# INFLUENCE OF IRON DEFICIENCY ON ELECTROMAGNETIC BEHAVIOUR OF NANOPARTICLE FERRITES

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## 1. Introduction and theoretical assumptions

This work is focused on the investigation of iron deficiency effect in the NiZn ferrites characterised by the spinel structure and chemical composition $(Ni_{0.33}Zn_{0.67})_{1+x}Fe_{2-x}O_4$ with $x$ = 0.00, 0.08, 0.12 and 0.20 ions per formula unit (i./f.u.) on resulting electromagnetic properties of prepared ferrite samples. The influence of various ratios of divalent ions $Ni^{2+}$ and $Zn^{2+}$ to trivalent ions $Fe^{3+}$ on hysteresis loop parameters of the samples subjected to thermal treatment at 1000°C and 1200°C was studied.

Spinel NiZn ferrites appertain to the group of widely used soft magnetic materials and thanks to their excellent magnetic properties (e.g., high initial permeability, electrical resistivity, low magnetic and dielectric loss, etc.) they are promising for high-frequency as well as many other applications in electronic devices. The magnetic and electrical properties of the ferrites are noticeably influenced by the microstructure, chemical composition and redistribution of cations within tetrahedral and octahedral sites of spinel lattice. The small iron deficiency in NiZn ferrite affects its electromagnetic and structural properties and, as a consequence, the electrical resistivity is increased due to the change of chemical composition and hopping of electrons between $Fe^{2+}$ and $Fe^{3+}$ ions within both sublattices [1]. However, the presence of minor second phase - zincite (ZnO), which is created besides major spinel phase in Fe-deficient NiZn ferrites, plays an important role as a grain growth inhibitor and thereby positive influences sintering and densification [2, 3].

## 2. Experimental details

The NiZn ferrite samples with the deficiency of iron were synthesized by innovative glycine-nitrate-acetate process which belongs to chemical wet methods of the preparation of the ceramic materials [4]. The calculated amounts of raw salts as $Ni(NO_3)_2.6H_2O$ and $Zn(CH_3COO)_2.2H_2O$ were dissolved in water solution of glycine $NH_2CH_2COOH$ and added into highly concentrated water solution of $Fe(NO_3)_2.9H_2O$. The homogenised mixture of metal-nitrate-acetate-glycine precursor was dried and the organic components of precursor were eliminated by means of auto-combustion reaction. The powder obtained from auto-combustion reaction was mixed with polyvinyl alcohol acting as binding material and pressed at 200 MPa in order to get tablets with the diameter 15 mm. The tablets were thermally treated at 1000°C or 1200°C for 6 hours; subsequently the circular hole was drilled into the centre of the tablets by means of water-beam drilling machine. The shrinkage of tablets sintered at temperature 1200°C achieved ~30%; samples calcined at 1000°C were shrinked by about ~20%. Ring-shaped samples prepared this way with the outer diameter of about 12 mm and inner diameter of 6 mm (or 10.5 mm and of 5 mm for samples prepared at 1200°C) were used for the measurement of hysteresis loops.

The magnetic properties of prepared ferrites were examined by means of experimental equipment built-up from commercially available instruments along with hardware modules and

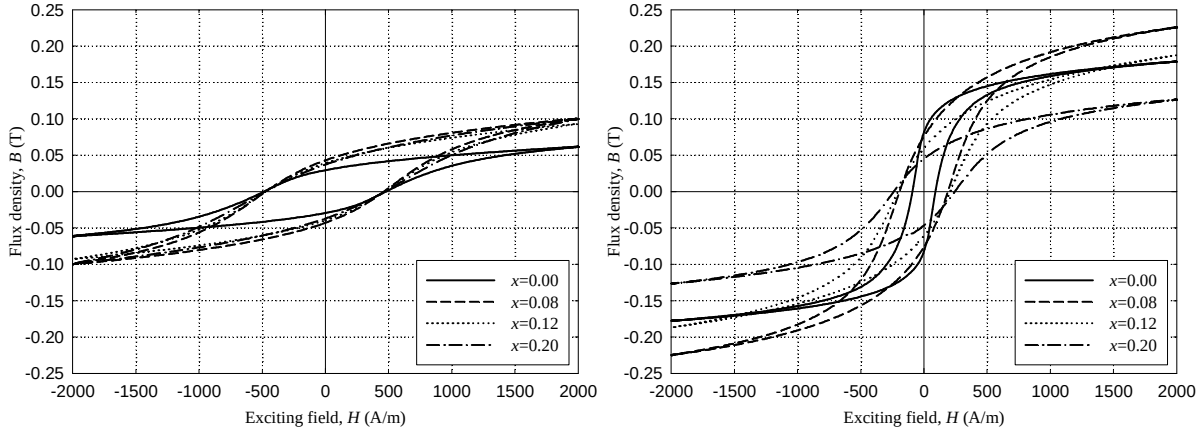
components developed at our institution controlled by customized software. Sets of hysteresis loops measured at feedback-controlled sinusoidal exciting field waveform shape with amplitude $H_{max}$ changing from 2000 down to 10 A/m with 10 A/m step were measured. The frequency used was 50 Hz, thus the dynamic effects in the investigated materials can be neglected. Various magnetic parameters were evaluated from these loops.

## 3. Results and discussion

In Fig.1 combined influence of sintering temperature along with iron deficiency on the hysteresis loops is demonstrated. As can be seen in Fig.1a corresponding to the samples sintered at lower temperature ($T_s$ = 1000°C) the maximum flux density $B_{max}$ at $H_{max}$ =2000 A/m reaches only about 100 mT. In this case, the coercivity $H_c$ almost does not depend on $x$, only the remanent magnetic flux density $B_r$ changes with decreasing of iron contents in the sample. Situation becomes very complicated in case of samples sintered at 1200°C, where the coercivity monotonously increases with $x$ meanwhile the remanent flux density decreases, Fig.1b. Also, the maximum flux densities significantly increased. This complexity can be explained by widely known correlation among the coercivity, saturation magnetic polarisation $I_s$ and the first anisotropy constant $K_1$

$$H_c = \frac{2K_1}{I_s} \tag{1}$$

since the magnetic anisotropy, represented by the first anisotropy constant is influenced by the size of ferrite particles (which varies with the conditions during the fabrication), significantly affects the coercivity and initial permeability, [5, 6]. The shape of hysteresis loop is thus dependent upon multiple mutually coupled factors.

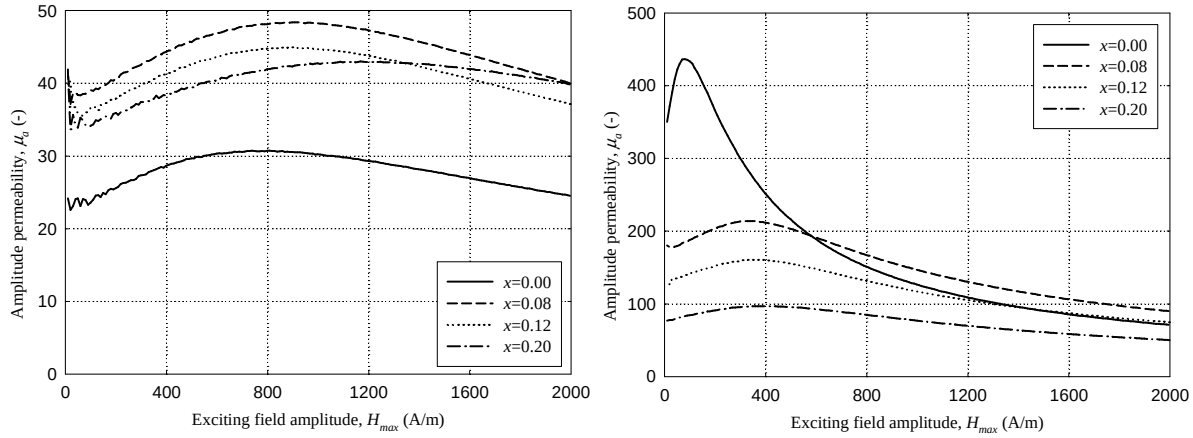



*a) sintered at 1000°C* *b) sintered at 1200°C*

Fig.1: *The hysteresis loops of* $(Ni_{0.33}Zn_{0.67})_{1+x}Fe_{2-x}O_4$ *ferrites.*

The dependencies of amplitude permeability $\mu_a$ upon exciting field amplitude $H_{max}$ obtained from the sets of minor hysteresis loops are shown in Fig.2. From these curves, the initial permeability $\mu_i$ was found as an extrapolation to zero fields. These values were compared to those directly measured at weak fields (1 A/m) with no significant differences (less than 1-2%). Again, complicated behaviour, observable already from the shape of hysteresis loops, depending on the sample composition as well as sintering temperature can be seen. Especially, huge increase of the peak value of amplitude permeability as well as the initial permeability associated with higher sintering temperature, reaching in some cases more than one order, is visible. One can see also substantially increased values of the amplitude permeability in all the interval of exciting fields of the samples sintered at 1200°C comparing to 1000°C. The

variations due to different sintering temperatures can be explained by the anisotropy effects that become more significant in the samples with larger crystalline grains, since the average grain size $D$ dependence upon $T_s$ in these materials can be usually fitted by the second-order polynomial function, [6, 7]. Another important effect can be observed when the iron content decreases - at $T_s$ = 1000°C the iron deficiency increases the permeability, meanwhile in case of samples with $T_s$ = 1200°C the amplitude permeability at weak fields decreases. Influence of iron deficiency can be attributed to the rearrangement of Ni, Zn and Fe ions within basic crystalline cell depending on the chemical composition resulting in changes of magnetic moments per unit cell corresponding to individual sublattices. Also, spin canting can be important and the presence of zincite influences this behaviour as well.




*a) sintered at 1000°C* *b) sintered at 1200°C*

Fig.2: *The amplitude permeability as a function of exciting field amplitude.*

Important magnetic parameters, including the hysteresis loop area $A_l$ representing the energy density or total power losses, obtained from the measured hysteresis loops and permeability dependencies are summarised in Table 1. As can be seen, in case of samples sintered at 1000°C the changes of parameters with increasing iron deficiency are less evident than for 1200°C; at higher sintering temperature the modifications are more pronounced and nearly linear ($B_r$, $H_c$), or quadratic ($\mu_i$). On the other hand, the hysteresis loop area $A_l$ as a function of $x$ shows qualitatively similar trend regardless of the sinterig temperature. Thus, elevated sintering temperatures offer the possibility to manage the magnetic parameters with $x$ more finely and precisely.

Tab. 1. *The properties of prepared* $(Ni_{0.33}Zn_{0.67})_{1+x}Fe_{2-x}O_4$ *ferrites.*

| $T_s$ (°C) | $x$ i./f.u. | $B_r$ (mT) | $H_c$ (A/m) | $A_l$ (J/m$^3$) | $\mu_i$ (-) |
|---|---|---|---|---|---|
| 1000 | 0.00 | 29.46 | 486.1 | 89.7 | 22 |
| 1000 | 0.08 | 42.87 | 469.9 | 135.6 | 38 |
| 1000 | 0.12 | 39.15 | 473.7 | 123.5 | 34 |
| 1000 | 0.20 | 37.01 | 475.4 | 132.5 | 33 |
| 1200 | 0.00 | 81.02 | 92.1 | 67.3 | 329 |
| 1200 | 0.08 | 75.75 | 193.5 | 117.8 | 172 |
| 1200 | 0.12 | 60.13 | 206.7 | 102.3 | 130 |
| 1200 | 0.20 | 45.84 | 241.6 | 90.1 | 76 |

## 4. Conclusions

Experimental results presented in this work clearly demonstrate the influence of chemical composition along with thermal treatment of the prepared materials with the aim of demonstrate the posibilities how to create materials devoted to the needs of any specific application simply by replacing iron by Ni and Zn ions as well as by varying sintering temperature.

Slight changes of constituing elements as well as preparation technology steps can bring about significant changes of resulting properties via the variations in crystalline structure associated with the relocation of magnetic and non-magnetic ions into both sublattices of ferrimagnetic material with spinel structure. Detailed knowledge and better understanding of all the physical-chemical mechanisms associated with the crystalline structure, particle size distribution, etc. allows the improvement of preparation procedure management leading to precisely targeted material properties.

Higher sintering temperature appears to be more convenient from the point of view of controlling final magnetic parameters, since they become more sensitive to the changes in chemical composition, in this case carried out by increasing the iron deficiency. On the other hand, higher temperatures mean higher energy consumption in mass production, thus the compromise needs to be found between the energy demands and the effectivity of material parameters handling. Moreover, if one asks for materials with the amplitude permeability less dependent upon applied field, lower sintering temperatures are better since the dependencies of permeabilty upon applied field are flatter than those at higher temperatures.

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