Research Article

Microstructure and Electromagnetic Properties of Ni-Zn-Co Ferrite up to 20 GHz

Charalampos Stergiou^{1,2}

¹Laboratory of Materials for Electrotechnics, Department of Electrical and Computer Engineering, Aristotle University, 54124 Thessaloniki, Greece

²Laboratory of Inorganic Materials, Centre for Research and Technology Hellas, Themi, 57001 Thessaloniki, Greece

Correspondence should be addressed to Charalampos Stergiou; stergiou@cperi.certh.gr

Received 3 January 2016; Accepted 31 March 2016

Academic Editor: Joke Hadermann

Copyright © 2016 Charalampos Stergiou. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The present paper examines the relation between different developed microstructures and the microwave electromagnetic properties in Ni-Zn-Co ferrite. To this end, the $\text{Ni}_{0.25}\text{Zn}_{0.25}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ composition has been prepared with the conventional ceramic process with varied prefiring T_p (750°C, 1000°C) and sintering T_s top temperatures (1200°C, 1250°C). When lower temperatures are applied in these production stages, incomplete microstructures with low density, higher porosity, or finer grains are achieved. On account of these features, the contributions of domain wall motion and spin rotation to the complex permeability $\mu^*(f)$ move to higher frequencies, whereas microwave dielectric permittivity $\epsilon^*(f)$ is decreased. In particular in conjunction with the high Co content, the wall relaxation and spin resonance are interestingly forced to occur at 850 MHz and 8.05 GHz, respectively. Regarding the electromagnetic wave attenuation, the ferrite annealed at lower temperatures exhibits strong return loss peaks at higher frequencies, but without other performance improvement. We should notice that the variations in sintering temperature T_s yield the maximum changes in the recorded parameters, including the coercive field, $\mu^*(f)$, and $\epsilon^*(f)$, indicating the inferior role of prefiring T_p in Ni-Zn ferrite.

1. Introduction

Among ferrimagnetic oxides, the cubic ferrite of Mn-Zn type has the largest production and market share due to their superior behaviour under ac magnetic fields at frequencies roughly reaching 1 MHz. However, for the growing electronic, telecommunication, and power applications at higher frequencies other types of magnetic oxides, such as Ni-Zn cubic and hexagonal ferrite, are preferably employed. These materials possess higher electrical resistivity and magnetocrystalline anisotropy, which ensure sufficiently low power losses and high magnetic response in this frequency range [1, 2]. In particular in the group of Ni-Zn spinel ferrite types, by introducing Co as a substituting element the operation band extends to even higher frequencies, which actually reflects the persistence of moderate magnetic permeability values up to a higher cutoff frequency limit. This effect basically occurs on account of the strong positive contribution of cobalt to the

ferrite anisotropy, which originates in the unquenched orbital moment of Co^{2+} cation in the octahedral crystal sites [3]. The induced anisotropy, even by low Co doping, inhibits the domain wall displacement and intensifies the ferromagnetic resonance, which may be exploited in the design of Ni-Zn ferrite with low loss above 1 MHz [4–7].

Except for defining the frequency region of operation through compositional control, the developed microstructure of the ceramic is also known to affect the electromagnetic (EM) performance of ferrite. In fact, advanced tailoring of the morphological features through adjustment of the processing parameters is one of the most significant technical objectives in ferrite industry over time [1, 8, 9]. Therefore, various recently published reports examine the strong relation between grain size, porosity, density, and magnetic properties of Ni-Zn ferrite at high frequencies, with a view of forming certain material design directions [10–14].

TABLE 1: Experimental variables under test.

Sample	Prefiring temperature T_p (°C)	Sintering temperature T_s (°C)
S1 (REF)	1000	1250
S2	750	1250
S3	1000	1200

Nevertheless, there is a deficiency in the respective literature focusing on the Ni-Zn ferrite with high Co concentration, which is enlarged by the necessity for knowledge of both complex magnetic permeability $\mu^*(f)$ and dielectric permittivity $\varepsilon^*(f)$ in order to design the final passive components. To this end, we probe into the impact of heat treatment and microstructure on the microwave EM properties of Co-rich Ni-Zn spinels by varying the top temperatures during the prefiring and sintering stages of the ceramic synthesis route.

2. Materials and Methods

In the present investigation, polycrystalline samples with the chemical composition $\text{Ni}_{0.25}\text{Zn}_{0.25}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ were synthesized by the conventional solid state reaction route. Specifically, stoichiometric amounts of the precursor oxides NiO (Alfa Aesar, >99.0%), ZnO (Merck, >99.0%), Co_2O_3 (Riedel-de Haën, >95.0%), and Fe_2O_3 (Riedel-de Haën, >99.0%) were mixed for 3 hours in distilled water, dried overnight, and calcined in air for 5 hours. The prefired powders were ball milled for 3 hours, dried, and subsequently granulated with the addition of polyvinyl alcohol solution. The granulated powders were then pressed under axial compaction (80 MPa) to form disc specimens of 12 mm diameter and were finally sintered in air for 10 hours. Table 1 depicts the applied variations of annealing temperatures and the respective sample designations.

Both the prefired and the sintered materials were pulverized and subjected to phase and crystal structure identification with the X-ray powder diffraction method (Seifert, XRD 3003 TT, CuK α). The microstructure of the developed ferrite was examined with scanning electron microscopy (JEOL, SEM JSM6300), from which the median grain sizes $Dv50$ were calculated by the linear intercept technique. With regard to the static magnetic characterization, the specific saturation magnetization (σ_s) and coercive field (H_C) were obtained from hysteresis loops recorded up to 10 kOe at room temperature by using a vibrating-sample magnetometer (Quantum Design, VSM VersaLab 3T). Moreover, the materials' constitutive EM properties (complex permittivity ε^* and permeability μ^*) were measured in the frequency range 10 MHz–20 GHz by means of impedance and vector network analysis (Agilent, E4991A and HP, 8720C) and by applying the Nicolson-Ross-Weir algorithm [15]. To this effect, the sintered discs were precisely ground to form ring samples with outer diameter of 7 mm, inner diameter of 3 mm, and height of 1.5 mm. Finally, the prepared ferrite was evaluated with reference to its ability to attenuate either the EM waves reflected from a conducting plane or the

FIGURE 1: X-ray diffraction patterns of the prefired samples.

FIGURE 2: X-ray diffraction patterns of the sintered samples.

waves propagating through it. Specifically, the return losses (RL) were calculated from the respective overall reflection coefficient (Γ) in decibels according to the formula $\text{RL} = -20 \cdot \log(|\Gamma|)$.

3. Results and Discussion

3.1. Structural Properties. The investigation with XRD technique of the powders prefired at 750°C and 1000°C has resulted in the patterns displayed in Figure 1. We thus observe that prefiring at 750°C results in a mixture of the desired Ni-Zn ferrite (ICDD-PDF no. 87-2337) and the cation oxides Fe_2O_3 (ICDD-PDF no. 33-0664), Co_3O_4 (ICDD-PDF no. 09-0418), and NiO (ICDD-PDF no. 89-7130), whereas after prefiring at 1000°C only the spinel ferrite phase is present. Due to this compositional variation, the pressibility of the two ceramic powders is altered, with the higher press density PD under constant pressure being achieved by the pure ferrite powder (Table 2). The lower PD of the multiphase material is attributed to its pressibility, as the theoretical densities of the cation oxides (Fe_2O_3 , Co_3O_4 , and NiO) are similar or even higher than that of ferrite. With regard to the sintered materials, despite their different heat treatment history described in Table 1, all the diffraction peaks were indexed according to a single phase of spinel ferrite (ICDD-PDF no. 87-2337) with inverse spinel structure (S.G.: Fd-3m), as it is depicted in Figure 2. In particular for the S1 sample, by applying the Rietveld analysis of the XRD data the cell constant was refined to $a = 8.3918 \text{ \AA}$ [16]. Beyond the similarities in crystal structure of the sintered ferrite, the respective SEM images reveal significant microstructural variations between them (Figures 3(a)–3(c)). Thus, we notice that the samples S2 and S3 with lower prefiring and/or sintering temperatures exhibit increased total porosity volume and suppressed grain

TABLE 2: Morphology-related properties of the sintered ferrite.

Sample	Press density PD (g/cm^3)	Median grain size $Dv50$ (μm)	Sintered density SD (g/cm^3)	Relative density (%)
S1	2.94 ± 0.02	3.4 ± 0.2	5.08 ± 0.01	94.1
S2	2.73 ± 0.02	3.0 ± 0.1	4.82 ± 0.02	89.3
S3	2.94 ± 0.02	2.1 ± 0.2	4.93 ± 0.01	91.3

FIGURE 3: SEM images of the samples (a) S1, (b) S2, and (c) S3. The scale bar length is approximately 20 μm .

growth, compared to that of sample S1. These variations are easily spotted by comparing the median grain size $Dv50$, the sintered density SD, and the respective relative density, which are cited in Table 2. In conclusion, it seems that the pores formed due to the insufficient pressibility of multiphase composition (lower T_p), are preserved during sintering, and finally yield the lowest SD. On the other hand, the lower sintering temperature T_s leads to incomplete densification process and a porous polycrystalline ceramic with the finest grains.

3.2. Static Magnetic Properties. In order to examine the impact of microstructure on the static magnetic properties of the spinel ferrite, we have extracted the values of the specific saturation magnetization M_s and coercive field H_C from the respective hysteresis loops under dc magnetic field (Table 3). Taking into account the measurement standard error of less than 1%, the magnetization M_s , expressing the magnetic moments per unit mass (emu/g), is practically unaffected by the morphological features of different samples with a fixed composition and crystal structure. Concerning

TABLE 3: Static magnetic properties of the sintered ferrite.

Sample	Spec. saturation magnetization M_s (emu/g)	Coercive field H_C (Oe)
S1	90.5	20.1
S2	89.4	20.4
S3	89.5	29.0

the coercive field, due to its strong dependence on the grain size, it is increased in sample S3 with the lowest $Dv50$ (2.1 μm). Actually, the increased volume concentration of boundaries in finer grains enhances the pinning possibility of magnetic domain walls, thereby raising H_C as the measure of the irreversible changes in magnetization.

3.3. Electromagnetic Properties. The dispersion of complex permeability with frequency, $\mu^*(f) = \mu'(f) - j\mu''(f)$, was measured in the range from 10 MHz to 20 GHz and the variations of the respective real and imaginary parts are

FIGURE 4: Complex permeability spectra of the sintered ferrite samples.

separately shown in Figure 4. The recorded curves include two dynamic magnetization mechanisms, which affect different frequency regions. Specifically, due to the multidomain nature of this polycrystalline ferrite, both the domain wall motion (relaxation-type) and the ferromagnetic resonance occur. The magnetization contribution of the domain wall bulging by its nature appears at much lower frequencies than the ferromagnetic resonance [17]. From the $\mu''(f)$ spectra of Figure 4, we derive that the characteristic frequency of domain wall relaxation is increased from 550 MHz in S1 to 650 MHz in the sample with low T_P (S2) and 850 MHz in the sample with low T_S (S3). The observed decline of the domain wall process and its movement towards higher frequency are consistent with the shrinkage of the median grain size of the samples when heat treated at lower temperatures [18, 19]. Similarly, the ferromagnetic resonance peak at higher frequencies takes place at 6.55 GHz in the S1 ferrite and shifts to 7 GHz in S2 and 8.05 GHz in S3. Since the resonance frequency f_R is proportional to an effective internal field, the higher f_R corresponds with a stronger internal field due to the demagnetization effects rising from the porosity and the finer grains [20, 21]. The shift of the spectrum towards higher frequencies is accompanied by the reduction of the respective permeability levels, which is in accordance with fundamental Snoek's law defining the product $(\mu' - 1) \times f_R$ [3].

It is also important to comment on the appearance of permeability dispersion characteristics at unusually high frequencies for cubic ferrite. This seems apparent controversy with the established notion of the existence of a cutoff limit for spinel applications far below 1 GHz. However, although it is not observed in the most common types of Mn-Zn and Ni-Zn ferrite, the occurrence of resonance peaks above 1 GHz has been reported in Co-rich Ni-ferrite and Ni-Zn ferrite [22, 23]. This crucial impact of Co on the permeability spectrum stems from its inherent strongly positive contribution to the first-order anisotropy constant.

FIGURE 5: Spectra of real part of permittivity of the sintered ferrite samples.

With regard to the dielectric behaviour of the prepared materials, the complex permittivity, $\epsilon^*(f) = \epsilon'(f) - j\epsilon''(f)$, was measured in the range of 1 to 20 GHz. We focus our investigation on the real part ϵ' , displayed in Figure 5, as the differences in the imaginary part ϵ'' of the samples lie within the confidence interval of the measurement. Thus, in the monitored frequency window, ϵ'' curves are indistinct and are decreasing monotonically with frequency from 0.5 to 0.1, whereas ϵ' curves show some noticeable variations. In fact, we get that sintering at 1200°C results in the lowest permittivity values of the S3 sample. Above 1 GHz the dielectric response of materials is ascribed to the mechanism of orientational polarization and is thus related to the dipole concentration

FIGURE 6: Return losses $RL(f, d)$ of metal-backed (a) S1, (b) S2, and (c) S3 ferrite.

[24]. Therefore, the minimum ϵ' value of the sample S3 sintered at the lowest T_S is most likely the aftereffect of low Fe^{2+} content in combination with the inferior density.

3.4. Absorber Performance. By using the measured $\mu^*(f)$ and $\epsilon^*(f)$ data, we have created the contour maps of Figure 6, which depict the return losses (RL) in dB of the different produced materials for a metal-backed single-layer configuration. RL are represented as a function of frequency (f) and material thickness (d). In these maps we notice narrow zones of high RL values, which coincide with the $\lambda_g/4$ curves, where $\lambda_g = \lambda / \text{Re}\{\sqrt{\epsilon^* \mu^*}\}$ is the wavelength in the material. We thus conclude that the dominant mechanism for reflection reduction in the tested ferrite is the destructive interference, when the layer thickness is an odd multiple of quarter wavelength. As only small differences are identified in the electromagnetic properties of the produced samples, the RL plots of Figure 6 possess similar qualitative characteristics. However, we should notice the shift of the high RL peaks to higher frequency region for samples S2 and S3, in correspondence with the permeability spectrum shift. That displacement of the high return loss performance

to higher frequencies in S2 and S3 is more clearly discerned in Figure 7, where we plot the maximum achievable return losses at each frequency point, for material thickness up to 5 mm. The represented curves actually constitute an envelope of the $RL(f)$ curves obtained for different d values. From this projection of the maps on the frequency axis we derive that by altering the heat treatment of the spinel ferrite we have moved the major peaks with magnitude above 30 dB from 6.2 GHz to 7.9 GHz. Still, the strong suppression of reflectance is achieved by ferrite layers with thickness of less than 2 mm.

4. Conclusions

We have investigated the impact of heat treatment during the production of cubic ferrite $Ni_{0.25}Zn_{0.25}Co_{0.5}Fe_2O_4$ on its microwave electromagnetic properties. By varying the top temperature values during prefiring (T_P : 750°C, 1000°C) and sintering (T_S : 1200°C, 1250°C), single-phase spinel ferrite with similar crystal structure and different microstructure was obtained. Specifically, the combination of high T_P and T_S gives rise to high-density magnetic ceramics, whereas low T_P forms large pores and low T_S leads to the finest

FIGURE 7: Envelopes of the $RL(f, d)$ curves of the S1, S2, and S3 ferrite. Thickness d ranges up to 5 mm.

grains. To this end, the latter conditions of low T_S result in the maximum coercive field H_C , according to the dc hysteresis loops. In respect of the ac magnetic properties, the high Co content has moved the characteristic frequencies of dynamic magnetization processes to unusually high values, due to the strong magnetocrystalline anisotropy. That is, the domain wall relaxation and ferromagnetic resonance occur, respectively, above 550 MHz and 6.55 GHz in the complex permeability spectrum $\mu^*(f)$. By decreasing any of the two temperatures, T_P or T_S , the resultant smaller grain size and higher porosity shift the permeability spectrum to even higher frequencies. The lower sintering temperature also affects the microwave dielectric properties by decreasing permittivity in the 1–20 GHz range, which indicates the reduced concentration of dipoles. These variations of permeability and permittivity drive the zero-reflection conditions from a metal surface from 6.2 GHz to 7.9 GHz. The underlying mechanism is the quarter wavelength phase cancelation of multiple reflections, which creates the conditions for narrowband EM wave absorption. Although the changes of temperatures T_P and T_S induce significant microstructural dissimilarities, we finally conclude that sintering temperature is a more critical parameter in affecting the microwave electromagnetic properties of Ni–Zn–Co ferrite ceramics.

Competing Interests

The author declares that there are no competing interests regarding the publication of this paper.

References

[1] V. A. Brabers, “Ferrimagnetic insulators,” in *Handbook of Magnetism and Advanced Magnetic Materials*, John Wiley & Sons, New York, NY, USA, 2007.

[2] M. Wu and A. Hoffmann, *Recent Advances in Magnetic Insulators—From Spintronics to Microwave Applications*, Elsevier, Academic Press, San Diego, Calif, USA, 2013.

[3] J. Smit and H. P. J. Wijn, *Ferrites*, Philips Technical Library, Eindhoven, Netherlands, 1959.

[4] I. Mikami, “Role of induced anisotropy in magnetic spectra of cobalt-substituted nickel-zinc ferrites,” *Japanese Journal of Applied Physics*, vol. 12, no. 5, pp. 678–693, 1973.

[5] A. Lucas, R. Lebourgeois, F. Mazaleyrat, and E. Labouré, “Temperature dependence of spin resonance in cobalt substituted NiZnCu ferrites,” *Applied Physics Letters*, vol. 97, no. 18, Article ID 182502, 2010.

[6] A. Lucas, R. Lebourgeois, F. Mazaleyrat, and E. Laboure, “Temperature dependence of core loss in cobalt substituted Ni–Zn–Cu ferrites,” *Journal of Magnetism and Magnetic Materials*, vol. 323, no. 6, pp. 735–739, 2011.

[7] E. Brun, R. Lebourgeois, and E. Laboure, “Low permeability ferrite with low losses at high frequency,” *Journal of the Japan Society of Powder and Powder Metallurgy*, vol. 61, supplement 1, pp. S227–S230, 2014.

[8] A. Goldman, *Modern Ferrite Technology*, Van Nostrand Reinhold, New York, NY, USA, 1990.

[9] A. J. Moulson and J. M. Herbert, *Electroceramics. Materials, Properties, Applications*, John Wiley & Sons, Chichester, UK, 2nd edition, 2003.

[10] C. A. Stergiou and V. Zaspalis, “Analysis of the complex permeability of NiCuZn ferrites up to 1 GHz with regard to Cu content and sintering temperature,” *Ceramics International*, vol. 40, no. 1, pp. 357–366, 2014.

[11] J.-L. Mattei, L. Huitema, P. Queffelec et al., “Suitability of Ni–Zn ferrites ceramics with controlled porosity as granular substrates for mobile handset miniaturized antennas,” *IEEE Transactions on Magnetics*, vol. 47, no. 10, pp. 3720–3723, 2011.

[12] X. Wu, S. Yan, W. Liu, Z. Feng, Y. Chen, and V. G. Harris, “Influence of particle size on the magnetic spectrum of NiCuZn ferrites for electromagnetic shielding applications,” *Journal of Magnetism and Magnetic Materials*, vol. 401, pp. 1093–1096, 2016.

[13] C. Clausell, A. Barba, L. Nuño, and J. C. Jarque, “Effect of average grain size and sintered relative density on the imaginary part $-\mu''$ of the complex magnetic permeability of $(\text{Cu}_{0.12}\text{Ni}_{0.23}\text{Zn}_{0.65})\text{Fe}_2\text{O}_4$ system,” *Ceramics International*, vol. 42, no. 3, pp. 4256–4261, 2016.

[14] I. R. Ibrahim, M. Hashim, R. Nazlan et al., “Grouping trends of magnetic permeability components in their parallel evolution with microstructure in $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$,” *Journal of Magnetism and Magnetic Materials*, vol. 355, pp. 265–275, 2014.

[15] J. Baker-Jarvis, M. D. Janezic, B. F. Riddle et al., “Measuring the permittivity and permeability of lossy materials: solids, liquids, metals, building materials and negative-index materials,” NIST Technical Note 1536, National Institute of Standards and Technology, US Department of Commerce, 2005.

[16] C. Stergiou and G. Litsardakis, “Structural and magnetic properties of yttrium and lanthanum-doped Ni–Co and Ni–Co–Zn spinel ferrites,” *AIP Conference Proceedings*, vol. 1627, pp. 117–122, 2014.

[17] R. Valenzuela, *Magnetic Ceramics*, Cambridge University Press, Cambridge, UK, 1994.

[18] S. Chikazumi, *Physics of Ferromagnetism*, Oxford University Press, Oxford, UK, 2nd edition, 1997.

- [19] D. Jiles, *Introduction to Magnetism and Magnetic Materials*, CRC Press, Boca Raton, Fla, USA, 2nd edition, 1998.
- [20] H. Igarashi and K. Okazaki, "Effects of porosity and grain size on the magnetic properties of NiZn ferrite," *Journal of the American Ceramic Society*, vol. 60, no. 1-2, pp. 51-54, 1977.
- [21] R. Valenzuela, "The temperature behavior of resonant and non-resonant microwave absorption in Ni-Zn ferrites," in *Electromagnetic Waves*, V. Zhurbenko, Ed., chapter 18, InTech, Rijeka, Croatia, 2011.
- [22] G.-J. Yin and S.-B. Liao, "Permeability spectra of Co substituted Ni ferrites," *IEEE Transactions on Magnetics*, vol. 27, no. 6, pp. 5459-5461, 1991.
- [23] J.-L. Mattei, E. Le Guen, and A. Chevalier, "Dense and half-dense NiZnCo ferrite ceramics: their respective relevance for antenna downsizing, according to their dielectric and magnetic properties at microwave frequencies," *Journal of Applied Physics*, vol. 117, no. 8, Article ID 084904, 2015.
- [24] M. T. Sebastian, *Dielectric Materials for Wireless Communication*, Elsevier, Amsterdam, Netherlands, 2008.