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Microstructural and Magnetic Characteristics of Divalent Zn, Cu and Co-Doped Ni Ferrites

M. Šoka*, R. Dosoudil and M. Ušáková

Institute of Electrical Engineering, Faculty of Electrical Engineering and Information Technology,
Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia

Divalent zinc, copper and cobalt doped nickel ferrites with the chemical formula $Ni_{1-x-y-z}Zn_xCu_yCo_zFe_2O_4$ where x values ranging from 0.4 to 0.6, $y = 0.1$, $z = 0.01$ and 0.02 have been synthesized by conventional ceramic method. The effect of Zn^{2+}, Cu^{2+} and Co^{2+} ions substitution on the selected microstructural and magnetic characteristics have been investigated to examine the utility of prepared ferrite materials for high-frequency applications. X-ray diffraction measurements confirmed the single-phase spinel cubic structure in all the samples and modifications in lattice parameter according to the ionic radii size of doped ions. The net magnetic moment, given by the differences between the magnetic moments of A and B sublattice, increased with raising substitution of Ni^{2+} ions. The measured frequency dispersion of complex permeability was discussed in terms of the changes in chemical composition, microstructure and the associated processes of resonance and/or relaxation due to domain wall movements and damping of spin rotations contributing to the fall of permeability and rise of magnetic losses.

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1. Introduction

Polycrystalline spinel ferrites have been very attractive soft magnetic materials for high frequency applications over a broad frequency range mainly due to their high value of saturation magnetization, high electrical resistivity, and moderate magnetic permeability. Electromagnetic properties of these ferrites are highly sensitive to chemical composition and synthesis method. There have been many reports on ferrites [1, 2] by substituting various ions of different valences to improve the required properties depending on the applications of interest. Among different types of soft ferrite, mainly nickel ferrites have potential applications in electronic devices such as inductors, dc/dc converters, and electromagnetic noise suppressors. At present, researchers have been searching for soft magnetic materials having high saturation magnetization, high permeability and low magnetic losses. Ni ferrites have high Curie temperature, high resistivity, and low dielectric and magnetic losses. The electromagnetic properties of these ferrites may be further improved by suitable substitutions [3]. In this paper, the effect of Zn^{2+}, Cu^{2+} and Co^{2+} ions substitution on the selected microstructural characteristics (such as X-ray diffraction (XRD) patterns, lattice parameter, average crystallite size) and magnetic properties (such as net magnetic moment, the Curie temperature and frequency dispersion of complex magnetic permeability) of NiZnCuCo ferrite systems has been studied with the aim to improve the magnetic properties of synthesized samples.

2. Experimental

The ferrite samples were synthesized by means of conventional ceramic route, where the raw oxides, such as Fe_2O_3, NiO, ZnO, CuO, and CoO of analytical grade (99% purity, GR grade, commercially available), were mixed to obtain required stoichiometric amounts. This raw mixture was homogenised by wet milling, filtered, dried out and subsequently calcined at 950 °C for 1 h. After repeated homogenization and drying, a small part of calcinate powder was thermally treated at 1200 °C for 6 h and used for the measurement of temperature dependences of magnetic susceptibility. Remaining part of calcinate was used for the fabrication of pellets with the diameter of 15 mm and consequently sintered at 1200 °C for 6 h as well. Sintered pellets were drilled into the centre by means of water-beam drilling machine. Thus, ring-shaped samples with the outer diameter of 8.2 mm, the inner diameter of 3.7 mm, and the height of 3.5 mm were obtained.

The structure and phase purity of all synthesized ferrite samples were verified by means of X-ray diffraction (XRD) patterns. XRD analysis was carried out at room temperature using Siemens Bruker D8 DISCOVER diffractometer equipped with X-ray tube with rotating Cu anode operating at 12 kW. All measurements were performed in parallel beam geometry with parabolic Goebel mirror in the primary beam. The XRD patterns of samples were recorded in the range from 15° to 100° in steps of 0.02°. The lattice parameter a and the average crystallite size d_{XRD} of the samples were determined by Rietveld refinement using the Topas 3.0 software from Bruker AXS.

The temperature dependences of magnetic susceptibility χ of sintered ferrites were carried out using a custom-made experimental setup based on commercial precision semi-automatic autobalanced inductivity bridge for magnetic susceptibility measurements. The susceptibility was measured in ac magnetic field with an intensity of 421 A/m and at a frequency of 920 Hz. The Curie temperatures of prepared samples were obtained from measured temperature dependences of susceptibility.

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*corresponding author; e-mail: martin.soka@stuba.sk

The frequency dependences of real ’ and imaginary μ'' parts of complex permeability $\mu = \mu' - \mathrm{j}\mu''$ have been measured within the frequency interval 100 kHz–3 GHz by means of an impedance method using a vector network analyser (Keysight E5063A).

3. Results and discussion

The microstructure and phase purity of prepared ferrite samples, investigated by means of XRD, are plotted in Fig. 1. Some microstructural and magnetic parameters for synthesized ferrite samples are shown in Table I.

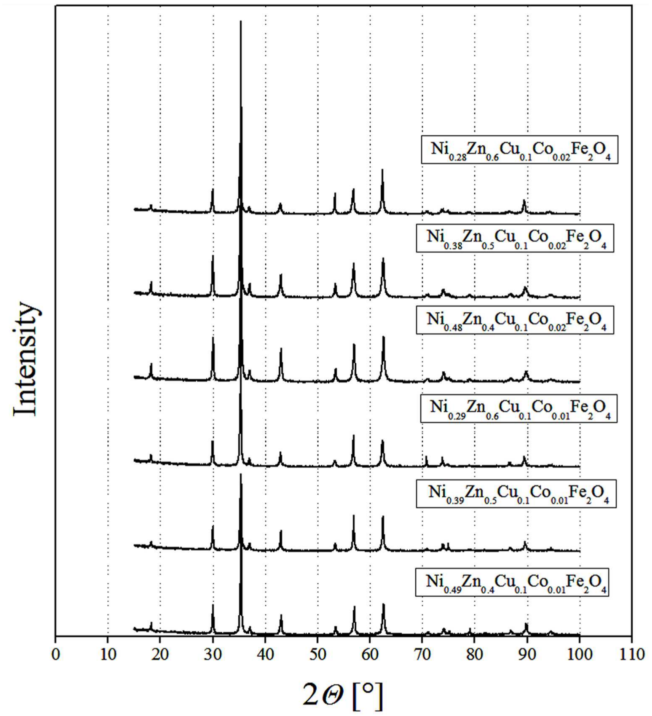

Fig. 1. XRD patterns for synthesized ferrites.

XRD analysis confirmed single phase spinel structure for all synthesized samples. No other crystalline phases were detected. Narrow diffraction peaks show good crystallinity of ferrite samples. Incorporation of substituting ions in a spinel structure caused slight deformation of crystalline array. Hereby the lattice parameter increases and simultaneously due to the substitution of Ni^{2+} by ions with higher value of ionic radius. It is well known that if the radius of the substituent ion is larger than the displaced ion, the lattice expands, and hence, the lattice parameter increases or vice versa. In general, an increase in the lattice parameter is expected for zinc, copper, and cobalt substitutions as the radii of Zn^{2+} (0.74 Å), Cu^{2+} (0.73 Å) and Co^{2+} (0.745 Å) are quite larger than that of the displaced Ni^{2+} ion (0.69 Å). The observed increase in lattice parameter for zinc, copper, and cobalt ions infers entry of all these ions into the spinel lattice. On the contrary, the average crystallite size decreases with the partial substitution of Ni^{2+} ions by Zn^{2+}, Cu^{2+} and Co^{2+} ions.

TABLE I

Microstructural and magnetic parameters for synthesized ferrites with composition $\mathrm{Ni}_{1-x-y-z}\mathrm{Zn}_x\mathrm{Cu}_y\mathrm{Co}_z\mathrm{Fe}_2\mathrm{O}_4$ ($y = 0.1$).

x	z	a [Å]	d_{XRD} [nm]	m [μ_B]	T_C [°C]
0.4	0.01	8.3918	48.9	5.11	324
0.5	0.01	8.4045	47.5	5.98	240
0.6	0.01	8.4127	46.0	6.76	145
0.4	0.02	8.3942	37.1	5.21	320
0.5	0.02	8.4030	33.4	5.99	240
0.6	0.02	8.4141	30.8	6.78	137

The observed variations in the net magnetic moment of the lattice, given by the difference between the magnetic moments of B and A sublattices ($m = 4|m_\mathrm{B} - m_\mathrm{A}|$), can be understood on the basis of super-exchange interactions among both the tetrahedral (A) and octahedral [B] site in the spinel lattice. As these exchange interactions are greatly affected by the nature of the ions present at both A and B sublattices, it is necessary to understand the distribution of cations over both the sublattices. It is known that Zn^{2+} ions have strong preference for A sites, whereas Ni^{2+}, Cu^{2+}, and Co^{2+} ions have their tendency towards B sites, while Fe^{3+} ions occupy both A and B sites. As a result, the ions in investigated ferrite system with composition $\mathrm{Ni}_{1-x-y-z}\mathrm{Zn}_x\mathrm{Cu}_y\mathrm{Co}_z\mathrm{Fe}_2\mathrm{O}_4$ occupy A and B sites in agreement with the following alignment:

$$\left(\mathrm{Zn}_x^{2+}\mathrm{Fe}_{1-x}^{3+}\right)_\mathrm{A}\left[\mathrm{Ni}_{1-x-y-z}^{2+}\mathrm{Cu}_y^{2+}\mathrm{Co}_z^{2+}\mathrm{Fe}_{1+x}^{3+}\right]_\mathrm{B}\mathrm{O}_4^{2-}. \quad (1)$$

Considering the magnetic moments of Fe^{3+} (5 μ_B), Ni^{2+} (2.2 μ_B), Cu^{2+} (1 μ_B), Co^{2+} (3 μ_B) and Zn^{2+} (0 μ_B), in compliance with ion alignment (1), the value of net magnetic moment m increases with increasing substitution of Ni^{2+} ions (see Table I).

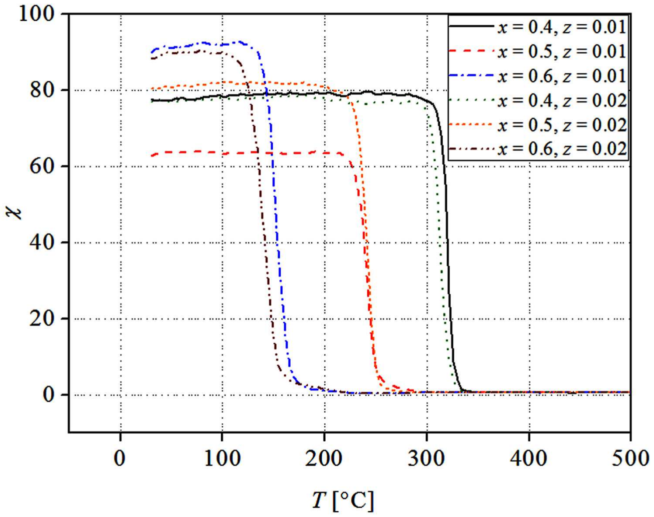

Fig. 2. Temperature dependences of magnetic susceptibility for synthesized ferrites.

Since thermomagnetic analysis is able to give a good information about the phase and chemical composition, the magnetic susceptibility temperature dependences of prepared ferrite samples were also studied, Fig. 2. Observed sharp fall of the curved lines approves occurrence of the single phase structure. Moreover, the decrease of the Curie temperature and variation of magnetic susceptibility value with the addition of Zn, Cu, and Co ions were detected. It can be attributed to the deformation of the crystalline array, which causes magnetic disorder in a spinel structure resulting in strengthening of A–B exchange ir

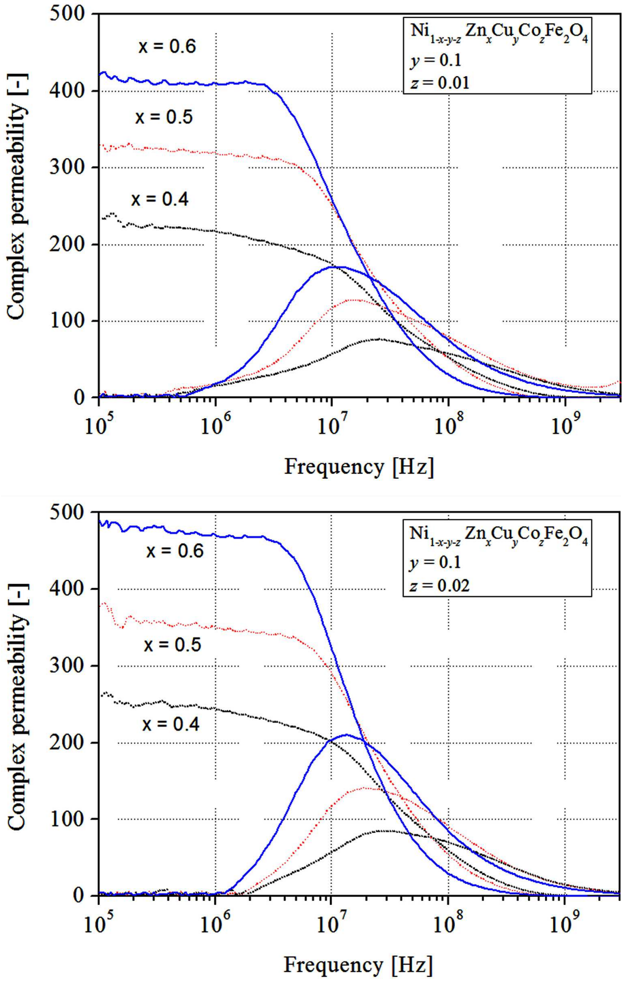

Fig. 3. Frequency dependences of real and imaginary parts of complex (relative) permeability for prepared ferrites with (top) $z = 0.01$ and (bottom) $z = 0.02$.

The frequency dependences of real μ' and imaginary μ'' parts of complex (relative) permeability $\mu = \mu' - \mathrm{j}\,\mu''$ for synthesized ferrite samples can be found in Fig. 3. The values of μ' slightly decreased with frequency up to about 4–7 MHz, then sharply drops down. The imaginary part μ'' increased with increase in frequency and takes a narrow maximum at about 10–30 MHz showing (ferromagnetic or ferrimagnetic) resonance of permeability loss. Permeability loss arises as a result of a lag of domain wall motion with respect to applied field and is attributed to imperfections in the lattice. The onset of resonance in the permeability loss spectrum varies also with composition and this resonance frequency (defined as a peak in $''-f$ dependence) determines the operational limit for any device utilizing the ferrite materials. An observation of composition dependence of μ' shows that it raised with Zn^{2+} and also Co^{2+} ions substitutions to obtain a maximum value at $x = 0.6$ and $z = 0.02$. The complex permeability is known to be the contributions from both the spin rotation and domain wall displacement [4] and is mainly controlled by the bulk properties of the prepared materials (like chemical composition, stoichiometry, ionic distribution, microstructure, impurity, crystal anisotropy and porosity). Since permeability is sensitive to many factors, it is difficult to draw a specific conclusion for the explanation of composition dependence of permeability. Higher values of permeability are favoured by higher density and saturation magnetization, better stoichiometry and bigger grains (or average crystal size) but it decreased with increased porosity, magnetocrystalline anisotropy and the Curie temperature. The present results of the compositional variation of μ may be interplay of all the above factors.

4. Conclusions

In this work, a systematic investigation was carried out on the microstructural and magnetic characteristic of synthesized ferrite systems with the chemical formula $Ni_{1-x-y-z}Zn_xCu_yCo_zFe_2O_4$ ($x = 0.4$, 0.5, 0.6, $y = 0.1$, $z = 0.01$, 0.02). XRD analysis confirmed single-phase spinel cubic structure and modifications in lattice constant. The lattice parameter and the net magnetic moment increased while the average crystallite size and the Curie temperature decreased with increase of substitution of Ni^{2+} ions. The frequency dispersion of complex permeability has been discussed in terms of the changes in various factors such as chemical composition, microstructure and the associated processes of resonance and/or relaxation due to domain wall displacements and spin rotations contributing to the fall of permeability and rise of magnetic resonance loss.

Acknowledgments

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