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MAGNETIC PROPERTIES OF Eu-SUBSTITUTED NiZn FERRITES

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Polycrystalline NiZn ferrites substituted by the rare-earth ions (Eu) with the chemical composition $Ni_{0.42}Zn_{0.58}Eu_xFe_{2-x}O_4$, where x = 0.00, 0.02, 0.04 and 0.06 prepared by ceramic technique based on solid-state reaction method at 1200°C are analysed. The paper is aimed at the investigation of the influence of small amount of Eu^{3+} ions on magnetic properties of prepared NiZn ferrite materials at low frequencies. Basic magnetic properties such as Curie temperature T_C, coercivity H_c, remanent magnetic flux density B_r, hysteresis loop area proportional to the total magnetisation loss, amplitude and initial permeability as well as the temperature dependence of magnetic properties were studied. Usual procedure of quick specimen evaluation is described.

Keywords: ferrite powder analysis, thermomagnetic analysis, substituted ferrite

1 INTRODUCTION

Substituted NiZn ferrites thanks to their good magnetic properties (high initial permeability, electrical resistivity and low magnetic and dielectric loss) are still perspective materials for various electronic devices. Magnetic and structural properties of these ferrites are strongly affected by the chemical composition, i.e. type and amount of the substituents, as well as sintering conditions, grain size, impurities and the procedure of preparation [1, 2]. Substitution is an effective way for changing properties of NiZn ferrite to achieve final properties proper for its application. From the point of view of their application, it is important to achieve low power losses, coercive field as well as thermal stability of the elements made of them.

Thermomagnetic analysis and hysteresis loop recording was used to evaluate properties of prepared specimens.

2 EXPERIMENTAL

Good high-frequency properties, small power losses as well as proper other parameters (amplitude permeability, saturation magnetization) make still NiZn ferrites widely used in various electronic applications e.g. for magnetic shielding, magnetic circuits of inductors.

From the point of view of team preparing new ferrite powders, it is mainly important to get quick information about the following parameters:

- Phase composition of powder
- Presence of possible impurities
- Estimation of powder particle size distribution

Several methods exist for material testing (X-ray diffraction, hysteresis loop recording, thermomagnetic analysis, etc), but some of them are time consuming and relatively expensive. During ferrite preparation tuning, it is necessary to test relatively high number of specimen.

In this paper, NiZn ferrites prepared by ceramic method substituted by Eu are analysed. Procedure of material testing is described concerned to quick evaluation of many prepared samples. In recent time, procedure for quick evaluation of prepared samples has been tuned and used. Measurement of temperature dependence of magnetic susceptibility and hysteresis loop recording is used for quick testing of prepared specimen. When these procedures show good results, other measurement methods follow (Mössbauer spectroscopy, electron microscopy analysis of particles, etc.).

Polycrystalline NiZn ferrite substituted by a rare-earts ions (Eu) with the chemical composition $Ni_{0.42}Zn_{0.58}Eu_xFe_{2-x}O_4$, where x = 0, 0.01, 0.02, 0.04 and 0.06 prepared by ceramic method based on solid-state reaction method at 1100°C/6h and 1200°C/6h was analyzed. The goal of substitution is to increase Curie temperature as in order to achieve better thermal stability of magnetic elements where applied as well as to improve their magnetic parameters (magnetic susceptibility and saturation magnetization).

3 ANALYSIS METHODS

The paper is aimed at the investigation of the influence of small amount of Eu^{3+} ions on magnetic properties of prepared NiZn ferrite materials at low frequencies. Basic magnetic properties such as Curie temperature, coercivity H_C, remanent magnetic flux density B_r, saturation magnetic flux density B_s, hysteresis loop area proportional to the total magnetization losses, amplitude and amplitude permeability were studied. The hysteresis loops of ferrite samples have been recorded. These two methods – thermomagnetic analysis and hysteresis loop recording – seem to be good way to get first information about the specimen quickly.

Self-balancing high sensitive bridge KAPABRIDGE KLY-2 equipped by online specimen heating has been used for thermomagnetic analysis. Initial magnetic susceptibility of the specimen is recorded periodically while it is heated possibly up to 850°C [3]. Measurement of temperature dependence of magnetic susceptibility (thermomagnetic analysis) is very sensitive to phase composition of ferrites and possible present chemical impurities.

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Hysteresis loop recording is important form the point of view of prepared ferrite application mainly. It was carried out using computer controlled experimental set-up which allows usage of analogue (hardware) as well as digital (software) feedback to control the waveform shape of either exciting field $H(t)$ or flux density $B(t)$.

4 RESULTS

The temperature dependences of magnetic susceptibility $\chi(T)$ of $Ni_{0.42}Zn_{0.58}Eu_xFe_{2-x}O_4$ (x = 0, 0.01, 0.02, 0.04, 0.06) ferrite, annealed at 1100°C and 1200°C, are shown in Fig. 1a-b. Moderate decline of $\chi(T)$ dependences, for ferrite powder annealed at 1100°C/6h, exhibit presence of the multiple-phase system, probably consisting of spinel-type ferrite and iron oxides such as maghemite and magnetite. Meanwhile sharp decline of $\chi(T)$ dependences, for ferrite powder annealed at 1200°C/6h, over the Curie temperature indicates presence of single-phase system, consisting of spinel-type ferrite. Moreover, absence of the Hopkinson's peak excludes attendance of small single-domain particles in super-paramagnetic state. Long-term annealing at relatively high temperature (1200°C/6h) leads to obtaining a thermally stable single-phase system with a large–particles structure and sufficiently high value of susceptibility.

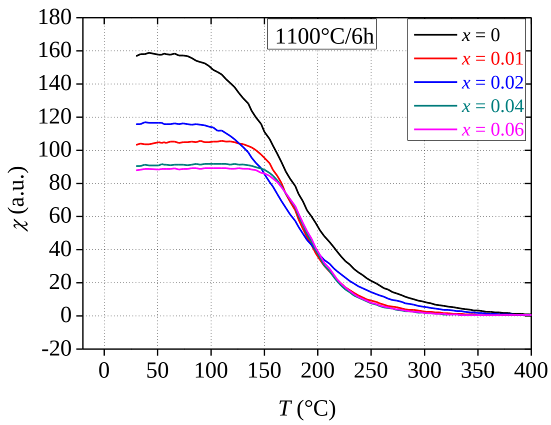

Fig. 1a. Temperature dependence of initial susceptibility of $Ni_{0.42}Zn_{0.58}Eu_xFe_{2-x}O_4$ ferrite powder annealed at 1100°C/6h.

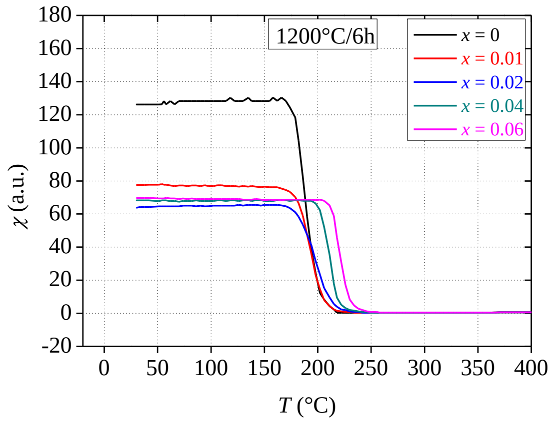

Fig. 1b. Temperature dependence of initial susceptibility of $Ni_{0.42}Zn_{0.58}Eu_xFe_{2-x}O_4$ ferrite powder annealed at 1200°C/6h.

The observed growth of Curie temperature (Fig. 2) with increasing content of paramagnetic Eu^{3+} ions can be analyzed using the model of ions distribution in a spinel structure. In the case of non-substituted composition, it is a mixed structure, where the part of Ni^{2+} ions is substituted by Zn^{2+} ions according to the schema

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

which includes the separation of the ions into tetrahedral A−site and octahedral B−site of spinel structure. It has been stated that the rare earth ions commonly reside at the octahedral sites by replacing Fe^{3+} ions and have limited solubility in the spinel lattice due to their large ionic radii [4] in accordance with the formula

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

Described slight deformation of the crystalline array leads to suppress the canting behavior of cations on B-sites, thus strengthening A-B interaction and consequently increase of Curie temperature. Meanwhile, the total magnetization is decreasing, which is also in relation with presence of iron oxide phases and consequently the decrease of the amount of Fe ions in system. Together with the changing of the demagnetizing field anisotropy, correlated to the expected changes of the particle size, causes amplitude permeability decrease, Fig. 3.

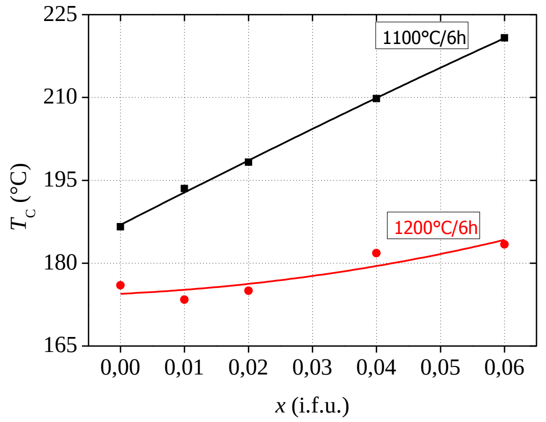

Fig. 2. Curie temperature dependences on x ions content of $Ni_{0.42}Zn_{0.58}Eu_xFe_{2-x}O_4$ annealed at 1100°C and 1200°C.

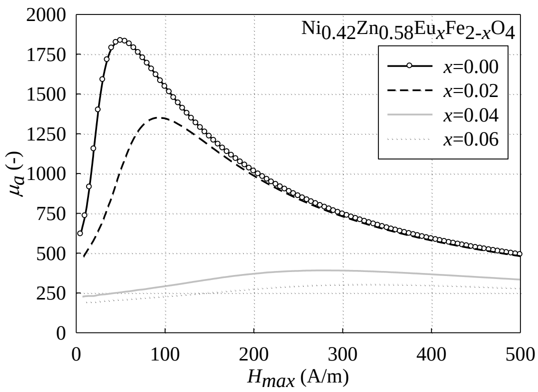

Fig. 3. Amplitude permeability dependences on exciting field H_{max} of $Ni_{0.42}Zn_{0.58}Eu_xFe_{2-x}O_4$ annealed at 1200°C/6h.

The hysteresis loops of $Ni_{0.42}Zn_{0.58}Eu_xFe_{2-x}O_4$ measured at frequency $f = 50$Hz, are shown in Fig. 4. Increment of relative small amount of Eu^{3+} ions at substituting Fe^{3+} ions in spinel structure causes noticeable variation of all magnetic parameters, i.e. H_c, B_r, B_s and hysteresis loop area, which is in relation with the presented results of the model of ions distribution in a spinel structure. Previous mentioned particle size variation is confirmed by the $H_c(x)$ dependences (Fig. 5), since the coercivity is proportional to the demagnetizing field anisotropy.

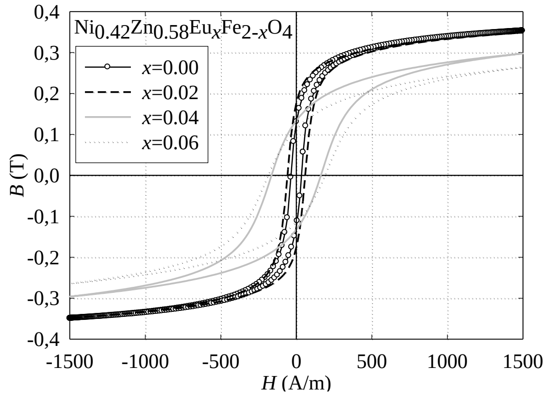

Fig. 4. Hysteresis loops of $Ni_{0.42}Zn_{0.58}Eu_xFe_{2-x}O_4$.

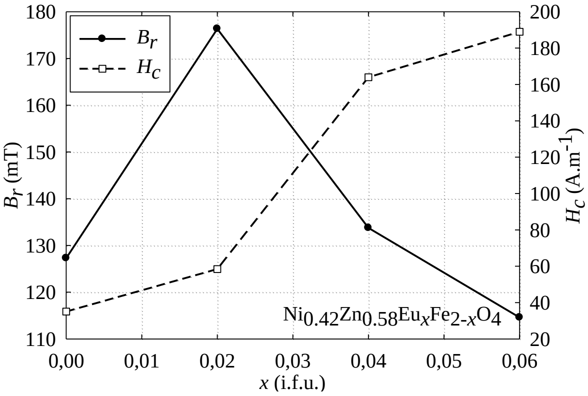

Fig. 5. Remanence and coercivity dependences on *x* ions content of $Ni_{0.42}Zn_{0.58}Eu_xFe_{2-x}O_4$ annealed at 1200°C/6h.

5 CONCLUSIONS

Temperature dependence of magnetic susceptibility and hysteresis loops of NiZn ferrite substituted by Eu ions was measured and analyzed. These two relatively cheap and quick analysis methods show that presented ferrites, annealed at 1200°C/6h, are of single-phase possibly without chemical impurities, so these specimens are candidates for other analyses and further interest. Contrary to ferrite powders annealed at 1100°C/6h, which consist of multiple phase system. Absence of the Hopkinson's peak reveals a larger-particles structure. Form the point of view of application of such substitutes ferrites, presence of rare-earth Eu ions yields decrease of saturation magnetization as well as magnetic permeability. On the other hand, increase of Curie temperature caused by this substitution can improve thermal stability of magnetic elements based on such ferrite.

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REFERENCES

[1] Ušáková, M – Lukáč, J. – Dosoudil, R. – Jančárik, V. – Grusková, A. – Ušák, E. –Sláma, J. – Šubrt, J.: Influence of Cu2+ ions on structural and magnetic properties of NiZn ferrites, J. Mater. Sci. - Mater. Electron 18, 2007, pp. 1183-1189

[2] Sláma, J. – Grusková, A. – Ušáková, M –Ušák, E. – Dosoudil, R.: Contribution to analysis of Cu-substituted NiZn ferrites, J. Magn. Magn. Mater. 321, 2009, pp.3346-3351

[3] Jančárik, V. – Grusková, A – Sláma, J. – Dosoudil, R.: Study of Sr and Ba hexaferrite prepared by low temperature auto-combustion method, J. Electr. Eng. 57 (8/S), 2006, pp. 163-166

[4] Sattar, A.A. – El-Shokrofy, K.M.: J. Phys. IV C1, 1997, p. 245

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