

MEASUREMENT OF PRINCIPAL MICROSTRUCTURE AND MAGNETIC PROPERTIES OF DOPED Ba FERRITE PARTICLES

Anna Grusková* — Jozef Sláma** — Alvaro González Angeles*** — Martin Šoka*

The magnetic and structural properties of substituted M-type Ba hexaferrites with composition $\text{BaFe}_{12-2x}(\text{Me}_1\text{Me}_2)_x\text{O}_{19}$ were prepared and studied. Divalent $\text{Me}_1 = \text{Ni}, \text{Zn}, \text{Sn}$ and tetravalent $\text{Me}_2 = \text{Ru}, \text{Zr}, \text{Ti}, \text{Sn}$ ionic combinations were used in various compounds. The phase purity of the samples was evaluated by temperature dependence of initial susceptibility $\chi(T)$ and specific saturation polarisation $J_{s-m}(T)$ and it was verified by Mössbauer spectroscopy. Mössbauer studies revealed that $\text{Ru}^{4+}, \text{Zr}^{4+}, \text{Ti}^{4+}$ replaced the Fe^{3+} ions in distinct sites. The $\text{Ni}^{2+}, \text{Zn}^{2+}$ and Sn^{2+} occupation sites were identified as well. Strong drop of $\Delta H_c(x)$ near $x = 0.1$ and slight decrease of $\Delta H_c(x)$ close to $x = 0.3$ for $(\text{NiRu})_x$ and $(\text{ZnRu})_x$ leads to the conclusion that the reached value of ΔH_c corresponds to planar anisotropy. The particles of all the ferrite samples exhibit a plate-like, nearly hexagonal shape with the diameter under 100 nm.

Keywords: Hexagonal ferrites, substitution effect, magnetic properties, magnetic susceptibility, Mössbauer spectra

1 INTRODUCTION

The M-type barium hexagonal ferrites (denoted as BaM) are considered to be the best magnetic material for electromagnetic wave absorbers due to their excellent magneto-dielectric properties, such as the high coercive force and saturation magnetisation, as well as an excellent chemical stability and corrosion resistivity. Moreover, due to their higher intrinsic magnetocrystalline anisotropy field, BaM can be used at much higher frequency than the ferrites with spinel and garnet structure. The M-type magnetically hard barium hexaferrites with appropriate substitutions are the most potential material for high-density magnetic particle media on account for their chemical stability and required magnetic characteristics [1-9]. Various substitutions are possible in $\text{BaFe}_{12}\text{O}_{19}$ composition. There are divalent Me_1 (Ni, Zn, Sn) together with tetravalent Me_2 (Ru, Zr, Ti, Sn) ionic combinations in the Fe^{3+} sites in the presented examples. Also, differently charged ions are possible, requiring the compensation of charge in another site. Substitutions of Fe^{3+} ions have a noticeable influence, directly affecting the magnetic infrastructure - changes of saturation polarisation, Curie temperature, coercivity, saturation and remanent magnetic flux density and other properties. According to ligand field theory the ions with d^1 up to d^4 orbitals prefer tetrahedral positions, meanwhile the ions with $d^6 - d^9$ orbitals occupy octahedral positions. Ions with d^0, d^5, d^{10} orbitals have no preference. It is also known, that less electronegative ions prefer tetrahedral coordination. However, the tendency to occupy a particular site depends also on the partner cation. In addition, ions with higher ionic radius prefer octahedral site. In this paper, the effect of metal ion combination (Ni, Zn, Sn with Ru, Zr, Ti, Sn) on the variation of magnetocrystalline structure and magnetic properties of the barium hexaferrite was investigated. One aim of the substitutions was to decline the easy magnetisation direction of one of the sublattices from the antiferromagnetic axis. It is an efficient way for controlling the value of coercivity H_c , which is preserving the value of J_s . This offers very effective media for data recording and microwave equipments.

The powdered samples with $0.0 \leq x \leq 0.6$ were prepared by two processing routes. Various Fe/Ba ratios were used for mechanical alloying and for the metallo-organic precursor method.

2 EXPERIMENTAL

The samples of $\text{Ba}(\text{Me}_1\text{Me}_2)_x\text{Fe}_{12-2x}\text{O}_{19}$ with divalent $\text{Me}_1 = \text{Ni}, \text{Zn}, \text{Sn}$ and tetravalent $\text{Me}_2 = \text{Ru}, \text{Zr}, \text{Ti}, \text{Sn}$ ionic combinations were synthesised by high energy milling (so-called mechanical alloying). The samples (assigned as Mx) were produced by using $\text{Fe}_2\text{O}_3, \text{BaCO}_3, \text{ZnO}, \text{NiO}, \text{SnO}$ and $\text{RuO}_2, \text{ZrO}_2, \text{TiO}_2$ and SnO_2 (all with purity of 98%). The mechanical milling was performed in a Segvay attritor using the ball/powder ratio of 15 and the Fe/Ba ratio of 10. The powders were milled within 28 hours in the air with an angular velocity of 400 rpm and with 250 ml of benzene added to avoid agglomeration at the bottom of mill. After mechanical milling, the samples were annealed at 1050°C for 1.5 hours. The samples of $\text{Ba}(\text{Me}_1\text{Me}_2)_x\text{Fe}_{12-2x}\text{O}_{19}$ with divalent $\text{Me}_1 = \text{Ni}$ and tetravalent $\text{Me}_2 = \text{Ti}, \text{Zr}, \text{Sn}$ ionic combinations (assigned as Sk) were prepared using a metallo-organic precursor method. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}, \text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}, \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}, \text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and other reagents (ZrOCl_2 , titanyl acetylacetonate $\text{TiO}(\text{acac})_2$) as soluble salts and citric acid, all of purity of 99%, were used as the initial materials. In this case Fe/Ba ratio of 10.8 was used. The amorphous citrate precursor was decomposed at 360°C for 5 hours. The samples were subsequently annealed at temperatures 700°C and 1070°C for 2 hours in a muffle furnace.

3 METHODS OF CHARACTERISATION

The phase purity of the samples was evaluated by the temperature dependence of initial susceptibility $\chi(T)$ and specific saturation polarisation $J_{s-m}(T)$ [10]. They were measured by using the bridge method in an alternating magnetic field of 421 A/m and 920 Hz and by a vibrating sample magnetometer Lake Shore 430 VSM applying an external magnetic field up to 1.2 T. The structure of samples was analysed

*Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Department of Electromagnetic Theory, Ilkovičova 3, 812 19 Bratislava 1, Slovakia, martin.soka@stuba.sk, **Evropský polytechnický institut, s.r.o., Osvození 699, 686 04 Kunovice, Czech Republic, ***Facultad de Ingeniería, Universidad Autónoma de Baja California, Blvd. Benito Juárez s/n, Cp 21280 Mexicali, BC, México

by the Mössbauer spectroscopy. The measurements were performed by a Mössbauer spectrometer with γ -ray source of ^{57}Co embedded in a rhodium matrix. The temperature dependences of $\chi(T)$ were measured by the bridge method at a constant rate of $4^\circ\text{C}/\text{min}$.

4 RESULTS AND DISCUSSION

The intrinsic magnetic properties (saturation polarisation J_s and Curie temperature T_C) and extrinsic properties (e.g. coercivity H_c) arise from the M-type structure with five distinct Fe sublattices, which are coupled by super-exchange coupling. The magnetic moments of the iron ions are arranged in parallel to hexagonal c-axis, but with opposite spin directions of the sublattices. Three sites named 12k, 2a and $4f_2$ have octahedral coordination, $4f_1$ has tetrahedral and 2b site has a fivefold (bipyramidal) coordination. Main aim of the substitution was to decline the magnetisation of one of the sublattices from anti-ferromagnetic axis, in order to the magnetocrystalline anisotropy become planar for a critical doping ratio x_c in some cases; while preserving the value of saturation polarisation J_s .

4.1 Coercivity decreasing

The changes of coercivity H_c were chosen as evaluation criteria of anisotropy variation. The evolution of H_c variation with x can be expressed by the coercivity difference, $\Delta H_c(x) = H_c(x) - H_c(0)$, where $H_c(0)$ is the coercivity of a sample with $x = 0$. Thus, $\Delta H_c(x)$ reflects the change of coercivity comparing to the pure BaM ferrite. The variation of $\Delta H_c(x)$ for selected (Me_1Me_2) substituent ions prepared by mechanical alloying (Mx) is presented in Fig. 1a, b, c where $\text{Me}_1 = \text{Ni}^{2+}$, Zn^{2+} , Sn^{2+} and $\text{Me}_2 = \text{Ru}^{4+}$, Zr^{4+} , Ti^{4+} . For substitutions with $(\text{Me}_1\text{Ru})_x$ the $\Delta H_c(x)$ displays decreasing tendency with x , as shown in Fig. 1a. Structural ionic configurations of $(\text{NiRu})_x$, $(\text{ZnRu})_x$ and $(\text{SnRu})_x$ are shown in Table 1. The strong decrease of $\Delta H_c(x)$ up to $x = 0.3$ for $(\text{NiRu})_x$ substitution in [11] leads to the conclusion that the anisotropy for $(\text{NiRu})_x$ becomes planar at a small substitution level. We observed the same trend of uniaxial anisotropy for $(\text{ZnRu})_x$. The strong fall of $\Delta H_c(x)$ near $x = 0.1$ and slight decrease of $\Delta H_c(x)$ observed near $x = 0.3$ for $(\text{NiRu})_x$ and $(\text{ZnRu})_x$ leads to the conclusion that the reached value of ΔH_c starts to correspond with planar anisotropy.

Structural changes on $(\text{NiRu})_x$ substitutions have shown, that Ru^{4+} ion preferably replaced the Fe^{3+} ions on 2b and then on tetrahedral sites $4f_1$ for Ni^{2+} as an associate ion, which occupies only octahedral sites $4f_2$ and 2a in this mixture.

Structural changes of $(\text{ZnRu})_x$ substitutions have shown, that Ru^{4+} preferably replaced the Fe^{3+} ions in bipyramidal 2b site for low x , and then in octahedral sites $4f_2 + 2a$ for Zn^{2+} as the associate ion, which occupies only tetrahedral sites $4f_1$ (see Table 1).

The fivefold site 2b has the strongest influence on high anisotropy of $\text{BaFe}_{12}\text{O}_{19}$ ferrite. We attribute the rapid

change of $\Delta H_c(x)$ and anisotropy in $(\text{NiRu})_x$ and $(\text{ZnRu})_x$ to preferential occupation of 2b site by Ru^{4+} ion. In addition, this tendency was observed also in the case of $(\text{CoRu})_x$ substitution in [12].

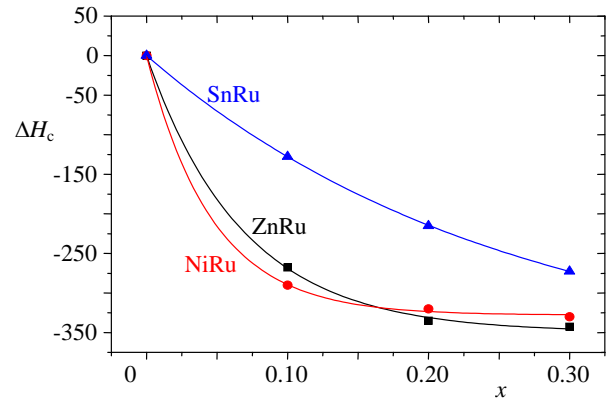


Fig. 1a. Change of coercivity difference $\Delta H_c(x)$ as a function of x for the samples $(\text{NiRu})_x$, $(\text{ZnRu})_x$ and $(\text{SnRu})_x$

Tab. 1. Ionic parameters and occupying sites preference of substituted mixtures

Substitution	orbital	radius	electronegativity	$4f_2$ o	2a o	$4f_1$ t	12k o	2b h
Zn^{2+} - Ru^{4+}	Zn^{2+} Ru^{4+}	$3d^{10}$ $4d^{10}$	0.074 0.067	1.65 2.20		*		*
Sn^{2+} - Ru^{4+}	Sn^{2+} Ru^{4+}	$4d^{10}$ $3d^8$	0.112 0.072	1.96 1.91	*	*		*
Ni^{2+} - Ru^{4+}	Ni^{2+} Ru^{4+}	$4d^4$	0.067	2.20	↓	↑	↓	↑
Lattice momentum (μ_B)					-	+	-	+
					10	5	10	30

o – octa, t – tetra, h – hexa

The $(\text{SnRu})_x$ mixture [13] produces a visibly smaller change of ΔH_c comparing to $(\text{NiRu})_x$, $(\text{ZnRu})_x$ or $(\text{CoRu})_x$ [12] substitution for $x \leq 0.3$. In spite of that, Sn^{2+} probably occupies the same $4f_2$ and 2a sites in $(\text{Sn}^{2+}\text{Ru}^{4+})_x$ as well as Ni^{2+} does in $(\text{NiRu})_x$ samples, while Ru^{4+} occupies also the identical 2b and $4f_1$ sites in both mixtures (Table 1). Thus we observed that not only Ru^{4+} ions, but also divalent Me^{2+} (Ni , Zn , Sn , Co) ions have an influence on ΔH_c reduction. However, Me^{2+} ions effect is much less significant. Different influence of divalent Ni^{2+} ion to comparison with Sn^{2+} ion on the behaviour of ΔH_c as a function of x may be probably explained by the fact that $\text{Ni}^{2+}(3d^8)$ has only 3d orbitals structure, whereas divalent Sn^{2+} (diamagnetic ion) has $(3d^{10}, 4d^{10})$ orbital structure and has too large ionic radius (0.112 nm). In $(\text{CoRu})_x$ mixture the $\text{Co}^{2+}(3d^7)$ ions displays also similar occupation of sites as Ni^{2+} cation in $(\text{NiRu})_x$ and both mixture have roughly the same behaviour of ΔH_c as a function of x . In $(\text{ZnRu})_x$ the $\text{Zn}^{2+}(3d^{10})$ cations again replaces the $\text{Fe}^{3+}(3d^6)$ ions, therefore this mixture exhibits similar $\Delta H_c(x)$ behaviour to $(\text{NiRu})_x$.

The coercivity variation of $(\text{NiZr})_x$ and $(\text{ZnZr})_x$ substituted BaM ferrites, up to $x = 0.6$, were prepared by mechanical alloying and are shown in Fig. 1b. $\Delta H_c(x)$ decreases visibly slowly in $(\text{NiZr})_x$ and $(\text{ZnZr})_x$ to compare with $(\text{Me}_1\text{Ru})_x$ samples.

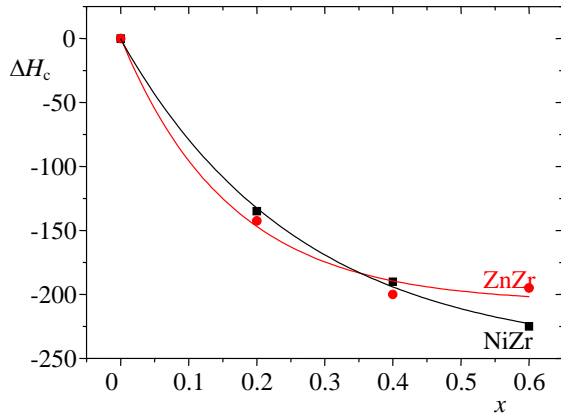


Fig. 1b. Change of coercivity difference $\Delta H_c(x)$ as a function of x for the samples $(\text{ZnZr})_x$ and $(\text{NiZr})_x$

Structural changes in $(\text{NiZr})_x$ substitutions have shown, that Zr^{4+} preferably replaced Fe^{3+} ions in 2b and then in tetrahedral sites $4f_1$ for Ni^{2+} as partner ion, which occupies octahedral sites $4f_2$ and 12k in this mixture. Regarding to $(\text{ZnZr})_x$ samples, Zn^{2+} ion has a strong preference for $4f_1$ tetrahedral coordination and Zr^{4+} preferably replaced Fe^{3+} ions in 2b and then in tetrahedral sites $4f_1$. The Zr^{4+} ion exhibits the same sites occupation as Ru^{4+} ion in $(\text{NiRu})_x$ and $(\text{ZnRu})_x$ but Zr^{4+} ion has somewhat larger ionic radius (0.073 nm) to comparison with Ru^{4+} (0.067 nm). Probably for this reason the $\Delta H_c(x)$ values are considerably lower than in $(\text{NiRu})_x$ and $(\text{ZnRu})_x$.

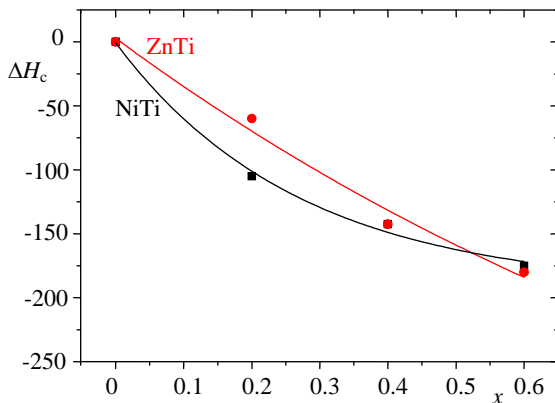


Fig. 1c. Change of coercivity difference $\Delta H_c(x)$ as a function of x for the samples $(\text{ZnTi})_x$ and $(\text{NiTi})_x$

The coercivity variation of $(\text{ZnTi})_x$ and $(\text{NiTi})_x$ substituted BaM ferrites (Fig. 1c), prepared by mechanical alloying, showed that ΔH_c decrease relative slowly in comparison with $(\text{Me}_1\text{Ru})_x$ and $(\text{Me}_1\text{Zr})_x$ samples. The behaviour of ΔH_c as a function of x decreased in all concentration rates for $(\text{ZnTi})_x$ and $(\text{NiTi})_x$ samples. Structural changes in $(\text{NiTi})_x$ substitutions have shown, that Ti^{4+} preferably replaced the Fe^{3+} ions in octahedral sites 12k and then in sites $4f_2$ for Ni^{2+} as the associate ion, which occupies octahedral sites $4f_2$ and 12k in this mixture. Regarding to $(\text{ZnTi})_x$ sample, Zn^{2+} ion has a preference for $4f_1$ and then in 2b position at higher substitution and Ti^{4+} preferably replaced the Fe^{3+} ions in 12k and then in octahedral sites $4f_2$.

4.2 Saturation polarisation variation

The resulting theoretical magnetic saturation polarisation J_s at a temperature T of $\text{BaFe}_{12}\text{O}_{19}$ per formula unit (p.f.u.) can be approximated by simple summation according to formula

$$J_s(T) = 6m_{12k}(T) - 2m_{4f1}(T) - 2m_{4f2}(T) + 1m_{2a}(T) + 1m_{2b}(T) \quad (1)$$

where m_n is the magnetic moment of Fe^{3+} ion in the n -th sublattice. Assuming a magnetic moment of $5\mu_B$ (Bohr magneton) per Fe^{3+} ion at 0 K we get a net polarisation of $20\mu_B$ (pfu) for the pure $\text{BaFe}_{12}\text{O}_{19}$ at this temperature. It is in agreement with the observed saturation polarisation for the pure compound J_s .

Influence of substitution on the net polarisation and coercivity H_c was investigated as well as possible limits of such an approach. Change of magnetic polarisation with doping ratio x is expressed by the difference $\Delta J_{s-m} = J_{s-m}(x) - J_{s-m}(0)$, where $J_{s-m}(0)$ is the measured specific magnetic polarisation of pure BaM ferrite ($x=0$). This dependence for selected samples prepared by mechanical alloying is shown in Fig. 2a, b.

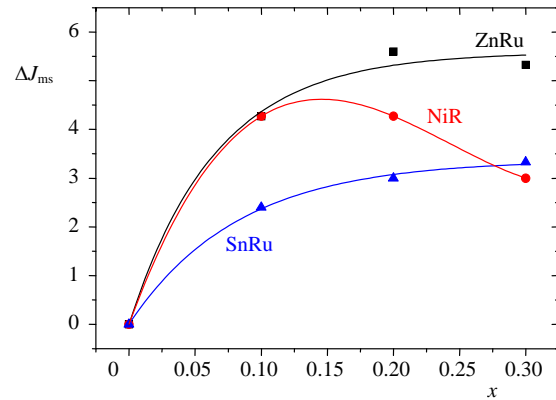


Fig. 2a. Change of specific polarisation ΔJ_{s-m} (a) as a function of x for $(\text{NiRu})_x$, $(\text{ZnRu})_x$ and $(\text{SnRu})_x$ samples

ΔJ_{s-m} increases with x (Fig. 2a) for $(\text{NiRu})_x$, $(\text{ZnRu})_x$ and $(\text{SnRu})_x$ substitutions presumably because the magnetic moments in the spin-down sublattices ($4f_1$, $4f_2$) decrease more than those in the spin-up sublattices (2a, 2b), (Eq. (1)). The Ru^{4+} ions seem to increase ΔJ_{s-m} , it can also be attributed to a strong preference of Zn^{2+} to tetrahedral, Ni^{2+} and Sn^{2+} to octahedral coordination and no particular preference of Ru^{4+} ions in $(\text{Me}_1\text{Ru})_x$ mixtures.

It can be seen that ΔJ_{s-m} decreases with x , (Fig. 2b) for $(\text{ZnZr})_x$, $(\text{NiZr})_x$, $(\text{NiTi})_x$ and $(\text{ZnTi})_x$ substitutions presumably because the magnetic moments in the spin-down sublattices ($4f_1$, $4f_2$) increase more than those in the spin-up sublattices (2a, 2b) (Eq. (1)).

The $\chi(T)$ dependences of $(\text{NiZr})_{0.4}$ and $(\text{NiSn})_{0.3}$ substituted BaM prepared by metallo-organic precursor method-Sk show a single phase structure with Hopkinson peaks. The $\chi(T)$ curve of the sample $(\text{NiTi})_{0.4}$ shows a weak maximum, probably owing to the presence of disordering in the composition which we can see in Fig. 3a.

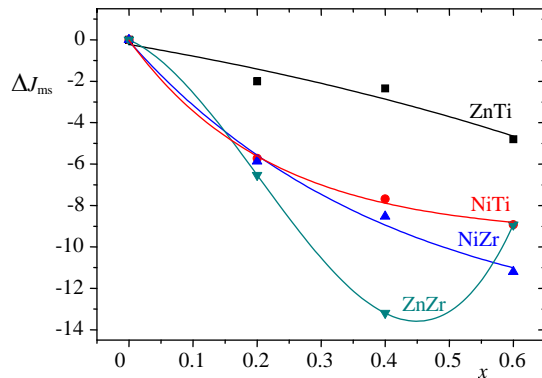


Fig. 2b. Change of specific polarisation ΔJ_{s-m} as a function of x for samples $(\text{ZnZr})_x$, $(\text{NiZr})_x$, $(\text{NiTi})_x$ and $(\text{ZnTi})_x$.

The soft drop of $T_C(x)$ dependences of $(\text{NiSn})_{0.3}$, $(\text{NiRu})_{0.3}$, $(\text{NiZr})_{0.4}$ and $(\text{NiTi})_{0.4}$, which were prepared by mechanical alloying, also showed the appearance of another phases at $\approx 585^\circ\text{C}$ which correspond to the nucleation of a secondary spinel phases (Fig. 3b).

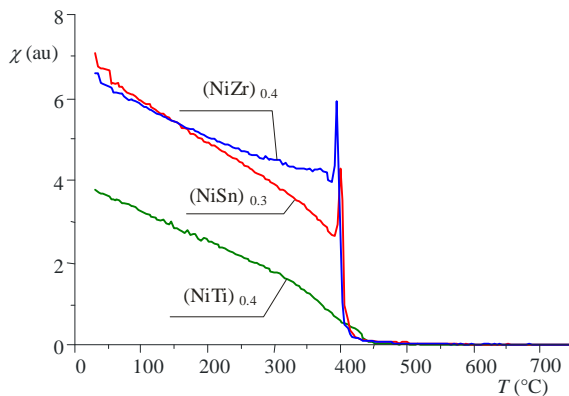


Fig. 3a. Temperature dependence of magnetic susceptibility $\chi(T)$ of (NiMe_2) . Substituted samples where $\text{Me}_2 = \text{Ti, Zr, Sn}$ prepared by metallo-organic precursor method-Sk.

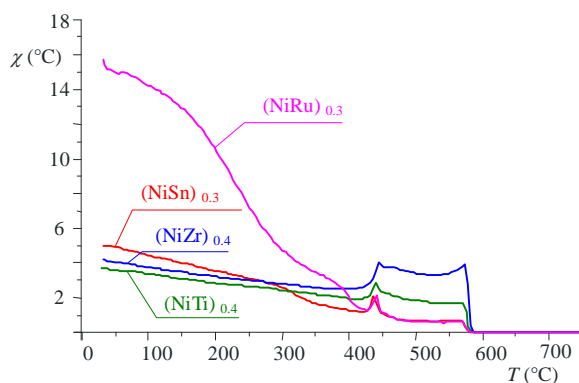


Fig. 3b. Temperature dependence of magnetic susceptibility $\chi(T)$ of (NiMe_2) . Substituted samples where $\text{Me}_2 = \text{Ti, Zr, Sn, Ru}$ prepared by mechanical alloying - Mx.

These phases were not detected by X-ray diffraction; it is most likely the NiFe_2O_4 (or magnetite Fe_3O_4) compound, with $T_C \approx 585^\circ\text{C}$. On the other hand, no signatures of spurious phases were found in BaM samples synthesised by the metallo-organic precursor method ($\text{Fe/Ba} = 10.8$) with x up to 0.4 substitution. NiFe_2O_4 spinel ferrite as a secondary phase was also obtained by Turilli et al [1] in strontium $(\text{NiTi})_x$ M-

type hexaferrite prepared by the metallo-organic precursor method. The ordering temperature T_C and the specific saturation polarisation J_{s-m} were reduced with x . This behaviour restricts the performance in terms of microwave absorption and the usable range of temperatures.

5 CONCLUSION

Small doping rate x was sufficient in some cases - nearly planar $(\text{NiRu})_{0.3}$ and $(\text{ZnRu})_{0.3}$ mixture with low temperature coefficient of H_c could be very promising medium for microwave devices and absorption at higher temperatures. There are several questions about meaning of future research on ferrites: a) new composite structures b) thin-film devices c) nano-particle sized magnetic media for high-density recording. New applications can arise when magnetic function is integrated with other functions (ferroelectrical, electrical and mechanical, etc.). It was found at certain doping ratio x that $(\text{Me}_1, \text{Me}_2)$ ions substituted Fe^{3+} in BaM ferrite and thus reduced the anisotropy by changing it to planar anisotropy, shifted the FMR frequency above 20 GHz. Consequently, substituted hexaferrites are very promising materials for using as electronic wave absorbers, especially at high frequencies up to 50 GHz. One of goals of this work was to develop compounds with great potential for electronic applications in the region of millimetre waves and with suitable properties for high density recording applications.

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