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THE DISPERSION CHARACTERISTICS OF THE COMPLEX PERMEABILITY OF NiZnCu Ferrite and its Composite Materials

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Summary
The paper deals with the frequency dependence of complex permeability for the Ni0.5Zn0.5Cu0.05Fe2O4 ferrite, sintered ferrite produced by conventional ceramic method and its composite materials made of this ferrite (in the form of powder) and non-magnetic polymer matrix (polystyryl chloride – PVC). The experimental and theoretical curves of the complex permeability were compared. The contribution of both domain wall motions and spin rotational magnetization process on the complex permeability in high-frequency region (up to 1 GHz) is discussed. In the case of composite materials, the simple magnetic circuit approach is taken into account. In composites, the real part of the complex permeability in the frequency region above 100 MHz is larger than that of the prepared sintered ferrite. This is attributed to the shift of the spin and domain wall resonance frequencies toward the higher frequency region by introducing demagnetising fields of magnetic particles in the composite.

1. INTRODUCTION

Nickel-zinc ferrites (NiZn) are widely used in high frequency applications (inductors, transformer cores, microwave devices, etc.) because of their high permeability, high electrical resistivity, low eddy current loss, mechanical hardness, chemical stability and reasonable cost, [1]. This system has a cubic spinel crystal structure with the unit cell consisting of eight formula units of the form \( \text{Ni}^{2+}\text{Fe}^{2+}\text{Fe}^{3+}\text{Fe}_{2}\text{O}_4 \), with 32 oxygen anions per unit cell forming a face centered cubic cage, while the metallic cations occupy interstices. The metallic cations outside the octahedral A-sites comprising the octahedral sublattice while those metallic cations enclosed by the octahedron cation octahedral B-sites comprising the octahedral sublattices [2]. The magnetic properties such as magnetic permeability of these ferrites depend strongly not only on the chemical composition, but also on the sintering density and the microstructure such as porosity, grain size and intergranular pores. These are attributed to the fact that the permeability of polycrystalline ferrite can be described by the superposition of different magnetizing processes: domain wall motion and spin rotation. Additionally, there exists a natural resonance due to the effective anisotropy field, resulting in magnetic losses. This provides some limitations (like a threshold frequency) of the application of polycrystalline ferrite to high-frequency device applications.

The task of this paper was to make a highly permeable NiZn ferrite with good thermal stability for preparation of ferrite polymer composite materials. For this purpose, the Ni-Zn ferrites are often doped with CuO. The choice of CuO is based on the fact that: (a) it increases the density and resistivity, and (b) it decreases the sintering temperature of the ferrite. The CuO reduces to Cu2O at 1026°C. The Cu2O has a low melting temperature (1235°C) and forms a liquid phase during sintering of ferrites that activates the sintering and increases the ferrite density (i.e. permeability). It allows producing highly permeable ferrites with less ZnO content and higher Curie temperature [3].

The ferrite polymer composite materials, on the other hand, consist of ferrite particles (filler) dispersed in a non-magnetic polymer matrix, which is not easily possible by ceramic (sintered) ferrites. The impregnation of magnetic fillers in the matrix imparts magnetic properties to the matrix and modifies the dielectric properties of the matrix [6-9].

The complex initial permeability spectra of NiZnCu ferrite and its composite materials have been studied in the frequency range from 10 kHz to 1 GHz and the contribution of domain wall motion and spin rotational magnetizing processes has been discussed. In the discussion, a simple magnetic circuit model is taken into account in the case of ferrite polymer composite materials.

2. EXPERIMENTS

The prepared NiZnCu ferrite with the chemical formula Ni0.5Zn0.5Cu0.05Fe2O4 came out of the composition Ni0.5Zn0.5Fe2O4 which had high initial permeability (~2500) but remarkably low thermal stability (the Curie temperature was only 70°C). The NiZnCu ferrite was prepared by the ceramic method at 1250°C in the sintered and also powder form (with the grain size distribution of 0–250 μm). The ferrite polymer composite materials were made of this ferrite and a non-magnetic polymer matrix (PVC) by the dry pressing method. Two series of composite samples were prepared to examine the effects of the ferrite particle size and the ferrite volume concentration on the complex permeability. These were: (1) constant ferrite volume concentration 73 vol% and different particle sizes 0–40, 40–80, 80–160, and 160–250 μm, and (2) constant particle size 0–250 μm and different ferrite volume concentrations 41, 48, 55, 63 and 73 vol%. All the prepared samples had the toroidal form with the dimensions: 12 × 6 × 3 mm. The complex permeability
In soft polycrystalline ferrites, the magnetisation changes are due to domain wall motion and spin rotation. The former is calculated using the equation of motion of the domain wall, and the latter is deduced from a harmonic oscillator equation describing motion of a planar 180° domain wall in the ferrite. The latter is calculated using the Landau-Lifshitz electromagnetic torque equation for spin dynamics. \[ \dot{M}(t) = \alpha \times \nabla \times \mathbf{H} \times \nabla H. \] Both the magnetising processes (domain wall motion and spin rotation) affect the magnetisation of the ferrite. Therefore, the complex initial permeability of a polycrystalline ferrite can be calculated as a superposition of these two contributions:

\[ \mu'(f) = \mu_{\text{d}}(f) + \mu_{\text{s}}(f), \]

Both the domain wall susceptibility \( \mu_{\text{d}}(f) \) as well as spin rotational one \( \mu_{\text{s}}(f) \) are of a resonance type and depend on the square of the frequency:

\[ \mu_{\text{d}}(f) = \frac{\mu_{\text{d}}^0}{f^2 - f_0^2 + i \frac{Q}{Q}}, \]

\[ \mu_{\text{s}}(f) = \frac{\mu_{\text{s}}^0}{f^2 - f_0^2 + i \frac{Q}{Q}}, \]

where \( \mu_{\text{d}}^0 \) and \( \mu_{\text{s}}^0 \) are static (or low frequency) susceptibilities for domain wall and spin rotational motions, \( f_0 \) and \( Q \) are resonance frequencies of domain wall and spin components, \( \alpha \) and \( \alpha_{\text{d}} \) are corresponding damping factors, \( \alpha_{\text{d}} \) is the effective mass of domain wall per unit of its area, and \( f \) is the frequency of external ac electromagnetic field. It should be noted that the domain wall component is affected by both the composition and the microstructure (which is sensitive to inner stress and/or distribution of grains), while the spin component is determined mainly by the chemical composition of the ferrite. If \( \alpha_{\text{d}} \) is large enough (\( \alpha_{\text{d}} \gg \alpha_{\text{s}} \)), the \( \mu_{\text{s}}(f) \) can be approximated by the relaxation–type frequency dispersion:

\[ \mu_{\text{s}}(f) = \mu_{\text{s}}^0 \left( \frac{1}{1 + f^2 \frac{Q}{Q}} \right), \]

where \( f_{\text{relax}} = f_0 \sqrt{2/\pi} \) is the relaxation frequency. We can decompose the complex permeability spectra presented in Fig. 1 into the domain wall component and the spin rotational contribution by use of Eqs. (1)-(4). The complex permeability spectra can be well reproduced by the superposition of these two components, where we used the numerically determined parameters using a non-linear least-squares fitting method: \( \mu_{\text{d}}^0 = 3973, \mu_{\text{s}}^0 = 5.2 \text{ MHz}, \beta_{\text{dmax}} = 8.1 \times 10^3 \). The dispersion characteristics of the complex permeability of NiZnCu ferrites...

![Image](image-url)

**Fig. 1.** The complex permeability spectra for the NiZnCu sintered ferrite.

\[ \lambda_0 = 608.4, \quad \lambda_0 = 172.1 \text{ MHz}, \quad \delta = 120 \text{ and } \lambda_{\text{avg}} = 9.8 \text{ MHz.} \] It can be noted that for more precise fitting we should consider distributions of these parameters. On the other hand, the ferrite polymer composite material is considered to be composed of ferrite particles (with intrinsic initial permeability \( \mu_i \)) surrounded by a non-magnetic polymer layer (with intrinsic initial permeability \( \mu_{\text{p}} = 1 \)). The elementary cell of idealised composite structure can be modelled using series–parallel magnetic circuit. Based on the approach described in [4, 8], it can be derived the following formula for the complex effective permeability of the composite sample:

\[ \mu_{\text{eff}} = \frac{\epsilon}{\epsilon + \frac{\mu_i}{\mu_{\text{p}}}}, \]

where \( \epsilon \) denotes the statistical mean value, \( \mu_{\text{eff}}(\omega) \) is the complex initial permeability (susceptibility) of the sintered ferrite (given by Eqs. (1)-(4)), \( \eta = dD/dt \) is the demagnetising parameter (\( d \) is the average thickness of the polymer layer and \( D \) is the average ferrite particle size). The demagnetising parameter has a distribution and is connected with the volume fraction \( s \) [8]. Thus, the \( \mu_{\text{eff}} \) value of composite can be influenced by granulometry \( d \) (i.e., polymer composite density or concentration \( k = 100 - v \)).

Figures 2 and 3 present the dependences of real \( \mu_{\text{eff}}' \) and imaginary \( \mu_{\text{eff}}'' \) parts of complex effective permeability \( \mu_{\text{eff}} = \frac{\mu_i}{\mu_{\text{p}}} \) for composite materials based on the NiZnCu ferrite powder and PVC polymer. The parameters of both these graphs are the particle size \( D \) (\( \mu_{\text{mic}} \)), Fig. 2, and ferrite particle concentration \( \kappa = (\%)/(\%) \), Fig. 3. In the case of composites, we can observe relaxation-type frequency dispersion in contrary to the sintered ferrite (see also Fig. 1). The values of \( \mu_{\text{eff}}' \) rise with ferrite volume concentration, but not very much with ferrite particle size. The increase in \( \mu_{\text{eff}}' \) due to a rise of \( \kappa \) is in a good agreement with our previous studies [4-8]. The important role in \( \mu_{\text{eff}}(\kappa) \) dependence has the demagnetising parameter \( \eta \), which decreases with increasing the \( \kappa \). On the other hand, the value of \( \mu_{\text{eff}}'' \) in the ferrite polymer composite materials becomes larger than that of the sintered ferrite in the high-frequency region (\( > 50 \text{ MHz} \)). As the ferrite particle concentration decreases, both the shoulder frequency of \( \mu_{\text{eff}}'' \) and peak frequency of \( \mu_{\text{eff}}'' \) shift higher. In the composite structure, magnetic poles, which are generated by the applied ac magnetic field produce the magnetic field \( H_0 \), causing permeability to be lower than that of the sintered ferrite. This feature can be explained in the following way. In composite, a magnetic inert component is introduced that causes a cut-off the magnetic circuit in the ferrite. Thus, the permeability is reduced remarkably as the \( \kappa \) decreases. The magnetic poles on the surface of magnetic particles dispersed in polymer matrix create the demagnetising field \( H_0 \) anti-parallel to the applied ac magnetic field. The \( H_0 \) reduces the induced magnetic moment more than that calculated from the volume concentration. Therefore, the \( \mu_{\text{eff}}' \) in low-frequency region decreases with the configuration change from the sintered ferrite to the composite.
In soft polycrystalline ferrites, the magnetisation changes are due to domain wall motion and spin rotation. The former is calculated using the equation of motion of the domain wall, and it damped simple harmonic oscillator equation describing motion of a planar 180° domain wall in the ferrite. The latter is calculated using the Landau-Lifschitz electromagnetic torque equation for spin dynamics, \( \Lambda = \nabla \times \mathbf{H} + \kappa \mathbf{M} \times \nabla \times \mathbf{m} \), where \( \Lambda \) is the angular frequency, and \( \kappa = \mathcal{N}^2 \kappa_p \) where \( \mathcal{N} \) is the number of turns, and \( c \) is a geometric parameter of the toroid, \([4]\). In the frequency range 1 MHz to 1 GHz, \( \mu_r \) was obtained by measuring the input impedance of samples by the coaxial line technique with another impedance analyser (HP 4191A). The impedance analysers were controlled by a PC computer via a GPIB interface.

3. RESULTS AND DISCUSSION

The frequency dependence of real and imaginary parts (\( \mu_r \) and \( \mu_i \)) of complex initial permeability \( \mu = \mu_r - j \mu_i \) for the prepared NiZnCu sintered ferrite sample is shown in Fig.1. The real part of the complex permeability \( \mu_r \), which is about 1.00 at 10 kHz, remained almost constant until the frequency was raised to a certain value, and then began to decrease at higher frequency (> 1.9 MHz). The imaginary part \( \mu_i \) gradually increased with the frequency, and reached a maximum of about 700 at 6 MHz, where the real part \( \mu_r \) of \( \mu \) in the frequency region from 2 to 60 MHz depends on the square of the frequency. This feature is well known as the natural resonance phenomenon \([1]\).

\[
\mu_r(f) = 1 \pm \frac{1}{2} \left[ f_0 \frac{f}{f_0 - f} \right] \quad \mu_i(f) = 0 \quad \text{for} \quad f = f_0
\]

where \( f_0 \) and \( f_r \) are static (or low frequency) susceptibilities for domain wall and spin rotational motions, \( \beta_0 \) and \( \beta_i \) are resonance frequencies of domain wall and spin components. \( \beta \) and \( \alpha \) are corresponding damping factors, \( \eta_0 \) is the effective mass of domain wall per unit of its area, and \( f \) is the frequency of external ac electromagnetic field. It should be noted that the domain wall component is affected by both the composition and the microstructure (which is sensitive to inner stress and/or distribution of grains), while the spin component is dominated mainly by the chemical composition of the ferrite. If \( f \) is large enough (\( f > f_0 \)), the \( \mu_i(f) \) can be approximated by the relaxation-type frequency dispersion:

\[
\mu_i(f) = \frac{1}{1 + \frac{f}{f_0}}
\]

where \( f_m, f_r \) are relaxation frequency. We can decompose the complex permeability spectra presented in Fig.1 into the domain wall component and the spin rotational contribution by use of Eqs.(1-4). The complex permeability spectra can be well reproduced by the superposition of these two components, where we used the numerically determined parameters using a non-linear least-squares fitting method: \( f_0 = 208.8, f_m = 1.3 \times 10^7, \mu_m = 8.1 \times 10^3 \), \( \mu_r = 688.4, f_0 = 117.2 \times 10^6, \eta_0 = 120 \) and \( f_m = 9.8 \times 10^7 \). It can be noted that for more precise fitting we should consider distributions of these parameters.

On the other hand, the ferrite polymer composite material is considered to be composed of ferrite particles (with intrinsic initial permeability \( \mu_i \)) surrounded by a non-magnetic polymer layer (with intrinsic initial permeability \( \mu_m = 1 \)). The elementary cell of idealized composite structure can be modelled using series-parallel magnetic circuit. Based on the approach described in \([4, 8]\), we can derive the following formula for the complex effective permeability of the composite sample:

\[
\mu_{\text{eff}} = \frac{1}{1 + \frac{1}{\mu_i} + \frac{1}{\mu_m}}
\]

where \( \mu_i \) is the statistical mean value, \( \mu_i \) (\( \mu_i \)) is the complex initial permeability (susceptibility) of the sintered ferrite (given by Eqs.(1-4)), \( \eta_0 = 4\pi D \) is the demagnetising parameter (\( D \) is the average thickness of the polymer layer and \( D \) is the average ferrite particle size). The demagnetising parameter has a distribution and is connected with the volume fraction \( v \). Thus, the \( \mu_i \) value of composite can be influenced by granulometry (\( D \)) and composite density (or concentration \( k = 100 - v \)).

Figures 2 and 3 present the dependences of real \( \mu_r \) and imaginary \( \mu_i \) parts of complex effective permeability \( \mu_i \) for composite materials based on the NiZnCu ferrite powder and PVC polymer. The parameters of both these graphs are the particle size \( D (\mu m) \), Fig.2, and ferrite particle concentration \( \kappa (\% \%) \). Fig.3. In the case of composites, we can observe relaxation-type frequency dispersion in contrary to the sintered ferrite (see also Fig.1). The values of \( \mu_r \) rise with ferrite volume concentration, but not very much with ferrite particle size. The increase in \( \mu_r \) due to a rise of \( \kappa \) is in a good agreement with our previous studies \([4-8]\). The important role in \( \mu_i (\kappa) \) dependence has the demagnetising parameter \( \eta_0 \), which decreases with increasing the \( \kappa \). On the other hand, the value of \( \mu_i \) in the ferrite polymer composite materials becomes larger than that of the sintered ferrite in the high-frequency region (> 50 MHz). As the ferrite particle concentration decreases, both the shoulder frequency of \( \mu_i \) and the peak frequency of \( \mu_i \) shift higher in the composite structure. Composite magnetic, magnetic poles, which are generated by the applied ac magnetic field produce the demagnetising field \( H_0 \), causing permeability to be lower than that of the sintered ferrite. This feature can be explained in the following way. In composite, a magnetic inert component is introduced which causes the cut-off magnetic circuit in the ferrite. Thus, the permeability is reduced remarkably as the \( \kappa \) decreases. The magnetic poles on the surface of magnetic particles dispersed in polymer matrix create the demagnetising field \( H_0 \) anti-parallel to the applied ac magnetic field. The \( H_0 \) reduces the induced magnetic moment more than that calculated from the volume concentration. Therefore, the \( \mu_i \) in low-frequency region decreases with the configuration change from the sintered ferrite to the composite.

Fig.1. The complex permeability spectra for the NiZnCu sintered ferrite.

Fig.2. The complex permeability spectra of the composite samples with constant particle size: 0-250 \( \mu m \).

Fig.3. The complex permeability spectra of the composite samples with constant concentration: 73 vol%.
increases with decreasing the value of $\kappa_c$. The $f_{sp}$ shifts higher due to the contribution of $H_D$.

As an example, the complex effective permeability spectra for composite sample with $\kappa_c = 73$ vol% and $\beta = 0.250$ μm were decomposed into the domain wall and spin rotational components with the following values of fitted parameters (Fig.4): $f_{sw} = 6.9$, $f_{sp} = 95.4$ MHz, $B_{sw} = 11.1 \times 10^7$, $X_{sw} = 1.9$, $f_{sp} = 5.4$ GHz, $\alpha = 1.4$, $f_{sp} = 384.7$ MHz and $\eta = 0.01$.

A quantitative agreement between the calculated curves and experimental data is obtained. Accordingly, it is possible to estimate the frequency dispersion of $\mu_r$ for composite materials using the dispersion parameters. It should be noted that the permeability of the domain wall component is sensitive to the microstructure of the ferrite. Therefore, domain wall permeability of the composites is difficult to analyse. In addition, we have no experimental information about the damping parameter $\beta$ of the domain wall permeability for composites at this stage. According to this fact, more detailed studies on the domain wall component of permeability will have to be studied in the future.

4. CONCLUSION

We have studied the variation of frequency dependence of complex initial permeability with ferrite volume concentration and particle size distribution for NiZnCu sintered ferrite of the chemical composition Ni$_{25}$Zn$_{75}$Ga$_{2}$O$_{48.5}$Fe$_{2}O$_{3} and its composite materials using the domain wall and spin resonance formulation combined with the magnetic circuit model approach. In the case of sintered ferrite, the dispersion character is of relaxation type and this is attributed to both the domain wall and spin rotational contributions. In the case of composites, the dispersion character is of a relaxation type and the permeability is larger than that of the sintered ferrite in high-frequency region. This is attributed to the shift of both the spin and domain wall resonance frequencies towards the higher frequency region by arising the demagnetising field in the composites. The magnetic circuit model can be applied to explain the effective permeability variation with ferrite concentration and particle size distribution in both the domain wall and spin components. Therefore, performance stability of some high-frequency devices can be improved using the ferrite polymer composite materials.

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Fig.4. The complex permeability spectra (measured and calculated) for composite sample with $\kappa_c = 73$ vol% and $\beta = 0.250$ μm.

**ELECTROMAGNETIC PROPERTIES OF SUBSTITUTED Ba–FERRITES BY SELECTED CATIONS**

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Summary

The powder samples of barium hexaferrite BaFe$_{12}$O$_{19}$, Me$_2$O$_3$, with x = varying from 0.0 to 0.6 were prepared by citrate precursor method. The cation preference of mainly four-valence Me$_2$O$_3$ (Zr, Ti, Sn) and two-valence Me$_2$O$_3$ (Co, Ni, Zn) ions and their combinations in substituted Ba ferrites were investigated. The Mössbauer spectroscopy and measurement of the magnetic properties. Mössbauer studies reveal that Zr$^{4\text{th}}$, Sn$^{4\text{th}}$ and less Co$^{4\text{th}}$, Zn$^{4\text{th}}$ ions have a strong preference to occupy $\text{B}_2$ position, this position has the greatest contribution to the magnetocrystalline anisotropy. The La$^{3\text{rd}}$, Sr$^{3\text{rd}}$ ions preferentially enter into $\text{B}_1$, sites and Zr$^{4\text{th}}$, Co$^{4\text{th}}$, Zn$^{4\text{th}}$ ions also prefer to occupy $\text{B}_2$, tetrahedral sites. The specific saturation magnetic polarization $\mu_s$ and remanence $J_r$ increased with $x$ due to the domination of non-magnetic and less magnetic ions in 4i and 4f sites. The coercivity $H_c$ was easily controllable by the substitutions level $x$.

1. INTRODUCTION

The M–type hexaferrites MFe$_{12}$O$_{19}$ (M = Ba, Sr or Pb) are extensively used for a wide range of the technological applications. To achieve the values of the various magnetic properties necessary for particular applications, either new processing method have to be used to change the morphology or the chemical composition has to be changed [1]. The hexagonal Ba ferrites have been extensively studied because of their large intrinsic uniaxial anisotropy and coercivity, which makes them widely used as permanent magnets [2], microwave devices and recording media [3]. Particular attention was paid to study of the magnetic characteristics of the ferrites, in which Fe$^{3\text{rd}}$ ions are substituted by various cations. Most of the studied substitutions is Ti-Co [4, 5], Zr-Co [6, 7], Sn-Co [8], Ir-Co [9], Zr-Ni [9], Sn-Ni [10], Zr-Sn [11] and Ti-Sn [3].

The temperature dependence of the coercivity in the range between −196°C to 227°C is for substituted Ba ferrites substantially lower than for nonsubstituted ferrites. Such difference can be caused by much steeper decrease of the magnetocrystalline anisotropy field and by the magnetization reversal mechanism to change from coherent to incoherent as temperature is varied [12].

It is known that the Ni$^{3\text{rd}}$ ion reduces the temperature coefficient of coercivity $\alpha_d/dH_T$, which is an important parameter for the stability of the recorded data [9]. In Zn-Sn substituted Ba ferrites, Sn$^{4\text{th}}$ ions decrease value $\alpha_d/dH_T$ more than other ions [13]. Zirconium salts are cheaper and more soluable than titanium salts, therefore it is suitable for wet preparation [14].

These ferrites are known to have great potential properties as tapes for perpendicular magnetic recording and, hence, higher information storage capacity [15]. Those technological applications require materials with strict control of the microstructure (such as homogeneity, particle size and shape) that govern the extrinsic magnetic behaviour.

The magnetic properties of the substituted hexaferrites strongly depend on the electronic configuration of the substituting cations as well as on their site preference among the five different Fe$^{3\text{rd}}$ sublattices of hexagonal structure, namely, tetrahedral (4f), bipyramidal (2b), and three different octahedral (12k, 4f) and (3a) [16]. On the other hand, it is known that more electronegative ions prefer octahedral coordination [14]. The electromagnetivity of selected ions La$^{3\text{rd}}$, Zr$^{4\text{th}}$, Ti$^{3\text{rd}}$, Zn$^{3\text{rd}}$, Co$^{3\text{rd}}$, Ni$^{3\text{rd}}$, Sn$^{4\text{th}}$ is 1.10, 1.33, 1.54, 1.65, 1.88, 1.91, 1.96, respectively. According to the ligand field [16], ions with d$^{4}$, d$^{5}$ and d$^{6}$ orbitals prefer tetrahedral and ions with d$^{3}$, d$^{4}$ and d$^{5}$ orbitals occupy octahedral positions mainly. Ions with d$^{3}$, d$^{4}$ and d$^{5}$ orbitals have no site preference. However, the tendency to occupy a particular site depends also on the ionic radii of the ions and their partners cations.

The influence of combinations of La$^{3\text{rd}}$, Zr$^{4\text{th}}$, Ti$^{3\text{rd}}$, Zn$^{3\text{rd}}$, Co$^{3\text{rd}}$, Ni$^{3\text{rd}}$, Sn$^{4\text{th}}$ ions with different values of the ionic radii (summarized in Tab. 1) to the magnetic properties and magnetocrystalline structure of the barium hexaferrite was investigated.

2. EXPERIMENTAL

High purity (99%) raw materials were used for preparation of polycrystalline powder samples of BaFe$_{12}$O$_{19}$, Me$_2$O$_3$ compounds. The hexaferrite with $x$ = 0.0 to 0.6 were prepared by citrate precursor method with an initial BaFe ratio 10:8 according to the method described in [6]. Finally, the powdered samples were annealed at the temperature 1050°C for 2 hours. The Mössbauer spectra were recorded using the constant acceleration source $^{57}$Co in Rh matrix at the room temperature. The temperature dependence of the magnetic susceptibility $\chi(0)$ and the Curie temperature $T_c$ were measured by the bridge method at constant rate 4 °C/min. The magnetic parameters were determined using the vibrating sample magnetometer with an external magnetic field of 540 kA/m.

3. RESULTS AND DISCUSSION

The temperature dependences of the magnetic susceptibility $\chi(0)$ and the Curie temperature $T_c$ are shown in Fig. 1, and for Ni-Zr (Zr, Ti, Sn) substituted Ba hexaferrite in Fig. 2a, 2b and 2c. The initial susceptibility is given in arbitrary units and it is related to the same amount of the sample (1 mg) for all dependences. The results show that the value of $\chi$ increases with substitution at room temperature. For pure samples ($x = 0$), a sharp