.20})_{0.979}\text{Co}_{0.021}\text{Fe}_{1.9-d}\text{O}_4$ ferrites synthesized by the Pechini type sol-gel method. Their structural and magnetic properties are characterized and compared to the ones of reference ferrites synthesized by classical solid-state reactions. Optimized parameters for Pechini method allow obtaining comparable low magnetic core-losses for both synthesis methods. The cores obtained by this sol-gel method present higher static permeability and lower coercive field than the ones obtained by classical solid-state reactions. Results suggest that the microstructure of ferrites synthesized by Pechini method can be considered as a promising alternative route for the design of low-loss magnetic components. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.4994035>

I. INTRODUCTION

Ni-Zn or Ni-Zn-Cu ferrites are exhibiting excellent magnetic properties at high frequencies above 1 MHz. They are consequently produced as low-loss magnetic materials for inductors for power converters. The magnetic properties of these ferrites are related to their composition and microstructure. The addition of cobalt in Ni-Zn or Ni-Zn-Cu ferrite is significant and lead to the reduction of magnetic core-loss at high frequency. The presence of cobalt changes the average magneto-crystalline anisotropy of the ferrite. Indeed, the constant of anisotropy K_1 is about $+300\text{kJ}\cdot\text{m}^{-3}$ for cobalt ferrite and $-1\text{kJ}\cdot\text{m}^{-3}$ for $\text{Ni}_{0.35}\text{Zn}_{0.65}\text{Fe}_2\text{O}_4$.^{1,2} The doping by cobalt can decrease the overall anisotropy of the ferrite. At a local scale, cobalt cation can induce locally a large anisotropy that tend to stabilize the domain wall in large grains and prevent further displacement (acting as a pinning defect).³⁻⁶ Energy dissipation by domain wall motions is then reduced and dynamic magnetization occurs mainly by spin rotation leading to low core-losses at high frequency. Moreover, it was highlighted by Lucas et al. that the core-losses of cobalt substituted ferrites depend on the temperature and are maintained low at around 80°C (typical working temperature of power converters).⁷

It is well-known that magnetic core-losses are closely related to the microstructure. To maintain very low losses (above 1 MHz and over 10mT), grain size has to be small enough to prevent domain wall nucleation inside the grain. To ensure that grains are mono-domain ones, size about $3\mu\text{m}$ is required.^{8,9}

The method of elaboration of ferrite is of significant influence on the microstructure and finally on the magnetic properties. Usually, ferrites are synthesized by the conventional ceramic method, because of industrial process maturity and because starting materials are fully available and not expensive. Nevertheless, it could be noticed that milling time remains very long and may result in

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some impurities in the material. Chemical syntheses are an alternative. These methods present the advantages of having finely spread powder and requiring low synthesis temperature. These should result in more homogeneous mixture in terms of composition and microstructure. The toxicity and the cost of some chemical components are the main drawbacks.^{10–12} Magnetic properties of ferrite synthesized by different types of sol-gel method were investigated and compared to ferrite produced by conventional ceramic methods.^{13–19} It results that ferrites which exhibit approximately the same permeability and coercive field are achieved by both sol-gel and solid-state methods. However, the magnetic performances at high frequency are not presented in these papers so it is difficult to know if this process is well-adapted to the production of low-loss ferrite. Consequently, we present an experimental study of ferrites synthesized by the Pechini type sol-gel method. Their structural and magnetic properties are characterized and compared to the ones of reference ferrite synthesized by classical solid-state reactions. The dynamic magnetic performances are also reported.

II. EXPERIMENTAL PROCEDURE

A. Powder synthesis

(Ni_{0.31}Zn_{0.49}Cu_{0.20})_{0.979}Co_{0.021}Fe_{1.9-d}O₄ powder samples were prepared by both conventional solid-state reaction and Pechini method. This composition was chosen following the results of previous studies. The presence of copper is useful to perform the synthesis at lower processing temperature and the low iron content is helping ionic diffusion and maintains high resistivity. Both Cu and Fe content are aiming to favor the ferrite densification whereas Ni/Zn ratio and cobalt content are fixed to minimize the magnetic core losses^{20,21} and match the chosen operating temperature.

For the solid-state method, stoichiometric amount of raw oxide materials (NiO, ZnO, Fe₂O₃, CuO, Co₃O₄) were mixed together during 4 hours. The powder was then calcined in air at 800°C for 2h. Then, the powder was grounded 2 hours. The powder was mixed with 2%wt of polyvinylacetate (PVA) binder. Powder was uniaxially pressed into toroid core with approximately 23mm of outer diameter, 14 mm of inner diameter and 5 mm of thickness. The sample was pre-heated to remove the binder and sintered at 980°C for 2 hours.

For the Pechini method, Stoichiometric amount of nitrate metals (Ni(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O, Co(NO₃)₂·6H₂O) were dissolved in distilled water and citric acid was added. The molar ratio of metal cation nitrates to citric acid was fixed to 1:3. Ethylene glycol was then added and the molar ratio of ethylene glycol to citric acid was fixed to 4:1. The solution was heated during 2 hours at 135°C. The water was evaporated by heating the solution at 80°C for 18 hours to form a gel. The gel was then calcined in two steps: 250°C for 30 minutes followed by a treatment at 600°C for 2 hours. The powder is sieved at 80µm and uniaxially pressed into toroid cores. The toroid cores are sintered with a two-step sintering process. This method was presented by Chen and Wang.²² It is used mainly for nanocrystalline powder to avoid grain growth while increasing the density. Some good results have been reported for Ni-Zn ferrite.^{23,24}

B. Characterization method

The phase formation was analyzed by XRD. The crystallite size on the powder is calculated using the Scherrer formula from the X-ray diffraction pattern.²⁵ The mean grain size was measured with the intercept method on images from Scanning Electron Microscopy (SEM) analysis. The density was measured with the Archimedes' principle. Static magnetic properties were determined for both powder and sintered samples on a magnetometer with extraction system between 0 and 7 T. Dynamic magnetic properties such as complex permeability, coercive field and magnetic core-loss were measured on the toroid cores. The complex permeability was measured over the frequency range from 10 kHz to 110 MHz using a precision impedance analyzer (4294A; Agilent) with a magnetic material test fixture (16454A; Agilent). The coercive field and magnetic core-losses were determined by flux metric measurement method (cores are wound as transformers). The magnetic field is derived from the current of the excitation winding and the induction is calculated from the open-circuit voltage of the sensing winding. For megahertz frequencies and low loss, it is necessary

to be less sensitive to phase discrepancy. The phase discrepancy is due to probe mismatch and delay due to oscilloscope acquisition time between channels. A 0.1ns acquisition delay between current and voltage measurement caused a 6% error on the magnetic core-loss measurement. To have an accurate measurement, an oscilloscope R&S RTO1024 with simultaneous 10Gs/s sampling rate is used and acquisition time delays are compensated according to specific apparatus (mutual inductance load). Then reactive power compensation method described by Mu, Lee, Li, Gilham, & Ngo²⁶ is used to decrease the influence of the phase discrepancy on core loss measurements. To avoid self-heating of the magnetic core under test, burst excitation waveform is also performed. The magnetic core-losses were determined at high frequencies ranging between 1.5MHz and 5MHz and for large amplitude excitation up to 40mT.

III. RESULTS

A. Structural characterizations

The samples and main structural characterizations are presented in the Table I.

The diffractograms of post-calcination powders and sintered samples are presented in the Fig. 1. Even if some oxides remain in the post-calcination powder, the ferrite phase is completely formed after sintering for all synthesis methods. The powder synthesized by Pechini method presents broader Bragg peaks. The measurements of crystallite size and specific area confirm that the Pechini powder is finer than the one from the solid-state reaction. This powder should be more reactive during the sintering.

The density of the sintered samples is above 90% of the theoretical density. The densities of C1 and P2 are almost the same around 93% of the theoretical density. The microstructures of the

TABLE I. Samples and structural characterizations.

No.	Synthesis	Calcination temperature (°C)	Crystallite size (nm) from diff. line (022)	Specific area (m ² /g)	Sintering cycle	Density (g/cm ³)	Density (%dth)	Mean grain size (μm)
C1	Ceramic	800	39	3.4	995°C-2h	5.01	93.6	1.3
P1	Pechini	600	20	10.3	975°C-915°C-6h	4.83	90.2	1.3
P2	Pechini	600	20	10.3	1000°C-940°C-6h	4.96	92.7	3

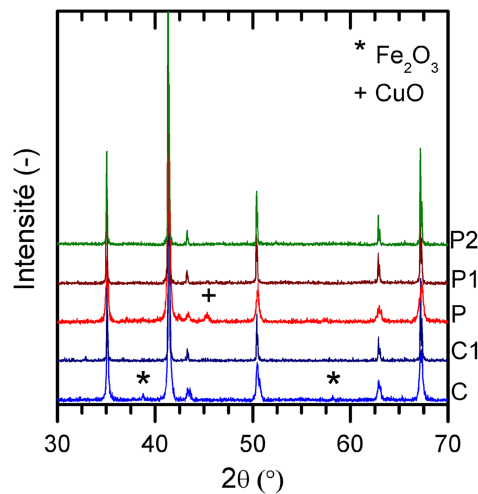


FIG. 1. Diffractograms of ceramic (C) and Pechini (P) calcined powders and ceramic (C1) and Pechini (P1) (P2) sintered ($\text{Ni}_{0.31}\text{Zn}_{0.49}\text{Cu}_{0.20}\text{Co}_{0.021}\text{Fe}_{1.9-d}\text{O}_4$) samples.

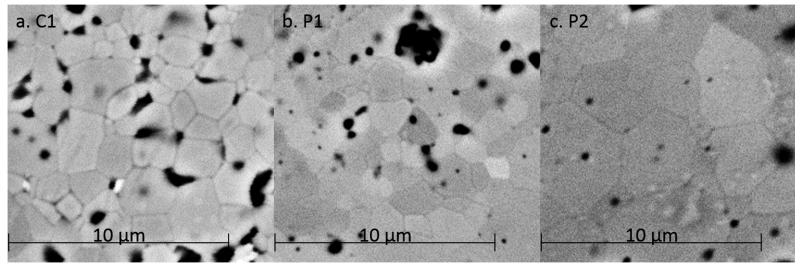


FIG. 2. Backscattering electron SEM images of the microstructure of $(\text{Ni}_{0.31}\text{Zn}_{0.49}\text{Cu}_{0.20})_{0.979}\text{Co}_{0.021}\text{Fe}_{1.9-d}\text{O}_4$ sintered samples: (a) C1 ceramic sample, (b) P1, (c) P2 Pechini samples.

sintered samples are presented in the Fig. 2. The black holes on the SEM images is the porosity due to incomplete densification. The mean grain size of samples C1 and P1 is the same at $1.3\ \mu\text{m}$ and remains greater for P2 at $3\ \mu\text{m}$.

B. Magnetic properties

The magnetization of the powders and the sintered samples are presented in the Fig. 3. The magnetization of the powders is really close despite a calcination temperature of only 600°C for the Pechini sample against 800°C for the solid-state sample. After sintering, the magnetization of P1 and P2 samples is higher than the one of C1 sample. This difference can be due to a more homogeneous composition or a different cationic repartition.

The complex permeability measured on the three samples is presented in the Fig. 4. The static permeability of the sample P2 is higher than the ones of P1 and C1. These results are consistent with the mean grain size measured of the samples.²⁷ The curves of complex permeability of samples C1 and P1 are nearly the same and the lower density of P1 seems to have no impact on the permeability. The production of ferrite with the same complex permeability is possible with both synthesis methods. The same properties are obtained with lower sintering temperature. During the sintering, the maximum reached temperature of P1 is 975°C which is 20°C lower than the maximum reached temperature of C1. The step temperature of P1 is only 915°C instead of 995°C for C1 sample.

The hysteresis loops at low frequency were measured and are presented on Fig. 5. The shape of the C1 loop is noticeably different from the ones of Pechini samples. The C1 hysteresis loop is broader but the approach to saturation seems to occur at lower induction compared to P1 and P2.

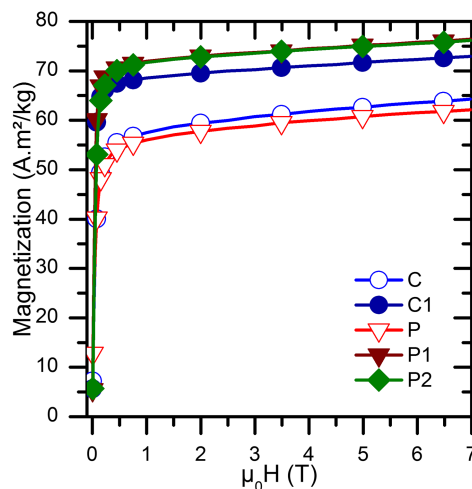


FIG. 3. Magnetization measurements of ceramic (C) and Pechini (P) powders and ceramic (C1) and Pechini (P1) (P2) sintered $(\text{Ni}_{0.31}\text{Zn}_{0.49}\text{Cu}_{0.20})_{0.979}\text{Co}_{0.021}\text{Fe}_{1.9-d}\text{O}_4$ samples.

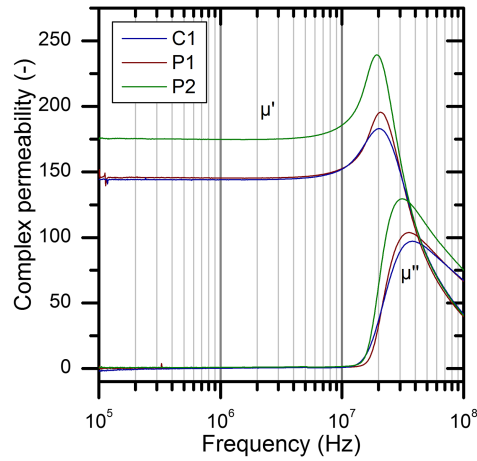


FIG. 4. Complex permeability of the ceramic (C1) and Pechini (P1) (P2) sintered $(\text{Ni}_{0.31}\text{Zn}_{0.49}\text{Cu}_{0.20})_{0.979}\text{Co}_{0.021}\text{Fe}_{1.9-d}\text{O}_4$ samples.

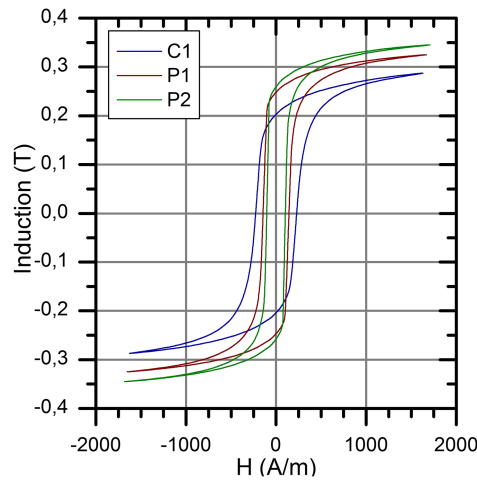


FIG. 5. Low frequency hysteresis loop of the ceramic (C1) and Pechini (P1) (P2) sintered $(\text{Ni}_{0.31}\text{Zn}_{0.49}\text{Cu}_{0.20})_{0.979}\text{Co}_{0.021}\text{Fe}_{1.9-d}\text{O}_4$ samples.

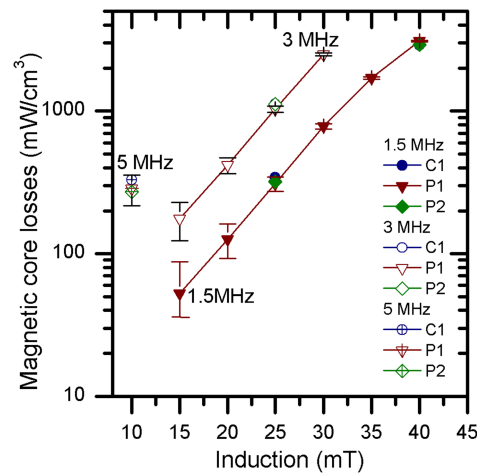


FIG. 6. Induction and frequency dependence of the magnetic core-losses measured for the ceramic (C1) and Pechini (P1) (P2) sintered $(\text{Ni}_{0.31}\text{Zn}_{0.49}\text{Cu}_{0.20})_{0.979}\text{Co}_{0.021}\text{Fe}_{1.9-d}\text{O}_4$ samples.

The coercive field of C1 is higher than the one of P1 even if the sample P1 is less dense and has the same mean grain size. The coercive field of P2 is lower than P1 which is consistent with the increase in mean grain size. The behavior of the samples synthesized by Pechini method is more interesting for a soft magnetic material.

The magnetic core-losses were measured at high frequencies ranging between 1.5MHz and 5MHz and for large amplitude excitation up to 40mT (Fig. 6.). The three samples have the same magnetic core-losses despite the differences noted on the other magnetic properties. The magnetic core-losses are low and comparable to the ones reported in the literature.^{7,28} The densities and the mean grain size of the samples are within the range required to obtain low losses.

IV. CONCLUSIONS

In conclusion, the synthesis of ferrite with low temperature Pechini reaction method was successful. The size of the powder can be tailored down to the desired scale and the obtained samples feature magnetic properties comparable to the ones of sample prepared by high temperature solid-state reaction. Sintered samples with at least 90% of theoretical density have been produced. Similar performances in terms of magnetic core-losses are obtained for both synthesis. The magnetic properties such as static permeability and coercive field are as good or better than the ones of solid-state reaction samples. The same properties can be obtained with a significant decrease in the sintering temperature which could be interesting for low temperature co-firing (LTCC) sintering. Results suggest that ferrites synthesized by Pechini method can be considered as an interesting basis for the design of low-loss magnetic components alternatively to the conventional route. Optimization of the sintering cycle could further improve the properties of Pechini method based ferrite.

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