The influence of selected ions on various characteristics of Nickel-Zinc ferrites

Mariana Ušáková*, **Elemír Ušák***, **Martin Šoka***, **Ján Lokaj*******

One of acknowledged methods remarkably improving structural, magnetic and electrical properties of spinel ferrite systems is the substitution of iron ions by some trivalent ions. In the family of spinel ferrites, thanks to its high saturation magnetization and electrical resistivity as well as low losses, the nickel-zinc ferrite is a very important magnetic material used in many applications in electrical engineering and electronics. The properties of these materials are in general dependent upon chemical composition, method of preparation, stoichiometry, sintering time, temperature as well as the atmosphere, *etc*. In this study the influence of appropriately selected ions (M = In^{3+}, Nd^{3+}, Dy^{3+} and Er^{3+}), partly replacing Fe^{3+}, on the microstructure and magnetic properties of spinel ferrite with the composition $Ni_{0.42}Zn_{0.58}M_{0.02}Fe_{1.98}O_4$ fabricated by means of standard ceramic technology was investigated.

K e y w o r d s: spinel nickel-zinc ferrites, rare earths, structural and magnetic properties

1 Introduction

NiZn ferrites are characterized by mixed spinel crystalline structure which is normal with respect to Zn and inverse for Ni according to the scheme

$$(Zn_xFe_{1-x})_A[Ni_{1-x}Fe_{1+x}]_B$$

where A and B represent the tetrahedral and octahedral sublattice, respectively. Its ferrimagnetic ordering is the result of super-exchange interactions among the ions in tetrahedral (A) and octahedral (B) sublattice. The $3d$ unpaired spins of transition metals exhibit an antiparallel arrangement which takes place through oxygen anions [1]. The substitution of ferric ions into ferrite systems by some trivalent ions causes the magnetic dilution due to the incorporation of diamagnetic atoms, such as In and Al or other, *eg*, rare earth elements (RE), and thus remarkably influences their structural, magnetic and electrical properties [2–4]. The increasing amount of In^{3+} ions in the spinel nickel ferrite structure where they occupy tetrahedral sites (A) (up to $x = 0.3$ ions per formula unit, i/fu) improves the magnetic as well as structural parameters [5]. Introducing of RE into spinel lattice is associated with the formation of the RE-Fe interactions which leads to small changes in the values of saturation magnetization M_s and Curie temperature T_C. These parameters are affected by the amount, type as well as ionic radius r_{ion} of substituting ions [6]. RE ions prefer the occupation of the octahedral position of the spinel lattice since the radii of RE elements are much larger than those of transition metal ions. Moreover, these large ions could probably cause lattice distortion which determines of the solubility

of RE^{3+} in the spinel structure; the overcome of solubility limit leads to the formation of the secondary phases. These secondary phases are usually the orthoferrite and oxides of RE [7].

It is known that the microstructure (*ie*, the distribution of ions into the magnetic sublattices of fundamental crystalline cells) of spinel ferrites associated with the chemical composition along with fabrication technology route noticeably influences their magnetic properties. Even a small content of additional components often results in significant changes in the microstructure associated *eg* with different ionic radii of substituting elements (even a lattice distortion can occur). As a consequence, the substitution of the original elements by various other ions allows fine control of the resulting magnetic parameters. Rare-earth (RE) elements are especially appropriate substituents for high-frequency applications, since already a small amount of RE ions causes the increase of the electrical resistivity and the relative loss factor. Good microwave absorption properties of rare-earth substituted NiZn ferrites were confirmed as well, [4].

In this work the effect of indium, neodymium, dysprosium and erbium on the microstructure and magnetic behavior of spinel nickel-zinc ferrite with composition $Ni_{0.42}Zn_{0.58}M_{0.02}Fe_{1.98}O_4$ has been studied. The choice of starting ferrite was based on the previous research where the magnetic characteristics of the ferrite with various ratios of Ni and Zn have been investigated; consequently, the sample with maximal remanent magnetization having the composition $Ni_{0.42}Zn_{0.58}Fe_2O_4$ was preferred for further substitutions [1].

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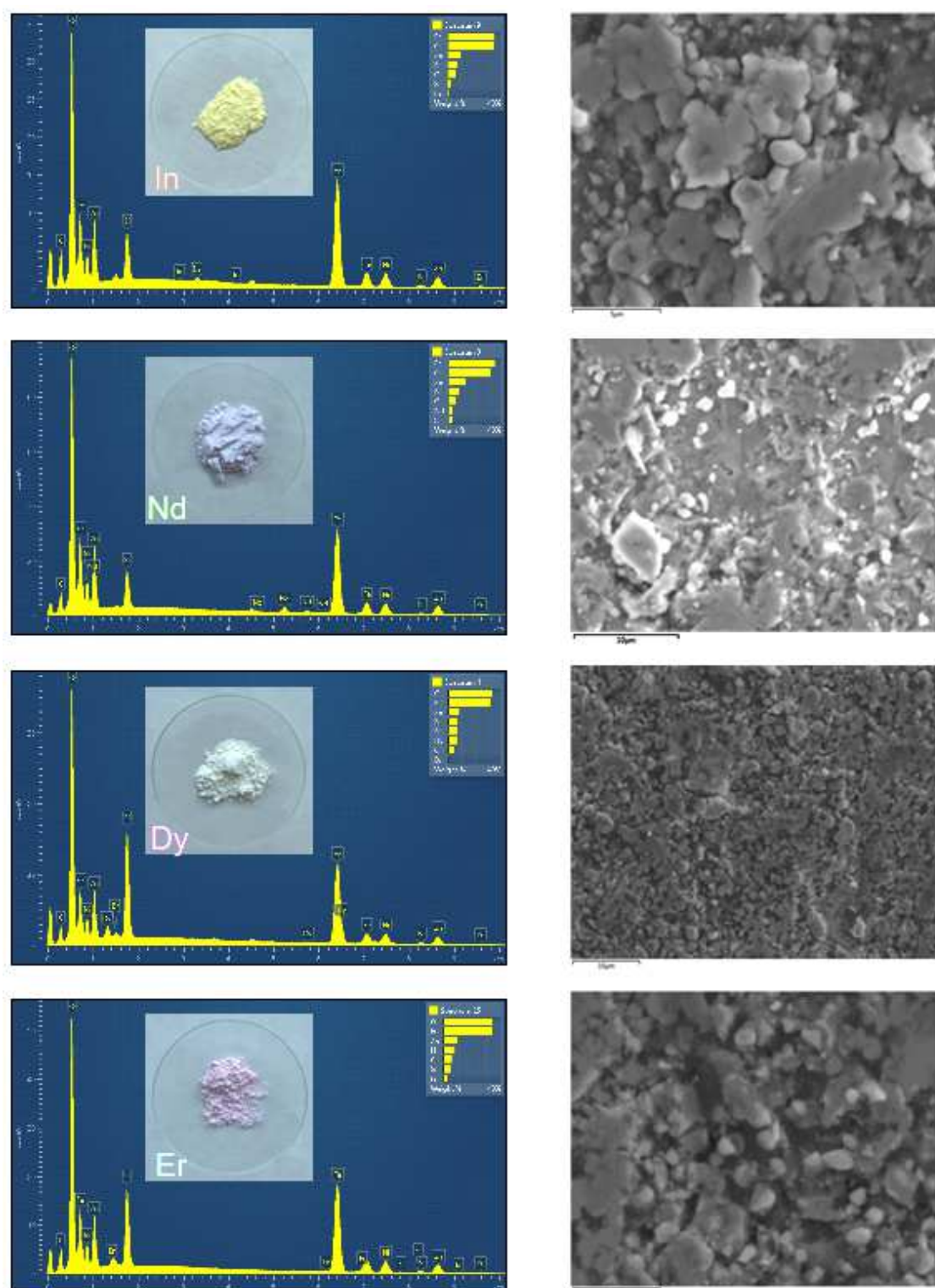
Fig. 1. (a) – EDX analysis and (b) – SEM images (b) of $Ni_{0.42}Zn_{0.58}M_{0.02}Fe_{1.98}O_4$ ferrite with $M = In^{3+}$, Nd^{3+}, Dy^{3+} and Er^{3+} ions

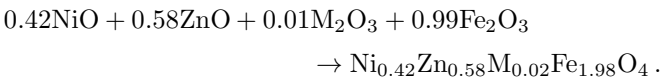## 2 Experiment

2.1 Materials and synthesis

Ferrite powders with the chemical composition $Ni_{0.42}Zn_{0.58}M_{0.02}Fe_{1.98}O_4$ with $M = In^{3+}$, Nd^{3+}, Dy^{3+} and Er^{3+} ions (partly substituting iron in the formula)

were prepared by means of standard double-sintering ceramic method based on solid-state reaction of relevant metal oxides of analytical reagent (AR) grade (purity better than 99 %). Dehydrated raw powders were weighed according to the required stoichiometric fractions and mixed in liquid ethanol medium in agate grinder. Further, the homogenized material was thermally treated in

two steps; firstly, it was pre-sintered at the temperature of 950 °C/1 hour followed by the final sintering at 1200 °C/6 hours has been carried out. Required spinel structure was created by means of solid state reaction expressed as

$$0.42\text{NiO} + 0.58\text{ZnO} + 0.01\text{M}_2\text{O}_3 + 0.99\text{Fe}_2\text{O}_3$$
$$\rightarrow \text{Ni}_{0.42}\text{Zn}_{0.58}\text{M}_{0.02}\text{Fe}_{1.98}\text{O}_4\,.$$

Ring-shaped samples with outer diameter D of about 12 mm, inner diameter $d = 6$ mm and thinkness h about 3.5 mm were used for the measurement of low-frequency magnetic properties.

2.2 Characterization techniques

The microstructure as well as the chemical composition of prepared samples has been verified by means of scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) used for semi-quantitative analysis.

Curie temperatures T_C were determined from the temperature dependencies of ac magnetic susceptibility $\chi(T)$ of ferrite powder samples using balanced ac bridge method.

Important magnetic parameters of ferrite samples, such as the coercive field H_c, remanent magnetic flux density B_r, amplitude permeability μ_a, *etc*, were found from the series of minor hysteresis loops at measured at defined (sinusoidal) exciting field intensity waveform $H(t)$ with the frequency $f = 50$ Hz and maximum exciting field intensity amplitude $H_{\max}$ varying from 1 to 2500 A/m measured by means of computer-controlled BH-curve tracer. Also, the initial permeability μ_i was evaluated from the dependencies of amplitude permeability upon applied field amplitude $H_{\max}$ as an extrapolation to zero field.

All the experiments have been performed in accordance with relevant standards within the specifications provided by the instrument vendors.
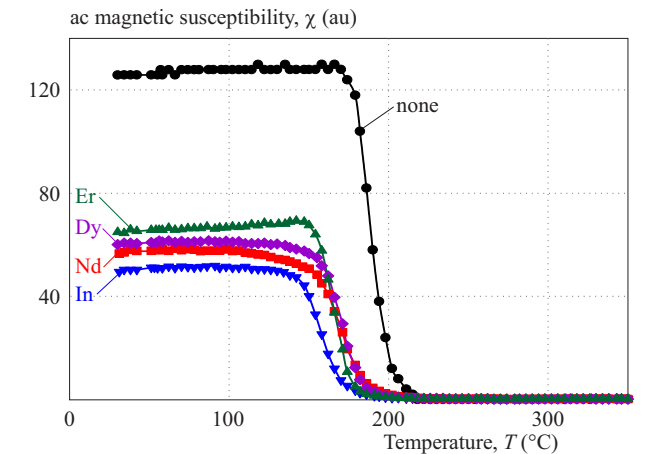
3 Results and discussion

3.1 Structural properties

The EDX analysis confirmed the presence of all expected elements, such as Ni, Zn, Fe, O and M (In, Nd, Dy, Er) in all the compositions of prepared ferrite samples, Fig. 1(a). The residual elements (Si and C) correspond to the carrier medium and conductive coating used for the testing. The differences against the theoretical values can be most likely attributed to the structural inhomogeneity and irregular location of particular ions in spinel structure resulting from the ceramic method of the preparation.

The weight percentage of individual elements is summarized in Tab. 1.

Table 1. The mass content of individual ions in $\text{Ni}_{0.42}\text{Zn}_{0.58}\text{M}_{0.02}\text{Fe}_{1.98}\text{O}_4$ ferrite

M	w_{Ni} (%)	w_{Zn} (%)	w_{M} (%)	w_{Fe} (%)	w_{O} (%)	w_{C} (%)	w_{Si} (%)
In	8.09	12.00	0.74	36.30	34.50	6.18	2.07
Nd	8.22	11.70	1.58	36.30	33.60	5.46	2.93
Dy	7.19	9.67	5.44	31.50	33.90	3.79	8.48
Er	7.80	9.80	2.68	34.60	34.80	5.46	4.79

The morphology of all the substituted NiZn ferrite samples is shown in Fig. 1(b). The SEM images show the presence of the ferrite particles of an irregular polyhedral shape with an average size of several micrometers. The ferrite particles are agglomerated into the clusters which are natural for magnetic materials. The presence of the second phase in ferrite samples is not visible due to the small amount of substituting element ($x = 0.02$) in all ferrite systems. This fact is in accordance with the results published in [4,8] where the second phase occurs in the spinel structure at higher contents of RE.
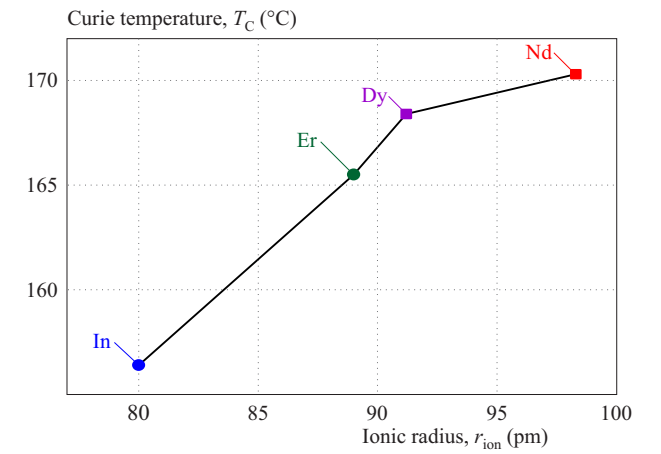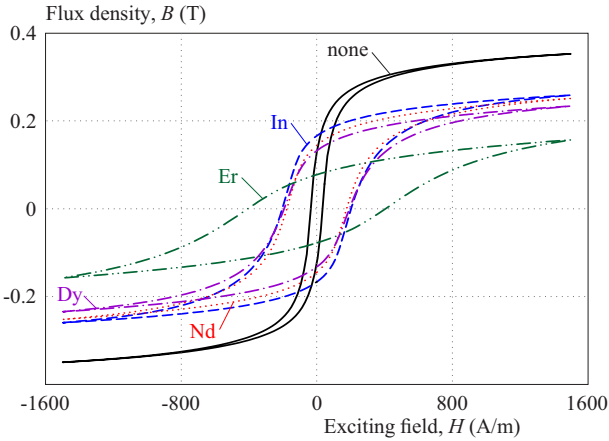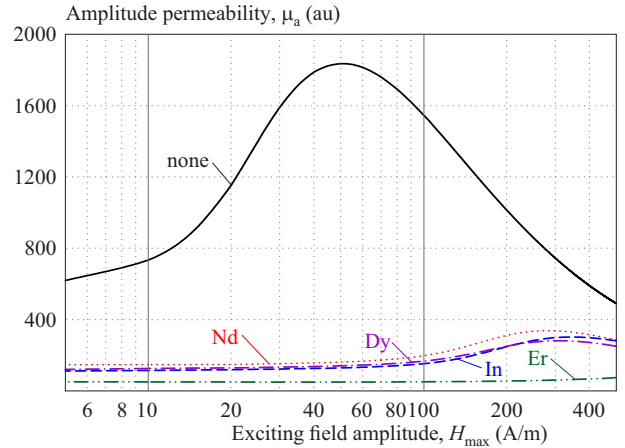

Fig. 2. The temperature dependencies of ac magnetic susceptibility $\chi(T)$

Fig. 3. Curie temperature T_C as a function of ionic radius r_{ion}

Table 2. Structural and magnetic parameters of $Ni_{0.42}Zn_{0.58}M_{0.02}Fe_{1.98}O_4$ ferrites

Ferrite composition	r_{ion}(pm)	T_C(°C)	H_c(Am^{-1})	B_r(mT)	μ_i(−)
$Ni_{0.42}Zn_{0.58}Fe_2O_4$	64.5	186.8	35.1	127.3	515
$Ni_{0.42}Zn_{0.58}In_{0.02}Fe_{1.98}O_4$	80.0	156.4	208.1	171.5	106
$Ni_{0.42}Zn_{0.58}Nd_{0.02}Fe_{1.98}O_4$	98.3	170.3	181.5	149.1	147
$Ni_{0.42}Zn_{0.58}Dy_{0.02}Fe_{1.98}O_4$	91.2	168.4	198.5	136.2	121
$Ni_{0.42}Zn_{0.58}Er_{0.02}Fe_{1.98}O_4$	89.0	165.5	469.4	97.2	52

Fig. 4. The hysteresis loops of the ferrites with different substituents obtained at $H_{max} = 1500$ A/m

Fig. 5. The amplitude permeability μ_a as a function of maximum applied field value H_{max}

3.2 Magnetic properties

In Fig. 2, the temperature dependencies of ac magnetic susceptibility per unit mass $\chi(T)$ can be found. From these curves, the Curie temperatures T_C of all the samples are determined from the dominant points of inflection. As can be seen, the room temperature susceptibility significantly depends on substituting ions. The non-substituted ferrite $Ni_{0.42}Zn_{0.58}Fe_2O_4$, in more details studied in [9], is characterized by the highest value of $T_C = 186.8$ °C compared to the substituted ferrites, see Tab. 2. Apparently, this can be attributed to the knowledge reported earlier that the exchange interactions Fe^{3+}–Fe^{3+} are stronger than Fe^{3+}–M^{3+}, which results in the decrease of T_C as a result of thermal misalignment of magnetic moments (acting against alignment due to the exchange interactions) taking place easier in substituted ferrites [6]. The largest decrease is observed for substitution by In^{3+} with the smallest ionic radius. The Curie temperature is thus observed to be influenced by the ionic radius of substituted element. M^{3+} ions entering the spinel lattice having the ionic radius substantially larger than that of substituted Fe^{3+} cause the deformation the lattice. An interesting observation in case of substituted ferrites is a nearly linear dependence of the Curie temperature upon the ionic radius $T_C(r_{ion})$ displayed in Fig. 3.

BH-loops of the ferrites with different substituents obtained at $H_{max} = 1500$ A/m is given in Fig. 4. Significant

differences in the shape of the loops and corresponding magnetic parameters (coercive field, remanent flux density, *etc*) are visible. The relative amplitude permeability μ_a was found as the ratio of the peak values of magnetic flux density B_{max} and applied field H_{max}, divided by the vacuum permeability μ_0. The amplitude permeability calculated from the peak values of all the measured minor hysteresis loops as a function of maximum applied field value $\mu_a(H_{max})$ is shown in Fig. 5. An extrapolation of these dependencies to zero fields yields the initial permeability μ_i. The measured values of important magnetic parameters of all the studied ferrite materials as well as the Curie temperatures and the effective ionic radii are summarized in Tab. 2.

4 Conclusions

Observed results indicate that even small quantities of M^{3+} ions replacing Fe^{3+} ions in octahedral position of spinel structure can act as the cause of considerable changes in the magnetocrystalline structure of the ferrites and, consequently, also in the magnetic behavior of ferrite materials. Thus, the required parameters of the material can be easily adjusted by embedding proper substituting ions into the spinel lattice. All the observations can be explained by the differences in magnetic moments of the ions replacing the iron in the octahedral B-sublattice and

also the lattice deformations depending directly on the ionic radii.

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