ELECTROMAGNETIC BEHAVIOR OF ZINC FERRITES OBTAINED BY A COPRECIPITATION TECHNIQUE

Simona A. POPESCU[1], Paulina VLAZAN[2], Ştefan NOVACONI[3], Ioan GROZESCU[4], Petru V. NOŢINGHER[5]

Ferite de Zinc cu stoichiometria $Zn_xFe_{3-x}O_4$ cu x = 0.2, 0.5, 0.8, 1, 1.2, 1.5 au fost preparate prin coprecipitare şi caracterizate cu difracţie cu raze X (DRX), microscopie electronică (SEM), tehnica de transmisie prin cablu coaxial şi măsurători de histerezis magnetic. DRX arată că $ZnFe_2O_4$ are o structură spinelică la fel ca Fe_3O_4. Curbele de histerezis magnetic pentru $ZnFe_2O_4$ indică faptul că magnetizaţia atinge o valoare de saturaţie de cca. 450 A/m. În cadrul lucrării au fost făcute corelaţii între morfologia şi proprietăţile magnetice ale eşantioanelor şi s-a analizat posibilitatea aplicării acestora ca absorbţi de microunde (ecran electromagnetic).

Samples of $Zn_xFe_{3-x}O4$ with x = 0.2, 0.5, 0.8, 1, 1.2, 1.5 have been prepared by a chemical coprecipitation technique and characterized by: X-ray diffraction (XRD), scanning electron microscopy (SEM), coaxial transmission line technique and other magnetic hysteresis measurements. XRD shows that $ZnFe_2O_4$ had a spinel structure similar to Fe_3O_4. The magnetic hysteresis curves of $ZnFe_2O_4$ indicate that the magnetization takes a saturation value of about 450 A/m. Correlations between the morphology and samples magnetic properties were made in this work. Also the possibility of ferrites samples application in microwave absorption (electromagnetic shielding) was analyzed.

Keywords: zinc ferrites, morphology, magnetic properties

1. Introduction

Ferrites are usually non-conductive ferrimagnetic compounds derived from iron oxides such as hematite (Fe_2O_3) or magnetite (Fe_3O_4) as well as oxides of other metals. In terms of their magnetic properties, the different ferrites are often classified as "soft" or "hard", which refers to their low or high

[1] Eng., National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, Romania, e-mail: simona2008@gmail.com
[2] Eng., National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, Romania
[3] Physicist, National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, Romania
[4] PhD Physicist, National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, Romania
[5] Prof., Electrical Engineering Faculty, University POLITEHNICA of Bucharest, Romania

magnetic coercivity [1]. Soft ferrites are ferrimagnetic materials materials with spinel structure and general formula $MeFe_2O_4$ (Me = divalent metal ion, e.g. Zn, Ni, Co, Cu, etc.). The spinel structure has a close-packed structure of oxygen anions. Metallic cations, magnetic and nonmagnetic, reside on the interstices of the close-packed oxygen lattice. In the spinel structure these cations form tetrahedra and octahedra sub - lattices that are in themselves arranged in a close - packed arrangement.

The small amount of iron deficiency in the composition of ferrites can increase the electrical resistivity further by reducing the amount of Fe^{2+} ions and inhibiting electron hopping between Fe^{2+} and Fe^{3+} ions at the octahedral sites of the spinel unit cell [2]. The NiZn composites ferrites magnetic properties are determined by their chemical composition, crystallinity, porosity, grain size, etc. NiZn composites ferrites are widely used as soft magnetic materials for high frequency applications due to their high electrical resistivity and low hysteresis losses [3].

Ferrites can absorb variably electromagnetic radiation in microwave bands cast in various forms, e.g., sheets, paints, films, ceramic tiles, powders, and loads in matrix composites or mixed with conducting material [4]. These ferrites can be synthesized by a number of methods such as combustion, ceramic, co-precipitation, hydrothermal method and others [5]. Zn ferrites are still of great interest because of new technological applications especially at high frequencies [6] such as non-resonant devices, radio and microwave frequency circuits, high-quality filters, rod antennas, transformer cores, read/write heads for high speed digital tape, and magnetic operating devices [7]. Also the microwave absorbing properties of the $ZnFe_2O_4$ ferrites depend on thickness, chemical composition, crystalline structure, grain size and porosity.

The electrical and magnetic properties of Ni Zn ferrites are both strongly dependent on the purity of ferrite powder, its microstructure, grain boundary and chemistry of preparation [8]. Zn ferrites are advantageous over other ferrites for use at high frequencies because they possess high electrical resistivities and useful ferrimagnetic properties. As the use of electronic devices increases the research is focusing on the influence of the electromagnetic waves emited by them [9]. The most effective solution for this problem is to eliminate the emitted and reflected waves from such electronic devices by absorbing the electromagnetic waves. The key properties regarding these applications are permeability losses, at high frequencies as reported in literature [10].

In addition to ferrites advances, was found that an increased permeability allow for a wide frequency range an improved electromagnetic absorption [11]. Several investigations of the characteristics of Ni, Zn ferrites, such as their structure, electrical conductivity, chemical and elastic properties, dielectric behavior and magnetic properties, have been reported in the literature [12].

In this work the synthesis and analysis of zinc ferites without the inclusion of nickel (for electromagnetic shelding applications [13]) are presented. The magnetic behaviour at low and high frequencies of Zn ferrite and a investigation of the structures for different types of Zn ferrites powders (for obtaining the magnetic hysteresis and microwave absorption parameters at high microwave frequencies up to 6 GHz) was analyzed.

2. Samples

The $Zn_xFe_{3-x}O_4$, x = 0.2, 0.5, 0.8, 1, 1.2, 1.5 samples were prepared by coprecipitation method using the following powders: iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$], zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] and sodium hydroxide NaOH as reaction agents.
$Zn_xFe_{3-x}O_4$, x = 1 ($ZnFe_2O_4$) ferrite samples were obtained as powder form about 1.5 g weigh after 12 hours of chemical and thermal processing. For this, iron nitrate was mixed with zinc nitrate, sodium hydroxide with bidistilled water. The solution was heated to 90°C during 5 hours with a Magnetic Agitator at 400 rpm. The solution was then washed with bidistilled water and alcohol, filtered for 5 hours for neutral pH and calcinated in a Nabertherm Oven at 200°C for 2 hours.

3. Experiments

Zinc ferrite morphology was analyzed using Scanning Electron Microscopy (SEM), FEI Company microscope, type Inspect S. SEM is a type of electron microscope capable of producing high-resolution images of a sample surface. SEM images have a characteristic three-dimensional appearance and are useful for judging the surface morphology of the sample. Depending on the instrument, the resolution can fall somewhere between less than 1 nm and 20 nm.

The $ZnFe_2O_4$ ferrite structure was determined using X-Ray Diffraction (XRD), Philips difractometer, type X'Pert PRO MPD. X-rays, which are also produced by the interaction of electrons with the sample, may also detect the structure of the investigated sample at nanosize scale.

3.1. SEM analysis

The SEM morphology of a typical $ZnFe_2O_4$ ferrite is given in Fig.1. The micrographs of the $ZnFe_2O_4$ surface shows compact crystallites shapes with particles and chains formed by agglomeration with smallest particles sizes typically less then 30 nm. The structure of $ZnFe_2O_4$ here is comparable with structures identified in other works [14]. From the morphology investigation it was concluded that the zinc ferrite obtained corresponds to the spinel structure.

This structure includes some amorphous phases seen in ferrite morphology as agglomerated particles.

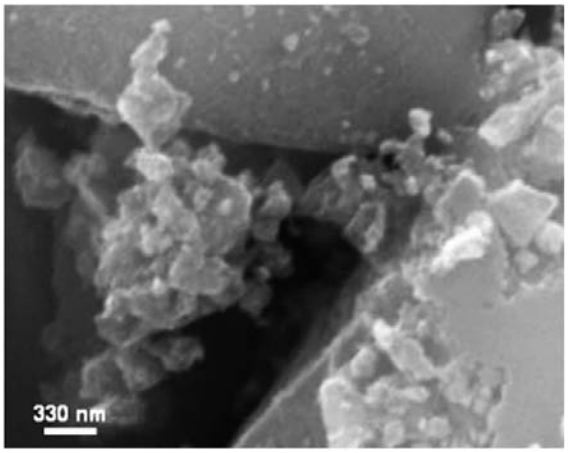

Fig. 1. SEM morphology of a typical $ZnFe_2O_4$ sample

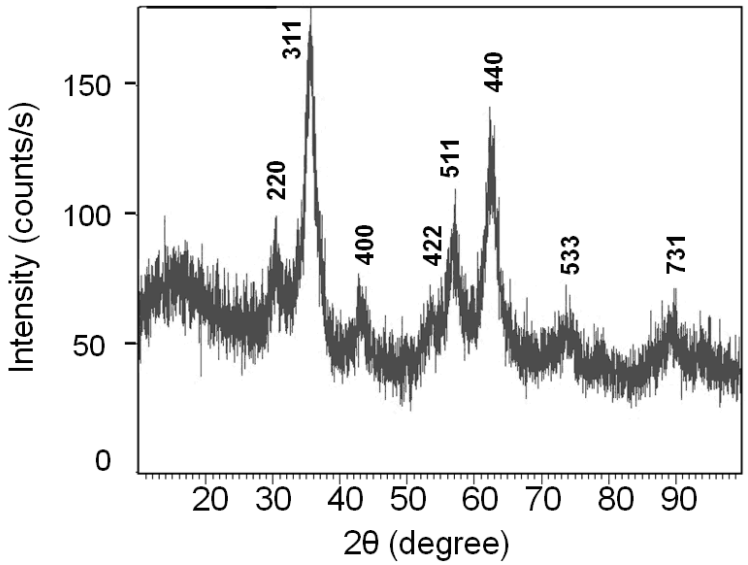

Fig. 2. XRD graph of a $ZnFe_2O_4$ sample

3.2. XRD analysis

The X-ray powder measurements were done in the 2θ range of 20–90° for the zinc ferrite obtained by the coprecipitation method using XRD technique.

Fig. 2 shows a typical X-ray diffraction pattern of a $ZnFe_2O_4$ ferrite, well defined diffraction peaks corresponding to the characteristic planes (311), (511) and (440) appear at 35°, 57° and 64°. The calculated distance between the main crystal planes was 0.2 nm. Other wide diffraction peak is also present with low relative intensities assumed to arise from an amorphous structure.

Using the Debye-Scherrer equation [15]

$$d = \frac{K \cdot \lambda}{B \cdot \cos(\theta_B)} \tag{1}$$

where d is measured mean size of zinc ferrites particles, K is a dimensionless constant that may range from 0.89 (for a perfect two-dimensional lattice) to 1.39 (depending on the specific geometry of the scattering objects), λ is wavelength (λ = 0.15 nm), B is the full width at half maximum of the main diffraction peak expressed in radian and θ is the Bragg angle.

The measured mean size of zinc ferrites particles was 10 nm.

3.3. Magnetic measurements

3.3.1. Hysteresis curves

The magnetic behavior of the $Zn_xFe_{3-x}O_4$ with x = 1 was investigated by measuring the magnetization due to a 50 Hz AC magnetic field. The magnetization was calculated from the time integration of voltage obtained through a primary coil to the sample [16].

In Fig. 3 the hysteresis curve of $ZnFe_2O_4$ ferrite sample is presented.

The ferromagnetic bahavior with a maximum magnetization of 450 A/m at 160 kA/m of zinc ferrite is evidenced due to specific occupancy of the tetrahedral and octahedral sites of Fe^{3+} and Zn^{2+} ions on the ferrite surface [2]. Low coercive fields may appear due to larger grain sizes [12].

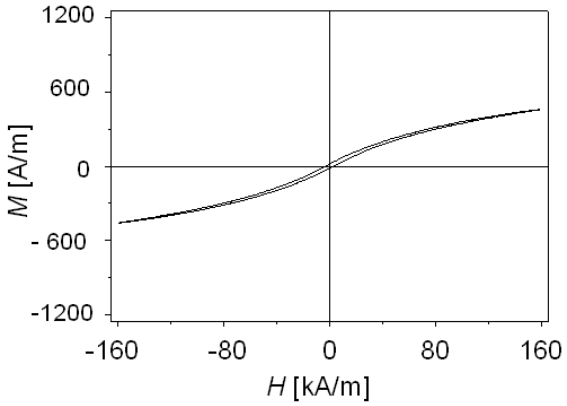

Fig. 3. Hysteresis loop for a $ZnFe_2O_4$ ferrite sample

3.3.2. Susceptibility and permittivity

The measurements of susceptibility and permittivity for the $ZnFe_2O_4$ samples were performed by the coaxial cell technique over the frequency range 0.1 - 6 GHz under computer control by the HP 8753C Network Analyser, Sweep Generator HP 8341 and Test Set type HP 8515 A [17]. The inner and outer diameters of the coaxial cell were 3mm and 7 mm, respectively, and its depth was 1.94 mm.

Variations of the real χ' and imaginary complex susceptibility χ" parts vs. frequency are presented in Fig. 4. It can be seen that a maximum value for the imaginary susceptibility apears at about 3 GHz, where the real susceptibility part has a minimum. This means that at 3 GHz the $ZnFe_2O_4$ samples presents relatively higher microwave absorbance.

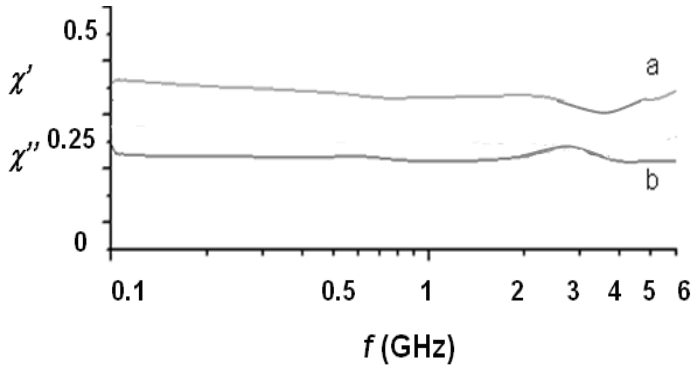

Fig. 4. Real χ'(a) and imaginary χ" (b) parts of the complex magnetic susceptibility vs. frequency f for $ZnFe_2O_4$ samples

The real ε' and imaginary ε'' complex permittivity parts of a $ZnFe_2O_4$ sample vs. frequency are presented in Fig. 5.

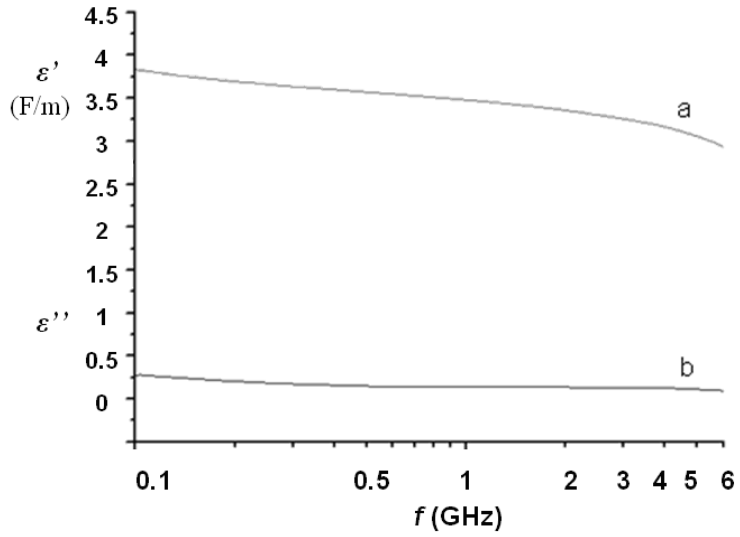

Fig. 5. Real ε'(a) and imaginary ε'' (b) parts of the complex permittivity vs. frequency f for $ZnFe_2O_4$ samples

It can be seen that the permittivity ε' decreases monotonously in the range 1-6 GHz. This behavior is a consequence of the dielectric relaxation processes in the samples [17] due to no interacting population of dipoles to an alternating external electric field.

4. Discussion

The analysis of the morphology and crystallinity by SEM and XRD for the zinc ferrites shows that the powders are composed of particles with diameters below 30 nm similar to NiZn ferrites obtained in other works [18]. From the x-ray diffraction measurements was observed also some amorphous material structure from the wide and small peaks corresponding to planes (220), (400), (533) and (731).

The amorphous phase may possibly affect the obtained electrical and magnetic properties of the Zn ferrites due to segregations of the sintering additives [21]. A recent investigation shows that the zinc ferrite, which is paramagnetic in the bulk form, becomes ferromagnetic in nanocrystalline powder form [20] due to synthesis parameters.

From the magnetic hysteresis measurements, a ferromagnetic behavior of $ZnFe_2O_4$ powders (with saturated magnetization of 450 A/m) was observed. By

increasing the synthesis temperature the ferrite powder will have a stronger ferromagnetic behavior [21].

The values of real magnetic permeability ($\mu' = (1 + \chi')\mu_0$, $\mu_0 = 4\pi.10^{-7}$ H/m) and permittivity ε' values of the $ZnFe_2O_4$ ferrite powder are shown in Table 1 along with additional parameters values presented in [19, 20, and 21]. Thus the results for μ' and ε' are the same with those from other autors.

Table 1

Magnetic and dielectric parameters for $ZnFe_2O_4$ sample

Sample	Mean value of size particles [nm]		Magnetic permeability [H/m] at 2 GHz	Dielectric permittivity [F/m] at 1GHz	Saturated magnetization [A/m]
	SEM	XRD			
$ZnFe_2O_4$	30	10	1.25	3.5	450
Zn ferrite, Ref. [19,20,21]	50	6	1.3	9	90

5. Conclusions

From the morphology investigation it was concluded that the zinc ferrite obtained corresponds to the spinelic structure including also some amorphous phases.

The magnetic permeability and dielectric permittivity was found to be similar to the values obtained in other works for Zn and NiZn ferrites in the GHz frequency domain.

Magnetic property measurements indicate that Zn ferrite powders exhibit the characteristic soft ferrite loops with high magnetization and low coercive field values. The Zn ferrites samples obtained by coprecipitation $Zn_xFe_{3-x}O4$ with x = 1 ($ZnFe_2O_4$) has shown the best magnetic behavior.

The properties of zinc ferrites at high frequencies differ considerably from the static or low-frequency behavior, resulting in a rich variety of microwave phenomena, utilized in ferrite devices.

R E F E R E N C E S

[1] *D. C. Kulkarni, U. B. Lonkar and V. Puri*, "High-frequency permeability and permittivity of NixZn(1_x)Fe2O4 thick film", Journal of Magnetism and Magnetic Materials, **vol. 320**, 2008, pp. 1844–1848.

[2] *Y. Li, Q. Li, M. Wen, Y. Zhang, Y. Zhai, Z. Xie, F. Xu and S. Wei*, "Magnetic properties and local structure studies of Zn doped ferrites", Journal of Electron Spectroscopy and Related Phenomena, **vol. 160**, 2007, pp. 1–6.

[3] *W. Yan, Q. Li, H. Zhong and Z. Zhong*, "Characterization and low-temperature sintering of Ni0.5Zn0.5Fe2O4 nano-powders prepared by refluxing method", Powder Technology, **vol. 192**, 2009, pp. 23–26.
[4] *A.C.F.M. Coasta, E. Tortella, M.R. Morelli and R.H.G.A. Kiminami,* "Synthesis, microstructure and magnetic properties of Ni–Zn ferrites", J. Magn. Magn. Mater. **vol. 256,** 2003, pp. 174–182.
[5] *A.D. Sheik and, V.L. Mathe*, "Anomalous electrical properties of nanocrystalline Ni–Zn ferrite", J Mater Sci, **vol. 43**, 2008, pp. 2018–2025.
[6] *A. Fujiwara, M. Tada, T. Nakagawa and M. Abe*, "Permeability and electric resistivity of spin-sprayed Zn ferrite films for high-frequency device applications", Journal of Magnetism and Magnetic Materials, **vol. 320**, 2008, pp. L67–L69.
[7] *M. Koledintseva, J. Drewniak, Y. Zhang, J. Lenn and M. Thoms*, "Modeling of ferrite-based materials for shielding enclosures", Journal of Magnetism and Magnetic Materials, **vol. 321**, 2009, pp. 730–733.
[8] *A. Dias, R. L. Moreira, N. D. S. Mohallem and A. I. C. Persiano*, "Microstructural dependence of the magnetic properties of sintered NiZn ferrites from hydrothermal powders", Journal of Magnetism and Magnetic Materials, **vol. 172**, 1997, pp. L9-L14.
[9] *B.W. Li, Y. Shen, Z.X. Yue and C.W. Nan*, "Influence of particle size on electromagnetic behavior and microwave absorption properties of Z-type Ba-ferrite/polymer composites", Journal of Magnetism and Magnetic Materials, **vol. 313**, 2007, pp. 322–328.
[10] *C. Calle, V.H. Calle, F. Cuellar, A. Cortes, D. Arias, W. Lopera, P. Prieto, O. Guzmana and G.A. Mendoza,* "Magneto-optical Kerr effect in NiZn ferrite films of variable thickness", Physica B, **vol. 384**, 2006, pp. 103–105.
[11] *K. Lakshmi, H. John, K.T. Mathew, R. Joseph and K.E. George*, "Microwave absorption, reflection and EMI shielding of PU–PANI composite", Acta Materialia, **vol. 57**, 2009, pp. 371–375.
[12] *B.K. Bammannavar and L.R.Naik*, "Magnetic properties and magneto electric effect in ferroelectric rich Ni0.5Zn0.5Fe2O4 + BPZT ME composites", Journal of Magnetism and Magnetic Materials, **vol. 321**, 2009, pp. 382–387.
[13] *N. Gupta, A. Verma, S.C. Kashyap and D.C. Dube*, "Microstructural, dielectric and magnetic behavior of spin-deposited nanocrystalline nickel–zinc ferrite thin films for microwave applications", Journal of Magnetism and Magnetic Materials, **vol. 308**, 2007, pp. 137–142.
[14] *Y.P. Fu and C.H. Lin*, "Microwave-induced combustion synthesis of Ni–Zn ferrite powder and its characterization", Journal of Magnetism and Magnetic Materials, **vol. 251**,2002, pp. 74–79.
[15] *R. Jenkins and R.L. Snyder*, Introduction to X-ray Powder Diffractometry, John Wiley and Sons Inc., New York, 1996.
[16] *I. Mihalca, A. Ercuta and C. Ionascu,* "The Villari effect in Fe–Cr–B amorphous ribbons", Sensors and Actuators A, vol. 106, 2003, pp. 61–64.
[17] *D. Vincent, L. Jorat, J. Monin and G Noyel,* "Improvement of the transmission/reflection method for dielectric and magnetic measurements on liquids between 0.1 and 20 GHz", Meas. Sci. Technol., **vol. 5**, 1994, pp. 990-995.
[18] *S. Sindhu, S. Jegadesan, A. Parthiban and S. Valiyaveettil,* "Synthesis and characterization of ferrite nanocomposite spheres from hydroxylated polymers", Journal of Magnetism and Magnetic Materials, **vol. 296**, 2006, pp. 104–113
[19] *T. Giannakopoulou, L. Kompotiatis, A. Kontogeorgakos and G. Kordas*, "Microwave behavior of ferrites prepared via sol–gel method", Journal of Magnetism and Magnetic Materials, **vol. 246**, 2002, pp. 360–365.
[20] *M. Wen, Q. Li, and Y. Li*, "Magnetic, electronic and structural properties of ZnxFe3−xO4", Journal of Electron Spectroscopy and Related Phenomena, vol. 153, 2006, pp. 65–70.

[21] *A.C.F.M. Coasta, E. Tortella, M.R. Morelli, R.H.G.A. Kiminami and M. Kaufman*, " Effect of heating conditions during combustion synthesis on the characteristics of Ni0.5Zn0.5Fe2O4 nanopowders", Journal of Materials Science, **vol. 37**, 2002, pp. 3569–3572.