

CHANGES OF NiZn PROPERTIES BY SUBSTITUTION OF Zn WITH Cu AND Co IONS

Jozef Sláma* – Martin Šoka* – Anna Grusková** – Mariana Ušáková*
– Vladimír Olah* – Vladimír Jančárik*

Partial substitutions of Zn^{2+} ions with Cu^{2+} and Co^{2+} ions in $Ni_{0.33}Zn_{0.67}Fe_2O_4$ ferrite were investigated. The temperature dependences of the magnetic susceptibility $\chi(T)$ were used on study of the superexchange A-B interaction, and A-A or B-B interaction for substituted NiZn ferrites.

Keywords: susceptibility, magnetic moment, Curie temperature, ferrites, super exchange interaction

1 INTRODUCTION

Electromagnetic interference has become a specific type of environmental pollution, due to the utilization of electrical and electronic devices in industrial, commercial and special applications; therefore attention has been paid towards finding suitable microwave absorber to solve this problem. Substituted NiZn ferrites have been found to be adequate materials for such an application and other microwave devices due to their low-price, high saturation magnetization, convenient Curie temperature and other hysteresis loop parameters. Their microstructure, intrinsic and extrinsic magnetic properties, as well as the atomic diffusivity and sintering kinetics can be modified by a doping with an adequate amount of the divalent metallic ions or rare-earth ions. It also leads to modification of their electromagnetic and therefore microwave absorbing properties.

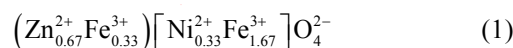
2 EXPERIMENTAL

The presented work is focused on the effects of two different substituents - Cu and Co on the microstructure and magnetic properties of NiZn ferrite with the chemical formula $(Ni_{0.33}Zn_{0.67})_{1-x(y)}Cu_x(Co_y)Fe_2O_4$, synthesized by a wet method from an organic-metallic precursor with glycine, using low-temperature auto-combustion. The samples were annealed at 850 °C for 6 hours. The aim is to study the effects of NiZn stoichiometry by a partial substitution of Zn^{2+} only with Cu^{2+} , or Co^{2+} ions and investigate the distribution of individual ions within the A and B sublattices within the spinel ferrite structure. The elementary cell of NiZn ferrite consists of eight molecules $(Zn_xFe_{1-x})_A [Ni_{1-x}Fe_{1+x}]_B O_4$. Measurements of the temperature dependence of magnetic susceptibility $\chi(T)$ was the main method of analysis. Partial substitution of Zn^{2+} ions by a divalent Cu^{2+} as well as Co^{2+} in $Ni_{0.33}Zn_{0.67}Fe_2O_4$ was investigated. The temperature dependences of the magnetic susceptibility

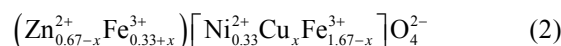
$\chi(T)$ were determined by the bridge method in an alternating magnetic field of 421 A/m at 920 Hz.

3 PARTIAL SUBSTITUTIONS OF DIVALENT Zn^{2+} IONS BY Cu^{2+} IONS

In the first step, change of ions distribution within the spinel structure is caused by partial substitution of divalent Zn^{2+} ions by Cu^{2+} ions. The $\chi(T)$ dependences are in Fig. 1a. The value of the Curie temperature T_C increases up to approximately 300 °C with the content of Cu^{2+} ions up to $x = 0.3$. The main reason can be that Cu^{2+} ions prefer the B sublattice of the spinel structure. In the case of non - substituted ferrite where the content of Cu^{2+} ions is $x = 0$; we can use the mode



There is a change of the substitution with Cu^{2+} with content x



where the magnetic moment of the Cu^{2+} ion is $1\mu_B$ [1-2] and therefore the magnetic moment related to per molecule of ferrite will be given by the expression

$$(0 \times (0.67 - x) + 5 \times (0.33 + x)) [2.2 \times 0.33 + 1 \times x + 5 \times (1.67 - x)] \mu_B \quad (3)$$

By entering of $x Cu^{2+}$ ions into B sublattice, the same amount of x of Fe^{3+} ions is moved from it into the A sublattice instead of $x Zn^{2+}$ ions. Increase of Fe^{3+} ions concentration in A sublattice causes increase of A-B interaction, from which the rises of T_C value were found, Fig. 1(a), (b)

* Department of Electromagnetic Theory; jozef.slama@stuba.sk, ** Department of Electrotechnology, Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia

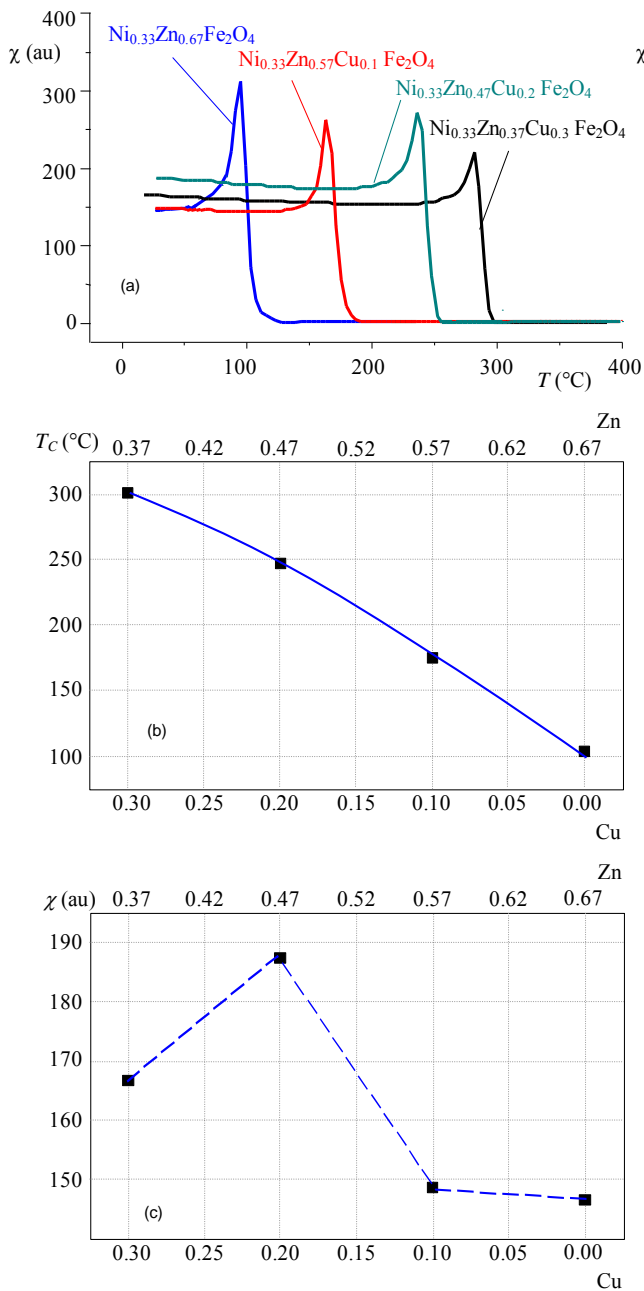


Fig. 1 (a) - temperature dependences of magnetic susceptibility of Cu²⁺ substituted NiZn ferrite, (b) - dependence of the Curie temperature on Cu²⁺ ions content, (c) - dependence of the initial susceptibility on Cu²⁺ ions content.

In this case, the rule, that the decrease of Zn²⁺ ions content causes increase of T_C is already valid. On the other hand, decrease of Fe³⁺ ions in B positions causes decrease of B-B interactions and consequently decrease of angle of Yafet-Kittel canting of sublattices up to the content of 0.47 Zn²⁺ [3] (ie $x \sim 0.2$ in our case). The total effective magnetic moment m_e (ie different between magnetic moment of B and A sublattice) reaches maximum value, because the value of magnetic moment of B sublattice is maximized and therefore also the saturation polarization J_s reaches maximum value.

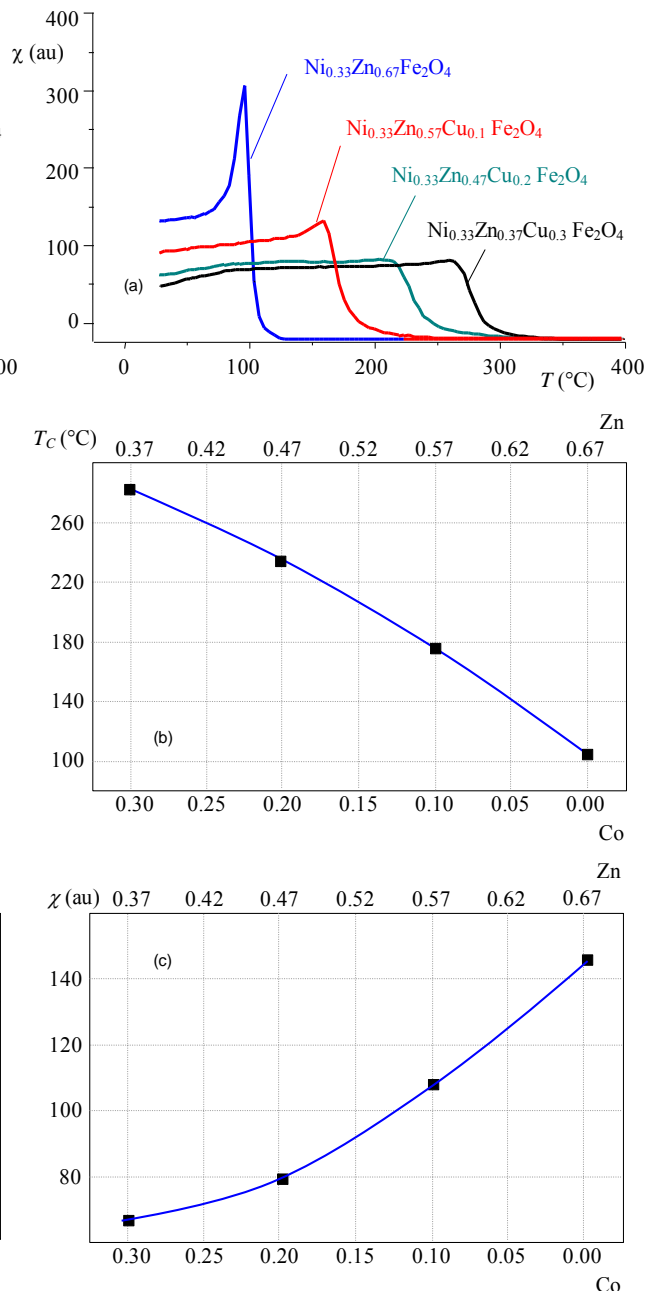


Fig. 2 (a) - temperature dependences of magnetic susceptibility of Co²⁺ substituted NiZn ferrite, (b) - dependence of the Curie temperature on Co²⁺ ions content, (c) - dependence of the initial susceptibility on Co²⁺ ions

Additional increase of Cu²⁺ ions (for $x > 0.2$) content causes decrease of m_e because the content Fe³⁺ ions increases in A and decreases in B sublattice, therefore also J_s decreases. When assuming, that the effective anisotropy does not change with the substitution of Zn²⁺ ions by Cu²⁺ ions within the range $x \in <0; 0.3>$, by the formula

$$\chi = J_s^2 / A_{ef} \quad (4)$$

implies that the change of $\chi(x)$ should be proportional to the change of $J_s^2(x)$. Consequently, according to the assumptions mentioned above, the change of χ caused by

Cu^{2+} substitution can be determined by the change of J_S^2 as a result of decrease of Zn^{2+} ions amount in A positions. Such substitution of Zn^{2+} by Cu^{2+} ions allows to prepare thermally stable sintered NiZnCu ferrites with relatively high permeability (susceptibility) [4-5].

4 PARTIAL SUBSTITUTIONS OF DIVALENT Zn^{2+} IONS BY Co^{2+} IONS

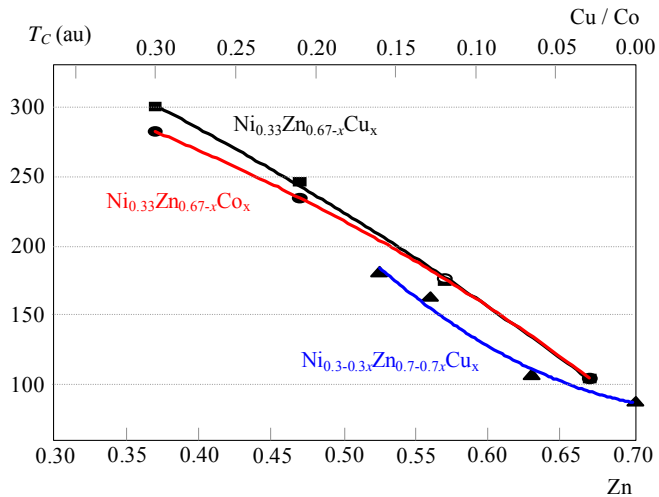
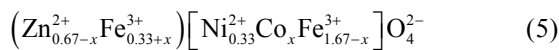


Fig. 3. Curie temperature dependencies on $\text{Cu}^{2+} / \text{Co}^{2+}$, resp. Zn^{2+} , ions content on $\text{Ni}_{0.33}\text{Zn}_{0.67-x}\text{Cu}_x$, $\text{Ni}_{0.33}\text{Zn}_{0.67-x}\text{Co}_x$ and $\text{Ni}_{0.3-0.3x}\text{Zn}_{0.7-0.7x}\text{Cu}_x$ ferrite samples annealed at $850\text{ }^\circ\text{C}/6\text{h}$.

Similar measurements were performed on $\text{Ni}_{0.33}\text{Zn}_{0.67}$ ferrite with partial substitution of divalent Zn^{2+} ions by Co^{2+} ions. The samples were also annealed at $850\text{ }^\circ\text{C}/6\text{h}$. The value of the Curie temperature increases with the content of Co^{2+} ions and for $x = 0.3$ achieves $T_C \approx 265\text{ }^\circ\text{C}$ (Fig. 2a, b). It can be caused by Co^{2+} ions behaviour which prefer B positions for substitution content. The model describing non-substituted state (1) will change by substitution of Co^{2+} ions with content x to



and the corresponding magnetic moment will be given by the formula

$$\begin{aligned} & (0 \times (0.67 - x) + 5 \times (0.33 + x)) [2.2 \times 0.33 + 3 \times x + \\ & + 5 \times (1.67 - x)] \mu_B \end{aligned} \quad (6)$$

magnetic moment of the divalent Co^{2+} ion is $3\mu_B$ [1-2]. The enter of x Co^{2+} ions into the B sublattice shifts the same

amount of Fe^{3+} ions into A sublattice instead of Zn^{2+} ions. Increase of the Fe^{3+} ions content in A sublattice causes A-B interactions to be stronger and therefore it causes higher value of T_C , Fig. 3. Again, as in the case by Cu^{2+} ions substitution, the rule is valid that decrease of the Zn^{2+} ions content causes observed increase of T_C . This rule could be extended so that when the substitution causes increase of Zn^{2+} ions in A positions, there will be decrease of A-B interactions and then also T_C [6-7].

5 DISCUSSION

Comparison of dependence of T_C on the substitution content $\text{Cu}^{2+} / \text{Co}^{2+}$, Zn^{2+} ions respectively, in $\text{Ni}_{0.33}\text{Zn}_{0.67-x}\text{Cu}_x$, $\text{Ni}_{0.33}\text{Zn}_{0.67-x}\text{Co}_x$ and $\text{Ni}_{0.3-0.3x}\text{Zn}_{0.7-0.7x}\text{Cu}_x$ ferrites is in Fig. 3. Substitution with Cu or Co ions causes just slightly different changes in $\text{Ni}_{0.33}\text{Zn}_{0.67-x}\text{Me}_x$ ferrites. In the case of $\text{Ni}_{0.3-0.3x}\text{Zn}_{0.7-0.7x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ferrite the value of the Curie temperature T_C is lower for any content of Zn^{2+} ions. Cu^{2+} ions prefer B sites and replace the respective part of Ni^{2+} ion, then a part of $0.7x$ Fe^{3+} ions shift from B to A sites, where take place of $0.7x$ Zn^{2+} ions. Consequently the A-B exchange has lower value. Dependences in Fig. 3 show that the content of Fe^{3+} ions particularly determinates the A-B interactions and therefore the T_C value.

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