MODIFICATION OF MAGNETIC PROPERTIES OF NiZn FERRITES BY APPROPRIATE SUBSTITUTIONS OF Gd IONS

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1. Introduction

NiZn ferrites became an attractive material for a wide range of applications thanks to an attractive set of properties: high resistivity, low dielectric losses, high Curie temperature and last, but not least – low cost. Many of its properties are sensitive to the composition and preparation technology (especially the heat treatment) and microstructure. By embedding of even a small amount of other ions into the basic composition it is possible to achieve significant modification of structure and properties. Our goal was to explore the influence of various amounts of Gd^{3+} ions on fundamental magnetic properties at low frequencies with the aim to find the correlation between the preparation technology (especially the material composition and heat treatment) and resulting magnetic properties from the point of view of a particular application at given frequencies and applied magnetic fields.

2. Theoretical background

In this work we focused on the investigation of polycrystalline NiZn ferrite materials with the chemical composition given by the general formula $Ni_{0.42}Zn_{0.58}Gd_xFe_{2-x}O_4$, where $x = 0.00$, 0.01, 0.02, 0.04 and 0.06 determines the amount of Gd ions substituting the iron in the crystalline cells in ions per formula unit (i.f.u.). Detailed description of the basic unsubstituted composition used, including the separation of the ions into tetrahedral A- and octahedral B-sublattice is given by the formula

$$\left(Zn^{2+}_{0.58}Fe^{3+}_{0.42}\right)_A \left[Ni^{2+}_{0.42}Fe^{3+}_{1.58}\right]_B O^{2-}_4 \qquad (1)$$

It is known from the literature that the rare-earth atoms, where belongs also Gd, influence the magnetocrystalline anisotropy of 4f-3d intermetallic compounds, [1, 2]. Gd^{3+} ionic radius is relatively large (about 9.35 nm against 6.45 nm in case of Fe). As a result, the substitution of Fe^{3+} with Gd^{3+} causes slight deformation of the crystalline array. Gd^{3+} ion replaces Fe^{3+} ion in the octaedric B-sublattice in accordance with the formula

$$\left(Zn^{2+}_{0.58}Fe^{3+}_{0.42}\right)_A \left[Ni^{2+}_{0.42}Gd^{3+}_{x}Fe^{3+}_{1.58-x}\right]_B O^{2-}_4 \qquad (2)$$

Since the total magnetic moment is $m = m_B - m_A$ and less magnetic Gd^{3+} ion substitutes Fe^{3+}, the total magnetisation (magnetic moment per unit volume) will decrease with increasing Gd amount in the compound as well. Moreover, XRD analysis confirmed the presence of small amount of the second phase $GdFeO_3$ (Gd orthoferrite) that deteriorates the magnetic properties, [3]

3. Sample preparation and experimental details

The samples were prepared by ceramic technique based on solid-state reaction method. The oxides of relevant metals, such as NiO, ZnO, Gd_2O_3 and Fe_2O_3 (in all cases with 99% purity, GR grade, commercially available) with the amounts corresponding to the required stoichiometric composition have been used as initial raw materials. After homogenisation by means of wet-milling in the agate mill, the semi-product was dried and subsequently sifted using the sifter with 500 μm meshhole size. Further, the raw materials were calcined in the furnace at the temperature of 950°C for 1 h. After repeated homogenisation and drying, the part of calcinate having the powder form was thermally treated at 1200°C for 6 h. This material was used for the measurement of physical-mechanical properties and the temperature dependencies of magnetic susceptibility. The rest of calcinate was mixed with binding material (polyvinyl alcohol), pressed to attain the shape of tablets with the diameter of 15 mm. The tablets were sintered at 1200°C for 6 h and a circular hole was drilled into the centre of the tablets by means of water-beam drilling machine. The ring-shaped samples with the outer diameter of about 12 mm and inner diameter of 6 mm have been obtained. These toroids have been used for the measurement of magnetic properties.

The temperature dependencies of magnetic susceptibility were measured by automated balancing bridge, see [4]. The magnetisation characteristics were measured by means of computer controlled experimental equipment built-up from commercially available instruments. The controlling software tailor-made to special needs was developed at our institution using commercially available graphical dataflow programming software development environment. Further information on hardware and software along with data evaluation procedure peculiarities can be found e.g. in [5, 6]. From the measured hysteresis loops various other important magnetic parameters (such as the coercivity H_c, remanent magnetic flux density B_r, hysteresis loop area proportional to the total magnetisation loss, amplitude or complex permeability, etc.) can be found.

4. Results and discussion

The temperature dependencies of magnetic susceptibility of the samples with given compositions are shown in Fig. 1. From these curves the Curie temperatures T_C were found as the temperatures of the inflexion point in the region where the susceptibility falls down to zero. The values of T_C for all the samples are given in Tab. 1. Another method of determining the Curie temperatures is based on the extrapolation of the tangent of the negative slopes to zero value of the susceptibility, giving in general higher values. As can be seen, an addition of Gd replacing iron ions causes almost linear increase of T_C, thus allowing higher operating temperatures of various components made of these materials in a wide range of applications.

The families of minor hysteresis loops at various values of maximum applied field $H_{max} = 10$ to $1500\ \mathrm{A.m^{-1}}$ (step $10\ \mathrm{A.m^{-1}}$) and sinusoidal exciting field waveform $H(t)$ were measured at the same conditions except the frequencies ($f = 50$ and 100 Hz) to validate the influence of eddy currents. No changes in measured curves were observed - it was confirmed that in case of these materials it can be neglected at such low frequencies, since they exhibit large specific resistivity. The loops measured at the highest applied field $H_{max} = 1500\ \mathrm{A.m^{-1}}$, for which the samples are close to technical saturation, are in Fig. 2. Similar families of loops were measured also in weak fields with smoother change (range of $H_{max} = 1$ to $200\ \mathrm{A.m^{-1}}$ with the step $1\ \mathrm{A.m^{-1}}$ to get more data points. No significant differences between coarse and fine curves were found. As can be seen, the replacement of Fe causes significant changes in the hysteresis loop shape – the loops become wider (the coercivity increases), meanwhile, as expected, the saturation flux density decreases as the magnetic moment reduces with decreasing iron content in the compound.

Fig. 3 displays the dependencies of the amplitude permeability μ_a upon maximum applied field H_{max}. The amplitude permeability was found from the peaks of measured minor hysteresis loops as (μ_0 = is the vacuum permeability)

$$\mu_a = \frac{1}{\mu_0} \cdot \frac{B_{max}}{H_{max}} \tag{3}$$

Similarly to the susceptibility and hysteresis loops, small addition of Gd caused massive change comparing to pure NiZn ferrite, but there were only slight differences in the hysteresis loop shape and permeability dependencies observed for $x = 0.01$, 0.02 and 0.04. Further increasing of Gd content ($x = 0.06$) causes again a substantial, step change of the magnetic properties, see Tab. 1.

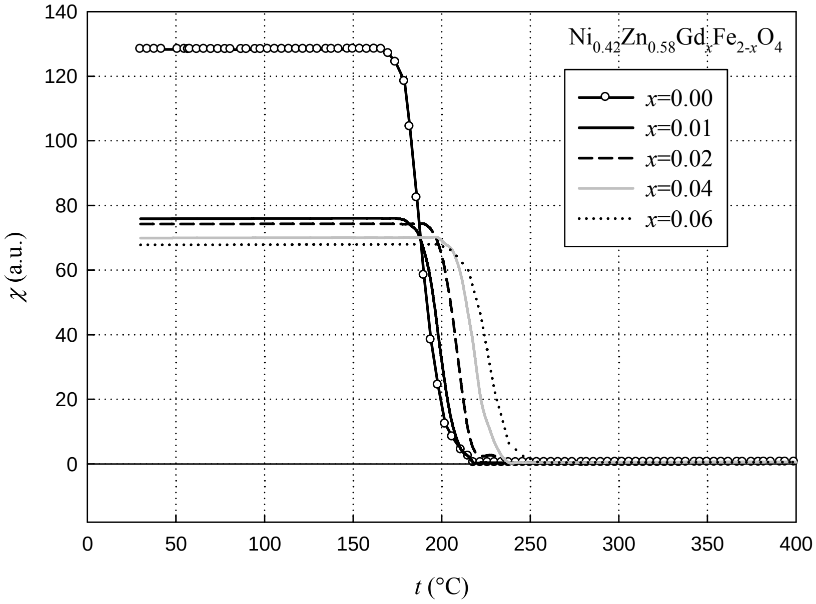

Fig. 1: *The temperature dependencies of magnetic susceptibility.*

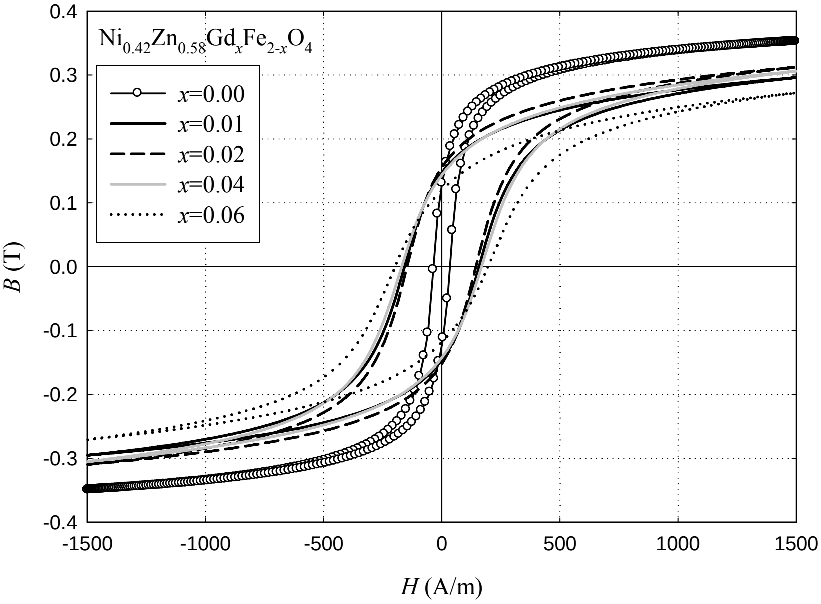

Fig. 2: *The hysteresis loops of materials with various Gd substitution, sinusoidal excitation, f = 50 Hz.*

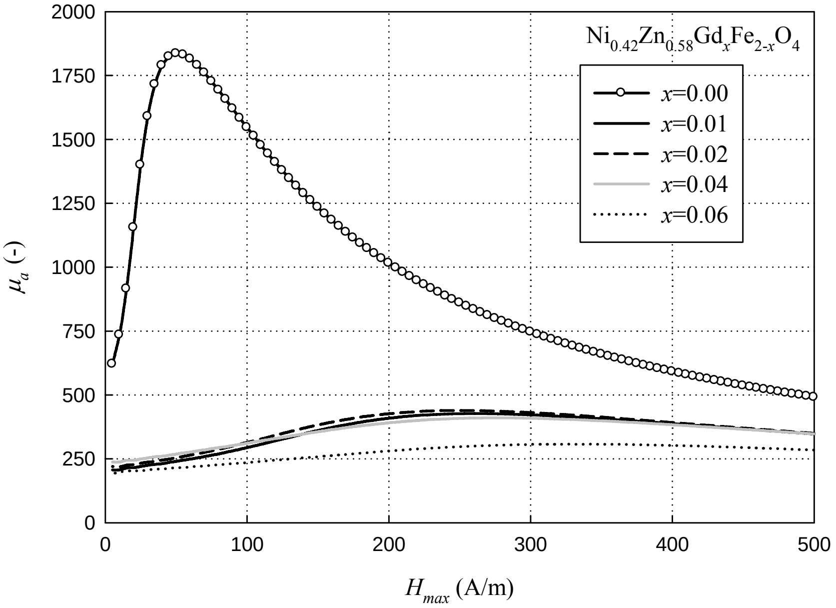

Fig. 3: *The amplitude permeability of materials with various Gd substitution as a function of maximum applied field value, sinusoidal excitation, f = 50 Hz.*

Basic parameters of the samples under investigation are summarised in Tab. 1. The Curie temperatures T_C were determined from the temperature dependencies of the magnetic susceptibility (Fig. 1), coercivity H_c and remanent flux density B_r was interpolated from the hysteresis loops data (Fig. 2) and the initial permeabilities μ_i were found from the dependencies of the amplitude permeability μ_a upon maximum applied field as an extrapolation to zero fields (Fig. 3). Note that these parameters can be assumed as static.

Tab. 1. *Basic magnetic parameters of samples.*

x (i.f.u.)	T_C (°C)	μ_i (-)	H_c (A/m)	B_r (mT)
0.00	188.8	538	35.07	127.27
0.01	197.7	209	157.76	147.24
0.02	209.3	212	145.91	154.95
0.04	217.7	234	169.62	143.45
0.06	226.8	191	197.58	119.72

5. Conclusions

The experiments carried out on the set of Gd-substituted NiZn ferrites have shown a significant changes of all the properties important from the point of view of practical applications. One can see a plateau of the magnetic properties for the substitution range $x = 0.01$ to 0.04, meanwhile the Curie temperature increases more-less linearly with x. This means that there is an optimum range of Gd substitution given as a compromise between sufficient Curie temperature and relatively good magnetic properties not too affected by the decrease of the total magnetic moment per crystalline cell.

Since these materials are intended mainly for high-frequency applications, further research focused on the examination of magnetic properties (e.g. the complex permeability spectra) at elevated frequencies up to few GHz will be the subject of further studies.

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