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MAGNETO-CHEMICAL COMPOSITION AND MAGNETIC PROPERTIES OF THE SELECTED SPINEL FERRITES

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The aim of the presented research is to prepare thermally stable nickel zinc ferrite, with suitable Ni^{2+}/Zn^{2+} ratio, and examine the effect of partial substitution of Zn^{2+} ions with Cu^{2+} and Co^{2+} ions on the structural and magnetic properties. For that purpose, there were prepared the $Ni_xZn_{1-x}Fe_2O_4$ (x = 0.30, 0.33, 0.36, 0.42, 0.50, 0.70) and $Ni_{0.33}Zn_{0.57}Me_{0.1}Fe_2O_4$ (Me = Cu^{2+}/Co^{2+}) ferrite compositions by the self-propagated combustion method at the temperature of 850°C. Applied method of preparation allows to obtain oxide based materials with small particles and low process temperatures.

Keywords: nickel zinc ferrites, structural properties, magnetic properties

1 INTRODUCTION

Spinel ferrites represent an important type of magnetic materials, which is confirmed by current continued interest in improving their physical properties [1, 2]. This can be achieved in several ways such as modification of classical preparation technology [3, 4], find out appropriate substituents in preparation process [5] and others. High initial permeability, high resistivity and therefore small power losses make these ferrites interesting for AC high frequency applications ranging from small power signal processing and transmission components up to high power switching power converters as well as electromagnetic interference absorbers used for shielding of various electronic devices. Minimization of electromagnetic components implies demand after high maximum magnetic field energy density, therefore high permeability and saturation magnetic flux density also at high frequencies as well as the thermal stability of magnetic parameters. When new magnetic materials are designed, or properties of existing materials are improved, it is necessary to reach a reasonable compromise between these requirements.

Our attention was focused on improvement of widely used NiZn ferrites. Optimal Ni:Zn ratio was chosen and partial substitution of Co^{2+} and Cu^{2+} ions for Ni^{2+} and Zn^{2+} ions was carried out. Phase composition, structure and selected magnetic parameters were evaluated by X-ray diffraction (XRD), scanning electron microscope (SEM), measurement of temperature dependence of the susceptibility and frequency dependence of complex permeability.

2 EXPERIMENTAL PROCEDURES

The samples of pure as well as substituted NiZn ferrites were prepared by means of self-propagated combustion method from the soluble metal salts of nickel, zinc, iron, cobalt and copper and glycine acting as the precursor [6]. Synthesized powder was annealed at the temperature of 850°C for 6 hours and used for thermomagnetic analysis. NiZn ferrite samples substituted by Cu and Co were pressed into the form of pellets with the diameter of about 10 mm and sintered at the temperature of 1000°C for 6 hours. Further, the circular hole was drilled into the pellet. Thus, the ring-shaped samples with the outer diameter of about 8 mm and inner diameter of 3.2 mm were obtained. These toroidal samples were used for the measurement of the frequency dependences of the real and the imaginary parts of complex permeability.

Since thermomagnetic analysis among other things afford quick and effective way to determine convenient Ni^{2+}/Zn^{2+} ratio in terms of phase composition and thermal stability of investigated samples, measurements of the temperature dependencies of magnetic susceptibility were carried out by a precision semi-automatic auto-balance inductivity bridge. It is equipped with automatic zeroing and automatic compensation of the thermal drift of the bridge unbalance.

The crystalline structure of selected substituted samples were investigated by means of X ray diffraction analysis (XRD) using commercially available diffractometer equipped with X ray tube with rotating Cu anode operating at 12 kW ($\lambda = 1.5418$Å). The size and shape of ferrite powder samples were examined by scanning electron microscope (SEM). The short-circuit (coaxial transmission line) method was used to determine the frequency dependences of the real and the imaginary parts of complex (relative) permeability over the frequency range 1 MHz to 3 GHz.

3 RESULTS AND DISCUSSION

Samples of ferrite powders with various values of Ni:Zn ratio were prepared as candidates for further structure modifications. Temperature dependence of magnetic susceptibility of $Ni_xZn_{1-x}Fe_2O_4$ ferrite powders was measured for x = 0.30, 0.33, 0.36, 0.42, 0.5 and 0.7 (Fig. 1). Such method is able to give a good information about the

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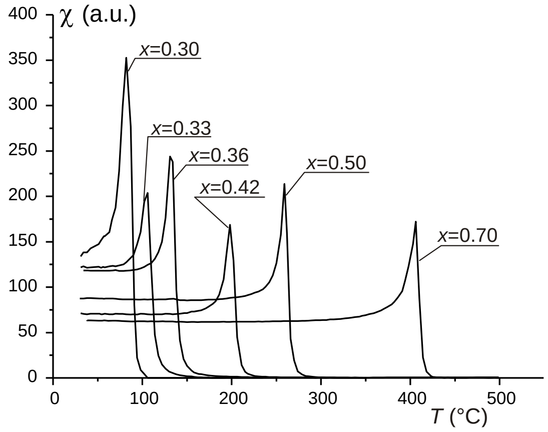


Fig. 1. Temperature dependence of magnetic susceptibility of $Ni_xZn_{1-x}Fe_2O_4$ ferrite

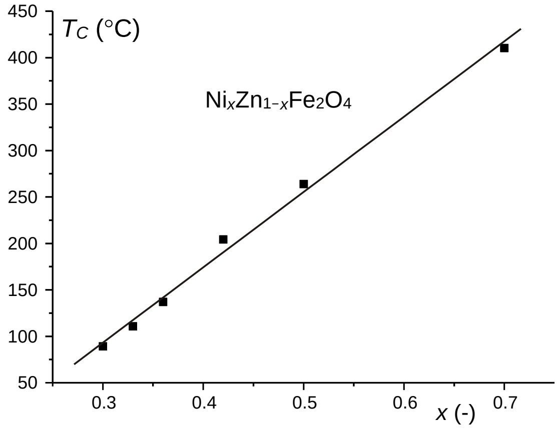


Fig. 2. Curie temperature dependence on ions content x

phase and chemical composition of specimen [7]. Sharp Hopkinson's peak with succeeded by a strong drop of susceptibility moves to higher temperature as the Ni content x increases. Curie temperature was determined for each dependence from a point of inflexion position, almost linear dependence on the substitution level x was found (Fig. 2.). From the point of view of magnetic susceptibility thermal stability, the best selection would be $x = 0.7$. However, amplitude permeability as well as the saturation magnetic flux density measured on toroidal samples of solid ferrites decreased with x [8]. Therefore selection of the specimen with $x = 0.33$ appeared to be a reasonable compromise for further work.

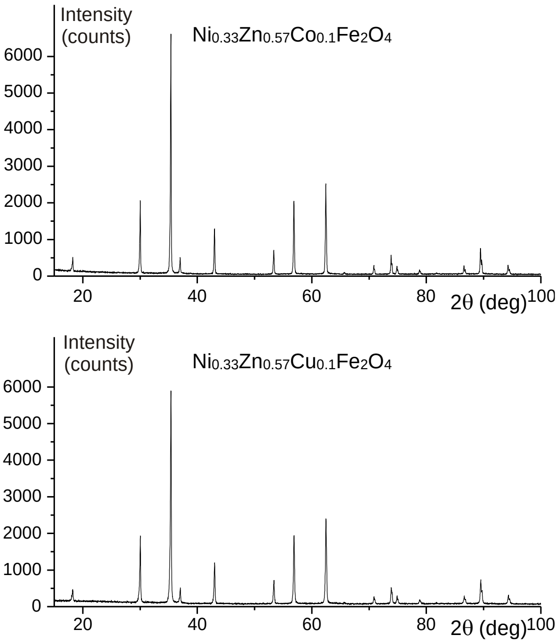


Fig. 3. XRD patterns of Co and Cu substituted NiZn ferrites

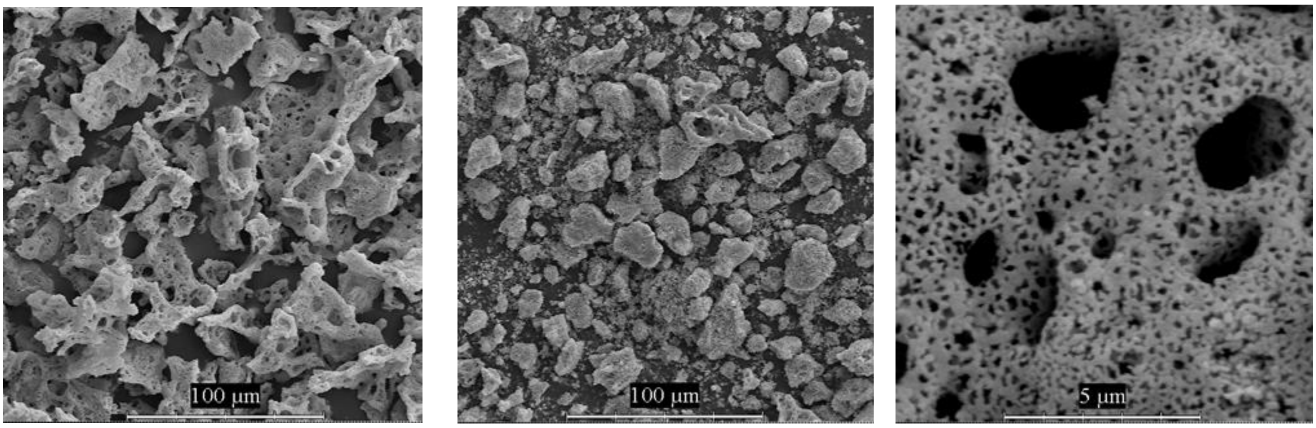
The X-ray diffraction analysis of NiZn ferrite samples substituted by Cu and Co ions sintered at temperature 1000°C for 6 hours indicates the presence of single-phase cubic spinel structure without other crystalline phases, (Fig. 3). The lattice parameter a and the crystallite size D were determined from XRD by the software TOPAS 3.0.

The lattice parameter of the $Ni_{0.33}Zn_{0.57}Cu_{0.1}Fe_2O_4$ (0.840866 nm) achieved only slightly higher value than for $Ni_{0.33}Zn_{0.57}Co_{0.1}Fe_2O_4$ (0.840626 nm) due to larger ionic radii of Cu^{2+} (0.96 Å) in comparison with Co^{2+} (0.72 Å), since the substitution of Fe^{3+} by the ions with larger ionic radii caused the lattice distortion. The crystallite size for Cu substituted NiZn ferrite reached the value $D = 294$ nm meanwhile for Co substituted NiZn ferrite it was 144 nm. These values are comparable with the crystallite size of NiZn ferrite without substitution, where $D = 157$ nm for the sample with composition $Ni_{0.33}Zn_{0.67}Fe_2O_4$ prepared by the same wet method [9].

The SEM of Cu and Co substituted NiZn ferrite powders as well as non-substituted ferrite thermally treated at 850°C for 6 hours are illustrated in Fig. 4. From these images, the presence of porous clusters with various size and irregular morphology is visible. Higher magnification shows that the clusters are created of small grains of submicrometer size.

Temperature dependence of magnetic susceptibility was measured on both Co- and Cu-doped ferrite samples. We can see that the Curie temperature increased from 107°C (pure NiZn ferrite) up to 177°C (doped ferrites). Moreover, the shape of dependence containing just one drop shows that no secondary phases are present in the ferrite. Presence of a strong Hopkinson peak near the Curie temperature caused by superparamagnetic state occurrence at the phase transition indicates small size of ferrite particles. Observed Curie temperature variation can be attributed to the strengthening of exchange interactions, between tetrahedral (A) and octahedral (B) sites of the spinel structure, as a consequence of Fe^{3+} ions content change on A and B sites due to presence of Cu^{2+}/Co^{2+} ions on B sites [10].

Frequency dependence of the of complex (relative) permeability $\mu = \mu' - j\mu''$ over the range 100 kHz to



$Ni_{0.33}Zn_{0.57}Co_{0.1}Fe_2O_4$ $Ni_{0.33}Zn_{0.57}Cu_{0.1}Fe_2O_4$ $Ni_{0.33}Zn_{0.57}Co_{0.1}Fe_2O_4$

Fig. 4. SEM picture of Co and Cu substituted NiZn ferrites

3 GHz for prepared ferrite samples $Ni_{0.33}Zn_{0.57}Me_{0.1}Fe_2O_4$ (Me = Cu^{2+}, Co^{2+}) are presented in Fig. 6. For both ferrites, the real component of permeability μ' remains almost constant up to a certain frequency, attains maximum value, beyond which μ' begins to decrease.

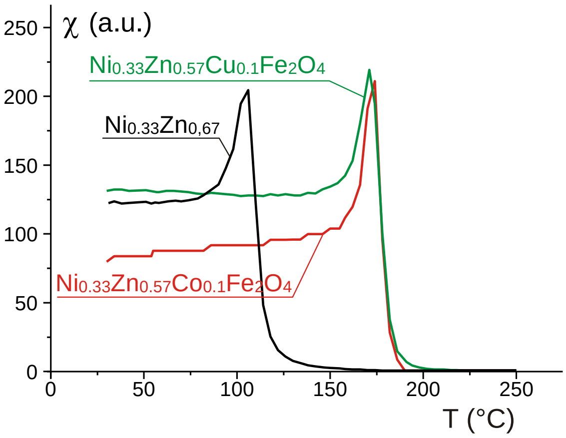


Fig. 5. Temperature dependence of magnetic susceptibility of pure and Cu/Co substituted NiZn ferrite powder.

The imaginary permeability μ'' remains very low for frequencies below several tens (for ferrite with Me = Cu^{2+}) or several hundreds (for ferrite with Me = Co^{2+}) of megahertz and increases above a certain frequency. A peak in μ'' corresponding to the dispersion of μ' can be identified at the resonance frequency of 19.8 MHz (Me = Cu^{2+}) and 131 MHz (Me = Co^{2+}), respectively. The observed resonance type of frequency dispersion of complex permeability is related to different magnetizing mechanisms (the domain wall displacements and spin rotations) and strongly depends on the dopant (Cu^{2+} or Co^{2+}) [11]. Incorporation of Cu^{2+} or Co^{2+} ions into the sublattices in the inverse NiZn spinel ferrite caused magnetic disorder accompanied with strengthening of the super exchange interaction and change of the magnetic moments, resulting in a variation of the spontaneous magnetization and also the permeability.

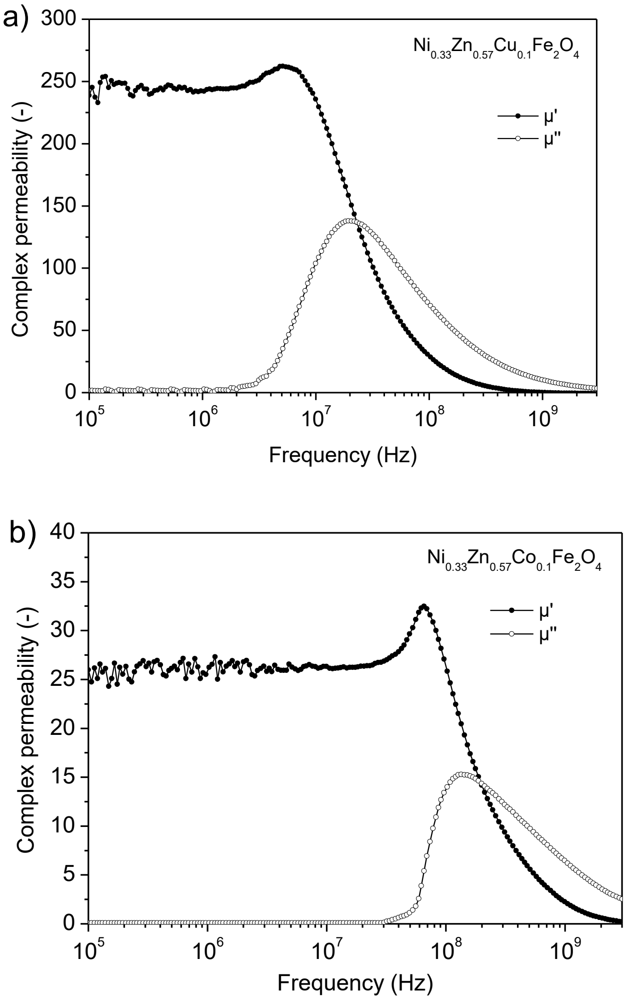


Fig. 6. Frequency dependences of real μ' and imaginary μ'' parts of complex (relative) permeability $\mu = \mu' - j\mu''$ for ferrite $Ni_{0.33}Zn_{0.57}Me_{0.1}Fe_2O_4$ with a) Me = Cu^{2+} and b) Me = Co^{2+}.

The smaller value of μ' (≈ 25) for ferrite with Me = Co^{2+} is due to the fact that cobalt has mostly an effect on the pinning of domain walls by inducing a magnetocrystalline anisotropy. The pinning force depends on cobalt content but it is also grain size (or crystallite size) dependent: the smaller the grain size, the stronger the pinning force. The small grain size has led to the reduction of contribution of domain wall displacements to the permeability.

5 CONCLUSIONS

The $Ni_xZn_{1-x}Fe_2O_4$ (x = 0.30, 0.33, 0.36, 0.42, 0.50, 0.70) and $Ni_{0.33}Zn_{0.57}Me_{0.1}Fe_2O_4$ (Me = Cu^{2+}/Co^{2+}) ferrite compounds were prepared by self-propagated auto-combustion method. The thermomagnetic analysis results of the first series of samples helped to find out and appropriate chemical composition of ferrite specimen with regard to thermal and magnetic order stability. The X-ray diffraction analysis of substituted NiZnMe ferrite indicates the presence of single-phase cubic spinel structure without other crystalline phases. Higher magnification on SEM shows that the clusters are created of small grains of sub-micrometer size. It proves the same fact concluded from the Hopkinson peak in $\chi(T)$ dependence. Complex permeability measurements exposed significant difference of the real component of permeability, related to the noticed crystallite size variation, between ferrites with Me = Cu/Co. Strong increase of the Curie temperature (by 100°C) enables these ferrites to use as stable core material for transformers in switching power supplies.

Acknowledgement

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