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STUDIES OF RARE-EARTH SUBSTITUTED NICKEL ZINC FERRITES

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Raw compounds with the chemical composition $Ni_{0.42}Zn_{0.58}La_xFe_{2-x}O_4$ (x = 0, 0.01, 0.02, 0.04, 0.06) were prepared using standard ceramic technique. The magnetic properties and magneto-chemical composition and structure of various doped nickel zinc ferrites were estimated by means of thermo-magnetic analysis of susceptibility temperature behaviour and magnetic hysteresis loop measurement.

Keywords: rare-earth, substituted ferrites, radio to microwave ferequencies

1 INTRODUCTION

In the present time, NiZn ferrites represent an important class of soft magnetic materials because of their vast technological applications, ranging from microwave to radio frequencies such as microwave devices, computer memories and magnetic recording [1]. In higher frequency range they exhibit high saturation magnetisation and initial permeability, sufficiently high Curie temperature and, on the other hand, low coercivity, magnetic and dielectric loss, high resistivity and subsequently low eddy current losses. The magnetic properties are most important for ferrites depending on the processing conditions, microstructure, chemical composition and the type of the small additives [2, 3]. The effects of different amounts of La_2O_3 on some properties of $Ni_{0.42}Zn_{0.58}La_xFe_{2-x}O_4$ ferrite have been investigated. Even small rare-earth (RE) additives play an important role in the modification of the structure and intrinsic/extrinsic magnetic properties of ferrites due to the magneto-crystalline anisotropy in the rare-earth doped compounds and the RE-Fe interaction [4].

2 MATERIAL PREPARATION AND METHODS OF CHARACTERIZATION

The samples were prepared by ceramic technique based on solid-state reaction method. The oxides of relevant metals, such as NiO, ZnO, La_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/1h. After repeated homogenisation and drying, the part of calcinate having the powder form was thermally treated at 1200°C/6h. 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/6h 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 [5].

The phase and chemical composition and purity of the samples was evaluated by the temperature dependence of magnetic susceptibility $\chi(T)$. It is possible to achieve the appropriate behaviour of $\chi(T)$ curve by changing the chemical composition and annealing temperature. Such thermomagnetic analysis is usually more sensitive to find small amount of extraneous phases in the sample than the Mössbauer spectroscopy. Moreover, measurement of $\chi(T)$ dependence is cheaper than Mössbauer spectroscopy and it takes less time than recording the Mössbauer spectrum. However $\chi(T)$ dependence sometimes does not detect presence of some magnetic phases, for example in the case of hematite particles [6].

The temperature dependencies of magnetic susceptibility were measured by automated balancing bridge Kappabridge KLY-2, based on the detection of inductance changes in a measuring coil due to the presence of the measured sample inside the coil. It is equipped with automatic zeroing and automatic compensation of the thermal drift of the bridge unbalance. Initial magnetic susceptibility of the specimen is recorded periodically while it is heated possibly up to 850°C. The magnetic hysteresis loop measurement was carried out using computer controlled experimental set-up, built-up from commercially available instruments, 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 $B(t)$.

3 EXPERIMENTAL

The magnetic susceptibility temperature dependences $\chi(T)$ of $Ni_{0.42}Zn_{0.58}La_xFe_{2-x}O_4$ ferrite (x = 0, 0.01, 0.02, 0.04, 0.06) annealed within 1100°C to 1300°C in linear steps of 100°C are shown in Fig. 1a-c. Over T_C the $\chi(T)$ curves fall from relatively high values to near zero. The slope of this drop gives the information about magneto-chemical composition of the sample. Perpendicularity indicates single-phase system, whilst bevel indicates multi-phase system. The multi-phase system, probably consisting of spinel-type ferrite and iron oxides such as maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4), was found for specimens annealed at 1100°C. Increasing of anneal-

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ing temperature leads to obtaining of a thermally stable single-phase system with sufficiently high value of susceptibility.

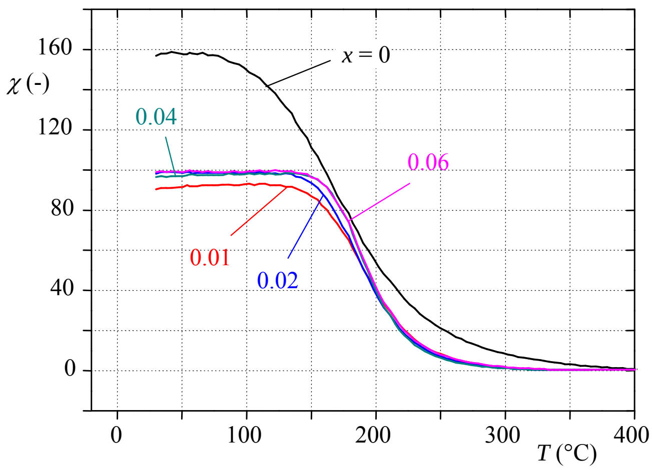

Fig. 1a. Magnetic susceptibility temperature dependences of $Ni_{0.42}Zn_{0.58}La_xFe_{2\text{-}x}O_4$ annealed at 1100°C/6h

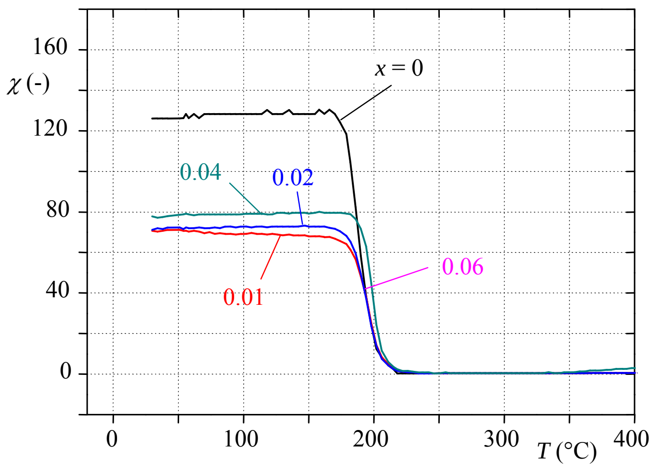

Fig. 1b. Magnetic susceptibility temperature dependences of $Ni_{0.42}Zn_{0.58}La_xFe_{2\text{-}x}O_4$ annealed at 1200°C/6h

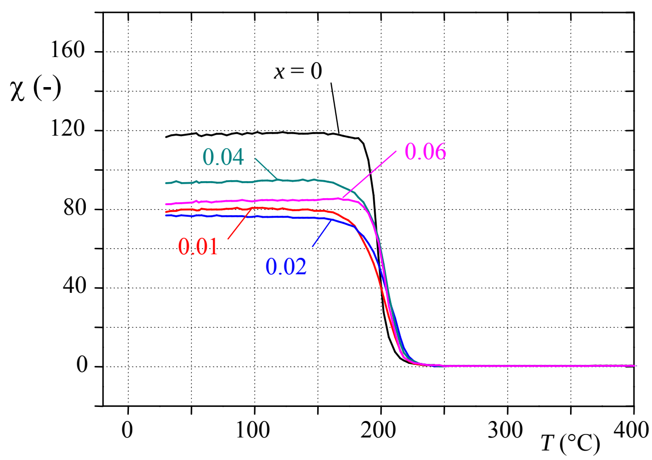

Fig. 1c. Magnetic susceptibility temperature dependences of $Ni_{0.42}Zn_{0.58}La_xFe_{2\text{-}x}O_4$ annealed at 1300°C/6h

Temperature responding to the point of inflexion from $\chi(T)$ dependence is considered to be a Curie temperature in this case. The point of inflexion is found by a numerical procedure. Measured points of the $\chi(T)$ curve are fitted by natural cubic splines around the expected Curie temperature and the temperature at which $\partial^2\chi(T)/\partial T = 0$ is find. Because this condition is usually valid at several points within the analysed region, the point it taken into account at which the slope is maximum [6]. The Curie temperature increases with the addition of La^{3+} ions and rising of annealing temperature, Fig. 1d. This is in relation with slight deformation of the crystalline array (schematically described later) and with presence of iron oxide phases and consequently the decrease of the amount of Fe^{2+} and Fe^{3+} ions in system due to the fact, that the magnetic behaviour of the ferrites is largely governed by iron-iron interaction via spin coupling.

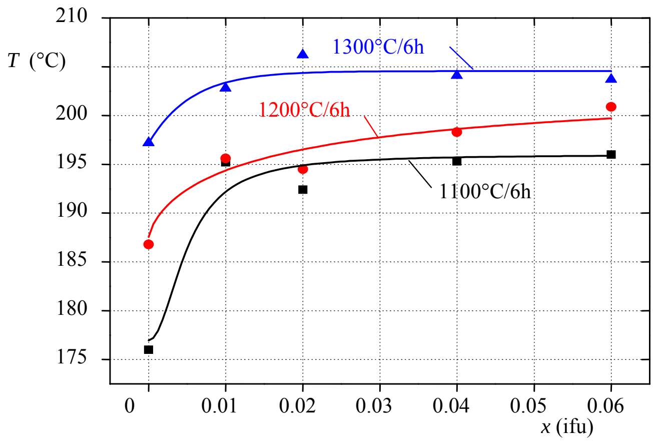

Fig. 1d. Curie temperature dependences on x ions content of $Ni_{0.42}Zn_{0.58}La_xFe_{2\text{-}x}O_4$ annealed within 1100°C to 1300°C in linear steps of 100°C

Observed decrease of amplitude permeability (Fig. 2a) is attributable to presence of iron oxides phases and La^{3+} ions, which has no unpaired electrons and it behaves as paramagnetic [7], in system. The placement of ions of basic composition $Ni_{0.42}Zn_{0.58}Fe_2O_4$ into the sites is governed by theoretical formula as follows

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

The () parenthesis brackets in the relation (1) express the placement of the ions in A sites and [] parenthesis express the placement of the ions in B sites. It has been accepted that the rare-earth ions commonly reside in octahedral sites [8]. Hence La^{3+} ions replace Fe^{3+} ions in the octahedral B sites in accordance with the formula

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

It leads to decrease of total magnetisation with increasing La^{3+} amount. The substitution of ferromagnetic Fe^{3+} by paramagnetic La^{3+} in the spinel is not useful for increasing magnetisation.

The hysteresis loops of $Ni_{0.42}Zn_{0.58}La_xFe_{2\text{-}x}O_4$ (x = 0, 0.01, 0.02, 0.04, 0.06) annealed at 1200°C, measured at frequency f = 50Hz, are shown in Fig. 2b.

As can be seen, despite the La^{3+} incorporation into the lattice was very small, the magnetic parameters, such as the remanent flux density B_r, coercivity H_c and loop area are markedly affected by increment of La^{3+} ions at the expense of Fe^{3+} ions in a spinel structure.

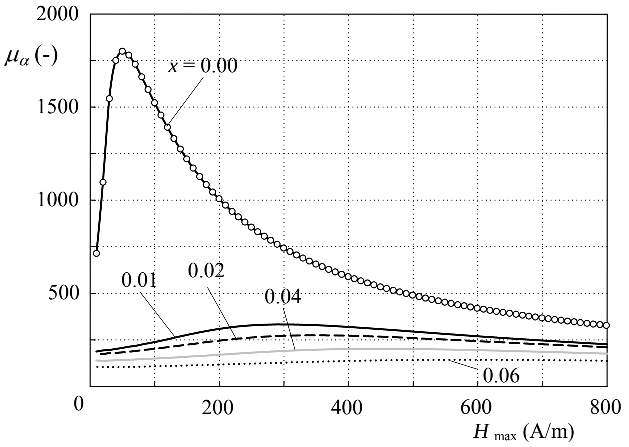

Fig. 2a. Amplitude permeability dependences on exciting field H_{max} of $Ni_{0.42}Zn_{0.58}La_xFe_{2-x}O_4$ annealed at 1200°C/6h

The loops become wider (the coercivity increases), meanwhile, the remanent flux density decreases as the magnetic moment reduces with decreasing iron content in the compound. It can be also demonstrated by the comparison of B_r and H_c variation as a result of linear content changes of paramagnetic La^{3+} and ferromagnetic Gd^{3+} [5] in $Ni_{0.42}Zn_{0.58}R_xFe_{2-x}O_4$ (R = La, Gd) ferrites annealed at 1200°C, Fig. 2c.

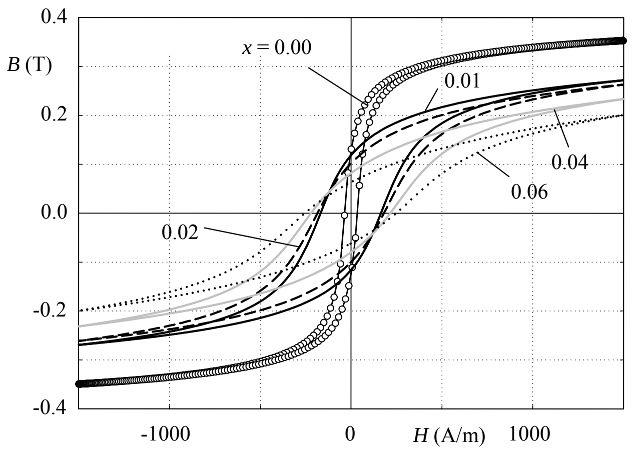

Fig. 2b. The hysteresis loops of $Ni_{0.42}Zn_{0.58}La_xFe_{2-x}O_4$ annealed at 1200°C/6h

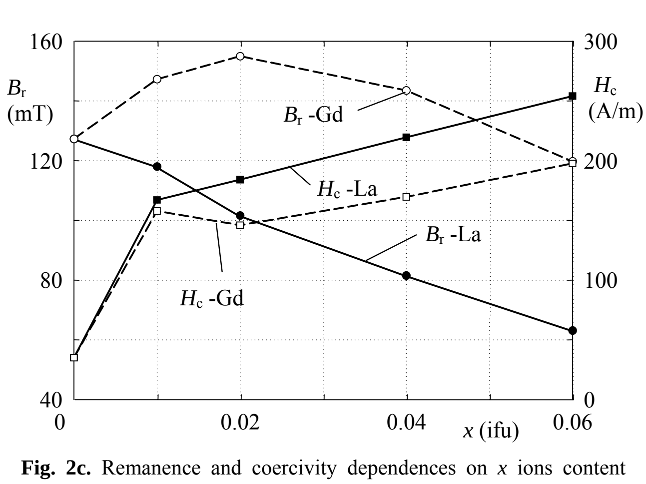

Fig. 2c. Remanence and coercivity dependences on x ions content of $Ni_{0.42}Zn_{0.58}La_xFe_{2-x}O_4$ and $Ni_{0.42}Zn_{0.58}Gd_xFe_{2-x}O_4$ annealed at 1200°C/6h

5 CONCLUSIONS

In summary, the effects of different amounts of La_2O_3 on intrinsic/extrinsic magnetic properties of $Ni_{0.42}Zn_{0.58}La_xFe_{2-x}O_4$, prepared by standard ceramic technique, have been investigated. Introducing a relatively small amount of La_2O_3 instead of Fe_2O_3 causes significant changes of the investigated properties. Curie temperature and coercivity increases with substitution, meanwhile initial susceptibility and remanent flux density decreases. In addition, the La^{3+} ions incorporated in the ferrite, because of its high radius, causes slight deformation of the crystalline array and may form the formation of the crystalline secondary phases. These changes are associated with modifications in the studied magnetic properties.

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