

# SUBSTITUTED NiZn FERRITES FOR PASSIVE SENSOR APPLICATIONS

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The paper is devoted to the preparation of NiZn ferrite with small substitutions of copper by means of ceramic technology. The influence of small Be and/or Cu substitution on various magnetic properties of NiZn ferrites (such as *eg* the Curie temperature  $T_c$ , coercivity  $H_c$ , initial permeability  $\mu_i$ , complex permeability  $\tilde{\mu}$ , saturation magnetisation  $M_s$  and hysteresis loop shape) has been analysed by means of various experimental methods and interpreted from the point of view of preparation technology optimisation and possible applications of such materials in sensor technology. A strong correlation between the substituent content and resulting properties has been observed, thus allowing preparation of material with the properties tailored for any particular application.

Keywords: substituted ferrites, magnetic properties, passive sensors

## 1 INTRODUCTION

NiZn ferrites with high permeability and high frequency are widely used in the telecommunications, electronic and information technology, surface-mount technology and various sensors. Currently, our attention is focused on two basic sensor types using these materials in the form of the composites of plastics (or rubber) and ferrite powders - active sensors using magnetically hard ferrites (acting mainly as permanent magnets with changing properties due to mechanical load, *etc*) and passive sensors using magnetically soft ferrites. Passive sensors are intended for contactless monitoring of the status of various objects. For passive sensors the NiZn ferrites with high permeability and high operating frequencies seem to be promising. The resulting change of magnetic properties is intended to be evaluated via the analysis of reflected or transmitted rf-signal. Passive sensors could be used even in the cases when other sensors do not withstand high operating temperature, pollution, mechanical load due to acceleration and vibrations of monitored object and/or electromagnetic interferences. For these applications the properties of NiZn ferrites have to be improved by means of proper substitution of selected ion types. Therefore the compositions of these ferrites include a high quantity of non-magnetic Zn ferrite leading to decrease of Curie temperature and thermo-stability.

Consequently, a search for new thermo-stable, highly permeable and low-loss composition on the basis of NiZn ferrites is very actual. The properties of ferrites are very sensitive to the method of preparation and the amount and type of substitution. It is known that high permeability could be achieved by increase of the density of ferrites.

## 2 GENERAL INFORMATION

The basic magnetic and electrical properties of NiZn ferrites depend on the types of cations present at different sites of the spinel structure. The spinel structure consists

of a cubic-closed packed oxygen ion with metallic ions occupying tetrahedral (A) and octahedral (B) interstitial sites. The magnetic structure of the spinel ferrites depends upon the types of magnetic ions residing in A and B sites. They interact with each other through the superexchange interaction A-A, B-B and A-B with magnetic polarisations relations  $J_{AB} > J_{BB} > J_{AA}$ . Thus, basic magnetic properties depend strongly on the oxidation states and the distribution of cations at A and B sites in the lattice. The anti-ferromagnetic A-B superexchange interaction is the main cause of the cooperative behaviour of magnetic dipole moments in the ferrites, known as ferrimagnetism of Ni-Zn ferrites below the Curie temperature. The basic magnetic properties of the examined Ni-Zn ferrites depend also on the types of cations at different lattice sites. As a result, it is possible to obtain a good soft magnetic material by optimising the choice of the substituents.

In the preparation process of NiZn ferrites many kinds of substituents are suitable to improve final properties. The aim of several works was the investigation of the effects of the change of NiZn stoichiometry by partial substitution of:

- i) only Ni<sup>2+</sup> with divalent cations such as Cu<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Be<sup>2+</sup> and other
- ii) only Zn<sup>2+</sup> with divalent (*eg* Cu<sup>2+</sup>, Be<sup>2+</sup>, *etc*)
- iii) both Ni<sup>2+</sup> and Zn<sup>2+</sup> proportionally with divalent cations (some of above mentioned along with V, As, Bi, Ge, Cr, Ti or rare-earth ions)

that can influence the microstructural properties, intrinsic parameters, atomic diffusivity and the sintering kinetics, [1-5]. The variation of properties can be accomplished also by means of introduction of non-magnetic trivalent Me<sup>3+</sup> ions (such as Y<sup>3+</sup>, Cr<sup>3+</sup>, *etc*) at the expense of Fe<sup>3+</sup> ions in the octahedral site. Me<sup>3+</sup> ions must have high preference for B site even at very low concentrations. The decrease of Fe<sub>2</sub><sup>3+</sup> to Fe<sub>2- $\delta$</sub> <sup>3+</sup> increases the A-B exchange interaction as well as the magnetic polarisation of the system. This peculiarity can be interpreted in the view of the replacement

of  $\text{Fe}^{3+}$  ions in the octahedral sites at low concentrations with  $\text{Me}^{3+}$  ions. This is due to the fact that the magnetic behaviour of the ferrites is largely governed by iron-iron interaction via spin coupling. It was apparent from several studies and our experiments and that the ferritisation process and electrical resistivity can be enhanced by a small range of iron deficiency in the chemical composition. It reduces the amount of  $\text{Fe}^{2+}$  ions in the ferrites and inhibits electrons from hopping motion between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions at the octahedral sites of the spinel unit cell.

It has been shown that the addition of tetravalent Ti influences the microstructural, electric and magnetic properties of the ferrites, too. Bhise *et al* [6] have studied the role of MnTi and MnSn substitutions on electrical properties of NiZn ferrites and Cr-substituted NiZn ferrites. The observed variation in *ac* conductivity for  $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Cr}_y\text{Fe}_{2-y}\text{O}_4$  as a function of Cr contents at various temperatures has shown that the conductivity was decreasing with increasing Cr contents. In the presented study  $\text{Fe}^{3+}$  ions were partially replaced with Cr ions

The Curie temperature  $T_c$  that depends on  $\text{Fe}_2\text{O}_3$  contents has also an external appearance. The maximum of  $T_c$  corresponds to equimolar composition. The ferrites with small lack of  $\text{Fe}_2\text{O}_3$  have shown decreasing of  $T_c$ . At the same time the ferrites with small surplus of  $\text{Fe}_2\text{O}_3$  (up to 0.5 molar % from equimolar composition) have also high Curie temperature, what can be explained by the strengthening of the exchange interaction according to Neél's model. On the other hand, the ferrite with small surplus of  $\text{Fe}_2\text{O}_3$  have minimum of initial permeability  $\mu_i$ . This can be explained by formation of magnetite ( $\text{Fe}_3\text{O}_4$ ). The positive magnetostriction constant ( $\lambda_s$ ) compensates the negative values of the other spinel ferrites in the composition, that increases the anisotropy of solid solution, and accordingly the initial permeability.

Satisfying results from the point of view of thermal stability have been achieved by doping the ferrite by Cu ions. The choice of Cu is based on the fact that

- (1) it increases the density and decreases sintering temperature,
- (2) it increases the resistivity of the material. At an optimum doping of Cu we have succeeded in developing a low power loss material operating in the MHz frequency region,
- (3) it increases the Curie temperature thus resulting in increasing the thermo-stability of the material.

The presence of Cu ions activates the sintering processes in ferrites.  $\text{Cu}_2\text{O}$  has a low melting temperature and forms a liquid phase during sintering of ferrites, increases the ferrite density. The increase of the density results in the reduction of demagnetising field due to the reduction of the pores, the maximum magnetic flux density and the remanent induction increase, but the coercivity  $H_c$  decreases. On the other hand, the real part of the complex permeability increases and the losses associated with the imaginary part decrease. The real part of complex permeability as well as the initial permeability depends on the sintering temperature, time and is strongly influenced by

the type of substituting ion.

### 3 EXPERIMENTS

Substituted NiZnMe ferrites with the chemical composition  $(\text{Ni}_{0.3}\text{Zn}_{0.7})_{1-x}\text{Me}_x\text{Fe}_2\text{O}_4$  with Me substituent being Cu or Be have been prepared by ceramic method. The substituent contents  $x$  was varied within the interval  $x \in (0, 0.25)$  ions per formula unit (i./f.u.) and the samples have been sintered at  $1250^\circ\text{C}$  in the air. The saturation magnetisation was measured by means of vibration sample magnetometer (VSM). The Curie temperatures were determined from the thermal dependencies of magnetic susceptibility measured by means of inductance bridge method. The frequency dependencies of complex permeability of prepared ferrites were obtained using two impedance analysers in the frequency range from 100 kHz to 100 MHz, [7].

### 4 RESULTS AND DISCUSSION

The variation of saturation magnetisation  $M_s$  as a function of substituent contents  $x$  for both substituting elements is shown in Fig. 1. In both cases,  $M_s$  was found to increase with increasing concentration of substituent  $x$ . The culmination point for both curves is about  $x=0.2$  within tested interval of concentrations.

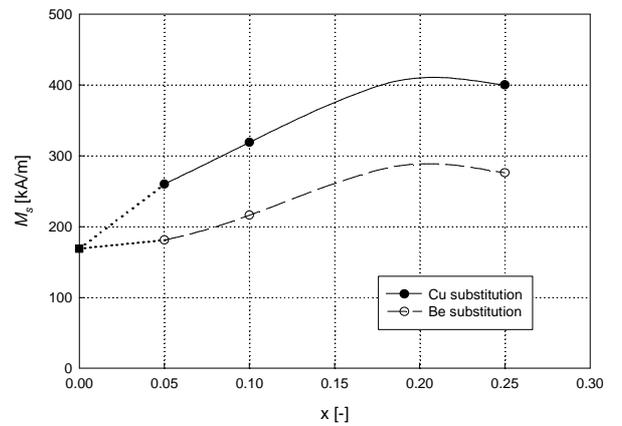
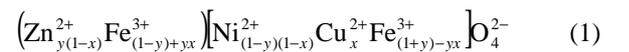


Fig. 1. The saturation magnetisation  $M_s$  of Be- and Cu- substituted NiZn ferrite as a function of substitution coefficient  $x$ .

If  $\text{Me}=\text{Cu}$ , the variation of saturation magnetisation depends on Cu cations occupying B-lattice sites.  $\text{Cu}^+$  ions have marked preferences for B-sites. The incorporation of Cu ions into the basic composition of  $(\text{Ni}_{0.3}\text{Zn}_{0.7})_{1-x}\text{Cu}_x$  yields higher magnetic moment according to the schema



$$\overbrace{\left( 0 + 5(1-y+yx) \right) \left[ m_B(\text{Ni})(1-y)(1-x) + m_B(\text{Cu})x + 5(1+y-yx) \right]} \quad (2)$$

where taking the  $\text{Fe}^{3+}$  magnetic moments as  $5\mu_B$ ,  $m_B(\text{Ni})$  and  $m_B(\text{Cu})$  are the moments of Ni and Cu ions, respectively, in Bohr magnetons. Theoretical schema indicates that the net magnetic moment for  $y=0.7$  and  $x=0$  reaches the value of

$$\begin{aligned} & \overrightarrow{(5(0.3))} \overleftarrow{2.2(0.3)+5(1.7)} \overrightarrow{\triangleq 1.5\mu_B + 9.16\mu_B} \\ & \triangleq |\overline{M}_A - \overline{M}_B| = 7.66\mu_B \end{aligned} \quad (3)$$

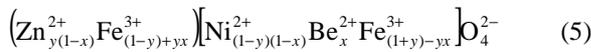
where  $m_B(\text{Ni})=2.2\mu_B$ . The measured saturation magnetic moment had lower value of  $\sim 4.6\mu_B$  due to B-sites canting into two sublattices B' and B''. The reason is that the non-magnetic Zn ions substitute the magnetic  $\text{Fe}^{3+}$  ions resulting in weakening the A-B interaction due to high magnetic dilution of A-lattice. For  $y=0.7$  the Cu substitution ( $x>0$ ) provides that the concentration of  $\text{Ni}^{2+}$  ions decreased by the adequate amount of  $\text{Cu}^{2+}$  ions in B-positions and the migration of some ( $yx$ )  $\text{Fe}^{3+}$  ions from B-sites to A-sites is provided by residual contents of  $\text{Cu}^{2+}$  ions. The magnetic moment (for  $y=0.7$  and  $x=0.25$ ) reaches the value of

$$\begin{aligned} & \overrightarrow{(5(0.3+0.7\cdot 0.25))} \overleftarrow{2.2(0.3\cdot 0.75)+1.9(0.25)+5(1.7-0.7\cdot 0.25)} \\ & \triangleq 2.375\mu_B + 8.59\mu_B \triangleq |\overline{M}_A - \overline{M}_B| = 6.215\mu_B \end{aligned} \quad (4)$$

where  $m_B(\text{Cu})=1.9\mu_B$ . The theoretical net moment has lower value than that for  $x=0$ , but the measured saturation moment had higher value of  $\sim 5.6\mu_B$  in comparison with  $\sim 4.6\mu_B$  for  $x=0$  (without Cu substitution).

The strength of A-B interaction was increased for  $x=0.25$  since it depends on the increase of Fe ions in A-positions. Thus, A-sites are able to align more moments of B-lattice ions antiparallel one to another, which increases the magnetisation of B-lattice due to decrease of canting between magnetisation vectors of B' and B'' sublattices. Therefore, total magnetisation increases with each substitution step up to  $x=0.2$  and then slightly decreases. The Curie temperature increases with  $x$ , resulting in increasing thermal stability of NiZnCu doped ferrite.

If a part of Ni and/or Zn ions is substituted with  $\text{Be}^{2+}$  ions, it has to be taken into account that  $\text{Be}^{2+}$  ions can occupy both A- and B-sites. Direct effect on A-B and B-B exchange interaction may have yield higher magnetic moment according to the next schema if the Be ions occupy B-sites only:



$$\overrightarrow{(0+5(1-y+yx))} \overleftarrow{2.2(1-y)(1-x)+0+5(1+y-yx)} \quad (6)$$

For  $y=0.7$  and  $x=0.25$  the net theoretical magnetic moment reaches the value of

$$\begin{aligned} & \overrightarrow{(5(0.3+0.7\cdot 0.25))} \overleftarrow{2.2(0.3\cdot 0.75)+5(1.7-0.7\cdot 0.25)} \\ & \triangleq 2.375\mu_B + 8.12\mu_B \triangleq |\overline{M}_A - \overline{M}_B| = 5.745\mu_B \end{aligned} \quad (7)$$

In case when Be ions will occupy B-sites only, theoretically  $yx=0.175$   $\text{Fe}^{3+}$  ions will move from B-sites into A-sites. Thus, the magnetic moment  $M_A$  increases from  $1.5\mu_B$  to  $2.375\mu_B$  (1.58 times) and the value of  $M_B$  decreases from  $9.16\mu_B$  to  $8.12\mu_B$ . This has direct effect on the decrease of B-

B interaction and the increase of A-B interactions resulting in reduction of canting within B lattice. As a consequence, the measured saturation magnetic moment has larger value comparing to the material without Cu-substitution ( $x=0$ ). On the other hand, the fact that the  $\text{Cu}^{2+}$  ions contribute and  $\text{Be}^{2+}$  ions do not contribute to the magnetic moment of B-sites  $M_B$  leads to the increase of theoretical as well as experimental value of the magnetisation of NiZnCu ferrite compared to NiZnBe material. This is in agreement with the measured data shown in Fig. 1. In case of Be-substitution the Curie temperature increases with  $x$ , resulting in the increase of thermal stability of NiZnBe ferrite.

The reduction of particle size is a well-known method to subdivide the ferrite into single-domain particles, which increases the coercivity  $H_c$  towards the maximum value controlled by the sample anisotropies. Our experimental results are shown in Fig. 2, where the coercivity of Cu or Be doped NiZn ferrites is plotted against the average grain size  $D$ . The dependence of initial permeability  $\mu_i$  for both Cu or Be substituted NiZn ferrites where  $x \in (0, 0.25)$  on the grain size is shown in Fig. 2, too. The presented experimental data of  $H_c$  and  $\mu_i$  fit well into the predictions following from the classical grain size theory. The relation of  $H_c$  proportional to  $1/D$  for relatively large grain sizes ( $D>100$  nm) reflects the classical rule that good soft magnetic properties require very large grains. The measured data of initial permeability show correspond to the theory as well, being essentially inversely proportional to the coercivity, i.e. proportional to  $D$ .

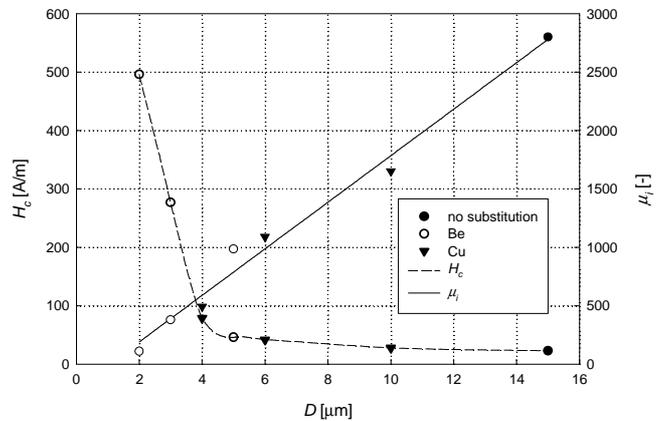


Fig. 2. The coercivity  $H_c$  and initial permeability  $\mu_i$  as a function of grain size  $D$ .

The frequency dependencies of the real part of the complex permeability  $\mu'$  have been studied as a function of the composition. In Fig 3, four frequency spectra of the real component of the complex permeability  $\mu'(f)$  are observed to decrease with increasing of Cu or Be contents. For both substituents at  $x=0.05$  the value of  $\mu'$  at low frequencies, referred to as the initial permeability  $\mu_i$ , can be explained mainly by the reversible domain walls displacement due to higher grain size values ( $>4\text{nm}$ ), [5]. The dependencies in Fig. 3 also show, that the value of  $\mu'$  is practically independent on the frequency up to few hundreds of kHz. Beyond this limit it shows a resonance peak whose frequency increases

with increasing of Cu dopant contents. The resonance peaks are more evident in case of copper substitution. In this case the initial permeability is higher in comparison with Be-substitution. The increase of Cu and Be contents probably enhances the influence of effective magnetic anisotropy and the resonance and/or relaxation dispersion is observed at higher frequencies.

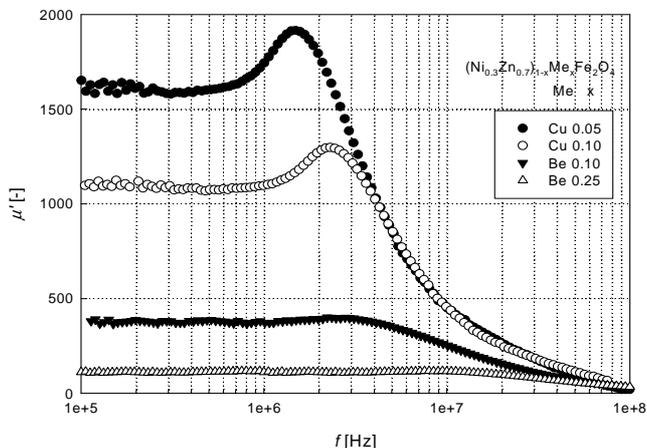


Fig. 3. The real component of complex permeability for Be- or Cu-substituted NiZn ferrites.

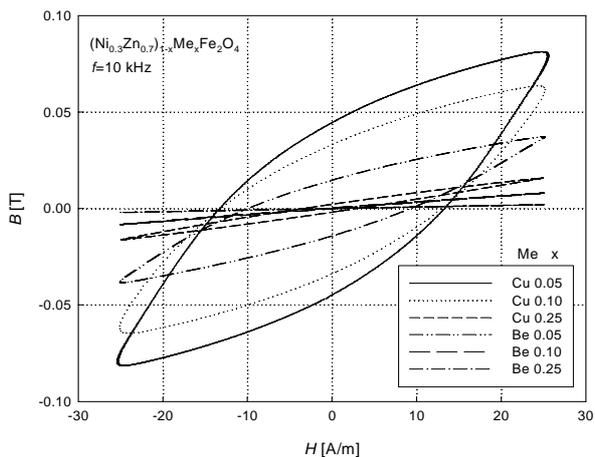


Fig. 4. The hysteresis loops for Be- or Cu-substituted NiZn ferrites.

The hysteresis loops for all ferrite samples were obtained at certain values of exciting magnetic field strength ( $H_m=25$  A/m and 100 A/m) and frequencies ( $f=1$  kHz and 10 kHz) by exciting the toroidal samples with a sinusoidal waveform. As an example, Fig. 4 presents the minor hysteresis loops for all ferrite samples, measured at the magnetic field intensity of  $H_m=25$  A/m and frequency  $f=10$  kHz. As can be seen here, increasing the substituent contents causes the hysteresis loops to be more narrow and the slope of line connecting opposite hysteresis loop peaks (main loop axis) decreases.

Both the  $\text{Be}^{2+}$  and  $\text{Cu}^{2+}$  ions have shown predominant impact on measured hysteresis loops. Be-substituted NiZn ferrites showed a little lower values of maximum magnetic flux density compared to Cu substituted NiZn ferrites. The

study of the minor hysteresis loops has also shown that with increasing the frequency the shape of the hysteresis loops at low exciting field amplitude ( $H_m=25$  A/m) changes from straight line to nearly „elliptical” one and the mean slope decreases, due to the relaxation processes.

## 5 CONCLUSIONS

The substituted NiZn ferrites offer an interesting system for study of the influence of divalent ions (Cu, Be, etc.) for the case in which the exchange correlation between tetrahedral and octahedral sublattices is controlled. The substitution ions offer probably one way for changing the grain size. In summary they offer a new possibility for tailoring superior soft magnetic properties comparable to those of NiZn and MnZn ferrites. The advantage is also a significantly better thermal stability of the soft magnetic properties.

The results confirmed, that the substitution of Cu or Be plays very important role in controlling the magnetic properties of  $(\text{Ni}_{0.3}\text{Zn}_{0.7})_{1-x}\text{Me}_x\text{Fe}_2\text{O}_4$  ferrites. Our experiments have shown a strong influence of Cu and Be contents on the initial permeability, saturation magnetisation, coercivity as well as hysteresis loop area associated with the energy loss. Thus, the substituent concentration along with proper technology becomes a strong tool for the preparation of the ferrites tailor-made for any particular application.

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