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Magnetic Properties of $Ni_{0.3}Zn_{0.7}Fe_2O_4$ Ferrites with Iron Ions Partly Substituted by Europium

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This work is devoted to the study of the impact of the substitution of iron by Eu on the properties of magnetically soft $Ni_{0.3}Zn_{0.7}Eu_xFe_{2-x}O_4$ ferrites aimed at enhancement of the knowledge related to the behavior of such materials in dependence on the amount of iron substitution. Our latest studies focused on the materials having similar chemical composition gave a hint of some possible approaches to manage the resulting magnetic properties in a precisely controlled way by the combination of several factors; choice of initial chemical composition of non-substituted ferrite, selection of substituted and substituting element, variations of final chemical composition, modifications of fabrication technology (sintering temperature and time), etc.

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1. Introduction

Recently, the influence of Eu^{3+} rare-earth (RE) ions on structural, electrical, and magnetic properties of ferrites was investigated by many researchers [1–3]. In this work, the effect of Eu substitution of Fe on the magnetic properties of NiZn ferrites was studied. The samples of soft magnetic spinel ferrite with the chemical composition $Ni_{0.3}Zn_{0.7}Eu_xFe_{2-x}O_4$ where the amount of substitution $x = 0.00$, 0.02, 0.04, 0.06, 0.08 and 0.10 ions per formula unit (i./f.u.) were prepared by means of standard ceramic technology at the sintering temperature of 1200 °C/6 h. Basic composition of non-substituted ferrite $Ni_{0.3}Zn_{0.7}Fe_2O_4$ was chosen owing to the fact that this ferrite is characterized by the largest value of the initial permeability among NiZn ferrites with larger amount of Ni whilst the coercivity is the smallest [4, 5]. A significant weakness of this material is relatively low Curie temperature. For this reason Eu was chosen as the substituent, since some other our studies proved Eu (along with Gd and La) as a good agent important for the increase of the Curie temperature, in case of Eu even linear with increase of substituting amount x, see e.g. [3, 6].

2. Experimental details

Fundamental magnetic properties such as e.g. the Curie temperature T_C, coercive field H_c, remanent magnetic flux density B_r, hysteresis loop area A_l proportional to the total magnetization loss, amplitude and initial permeability (μ_a and μ_i, respectively) at low frequencies were examined.

The Curie temperatures were determined from the temperature dependences of magnetic susceptibility $\chi(T)$ measured by the balancing bridge method using the experimental equipment based on commercially available measuring instrument (susceptometer) with the capabilities enhanced by tailor-made heating/cooling system and data acquisition hardware [7]. The magnetization characteristics along with fundamental magnetic parameters were measured on ring-shaped samples by an advanced measuring system consisting both of commercially available instrumentation units (arbitrary waveform generator, fast digital multimeters) and custom-made components (high-power operational amplifier). The acquisition and evaluation of experimental data is controlled by the software adapted to our specialized needs [8]. Newly developed software utilizing original enhanced algorithms of data processing allows to speed-up the experiments along with improving the accuracy.

3. Results and discussion

The series of quasi-static hysteresis loops measured at sinusoidal exciting magnetic field $H(t)$ waveform with constant frequency $f = 50$ Hz and the peak value $H_{\max}$ changed within the range of 1 to 1500 A/m were obtained. The hysteresis loops at maximum field $H_{\max} = 1500$ A/m are displayed in Fig. 1. From the peak values of all the hysteresis loops, the relative amplitude permeability μ_a, given as the ratio of the peak values of magnetic flux density $B_{\max}$ and applied field $H_{\max}$, divided by the vacuum permeability was found.

The dependences of μ_a upon $H_{\max}$ are shown in Fig. 2. As expected, the non-substituted ferrite exhibits very low coercivity of 8.5 A/m and high relative amplitude permeability reaching its maximum value of about 2380 at about $H_{\max} = 11$ A/m. As can be seen, the addition of Eu at the expense of iron causes significant changes, surprisingly almost independent of the europium contents, the only exception differing slightly from the general tendency is $x = 0.08$. Note that the hysteresis loops (as well

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as the amplitude permeability dependences) for $x = 0.06$ (solid blue line, almost invisible) and $x = 0.10$ (solid green line, covering the blue line for $x = 0.06$) are nearly identical. The general observation is that europium causes the increase of maximum flux density $B_{\max}$ at $H_{\max} = 1500$ A/m, that can be put into correlation with the saturation magnetic polarization, since such a field is large enough to saturate the samples (in any case $H_{\max} \gg H_c$). On the other hand, the amplitude permeability drastically decreases whilst the dependences become flat.

This finding is evident on the dependences of coercive field H_c and the remanent flux density B_r normalized to maximum value ($B_r/B_{\max}$ ratio) on Eu amount x, see Fig. 3. As can be observed, by adding some Eu the coercive field jumps from 8.5 A/m up to almost 60 A/m and further reaches its maximum of about 83 A/m at $x = 0.06$. Regardless of x, the values of coercive fields tend to increase roughly linearly. In contrast to the coercive field behavior, except for the non-substituted ferrite, the normalized remanent flux density is nearly constant.

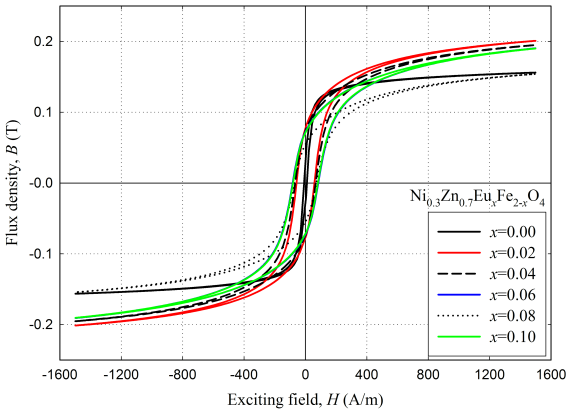

Fig. 1. The hysteresis loops of $Ni_{0.3}Zn_{0.7}Eu_xFe_{2-x}O_4$ ferrite for various Eu contents x measured at $H_{\max} = 1500$ A/m.

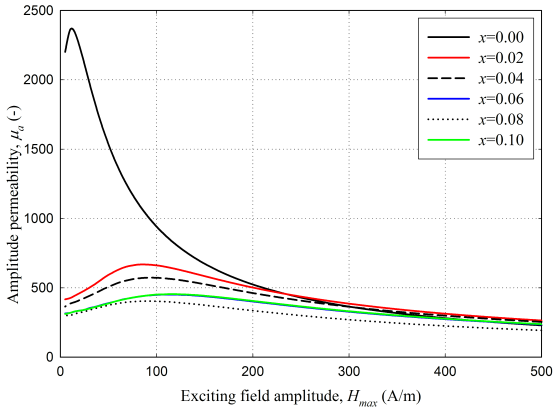

Fig. 2. The amplitude permeability μ_a of $Ni_{0.3}Zn_{0.7}Eu_xFe_{2-x}O_4$ ferrite for various Eu contents x as a function of $H_{\max}$.

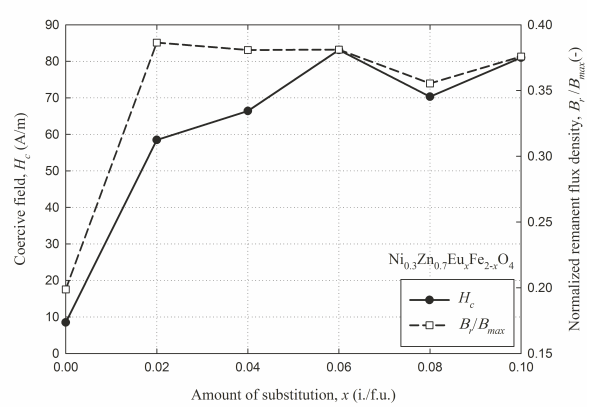

Fig. 3. The dependence of coercive field H_c (•, solid) and the ratio of remanent and maximum flux density $B_r/B_{\max}$ (□, dashed) on Eu contents x in $Ni_{0.3}Zn_{0.7}Eu_xFe_{2-x}O_4$ ferrite.

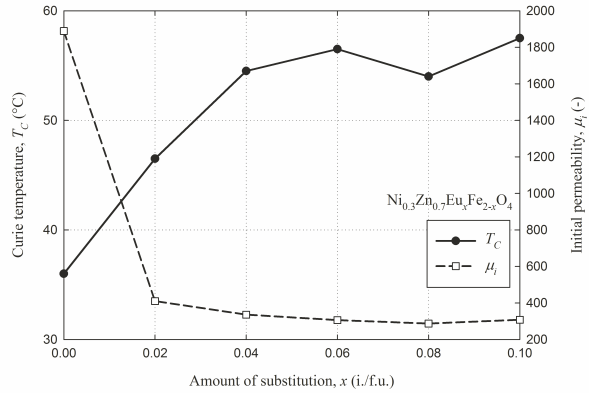

Fig. 4. The dependence of Curie temperatures T_C (•, solid) and the initial permeability μ_i (□, dashed) on Eu contents x in $Ni_{0.3}Zn_{0.7}Eu_xFe_{2-x}O_4$ ferrite.

The dependences of Curie temperatures T_C and initial permeability μ_i on the contents of Eu are in Fig. 4. The Curie temperature was found as an inflection point at the negative slope of the temperature dependences of magnetic susceptibility normalized to the room-temperature value χ/χ_{RT}, see Fig. 5. Adding of Eu increased T_C from 36 °C up to 57.5 °C roughly monotonically (except for $x = 0.08$ where a slight decrease was observed) with a relatively large slope for values of $x < 0.04$ and almost no change for larger europium amounts. The increase by about 22 °C seems to be promising, but the initial value is too low for practical applications even at room temperatures. Note that the uncertainty of T_C measurements (±4 °C) is greater than usual, since the dependences declined gradually (not as steeply as usual) already from the starting point (room temperature) and the step between successive measurements was as large as 4 °C. Thus, the determination of the point of inflexion from the measured data is rather coarse. Initial permeability was found as a linear extrapolation of the dependences in Fig. 2 (10 data points corresponding to $H_{\max} \leq 10$ A/m) to zero exci-

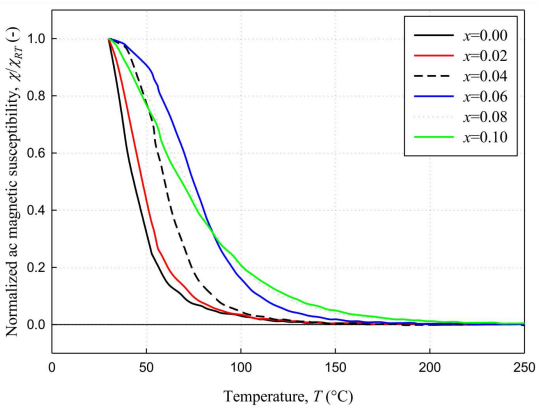

Fig. 5. Temperature dependences of normalized ac magnetic susceptibility χ/χ_{RT} for various Eu contents x in $Ni_{0.3}Zn_{0.7}Eu_xFe_{2-x}O_4$ ferrite.

ting field. This approach was verified long ago as being sufficiently accurate in comparison with conventional approach using low-level exciting fields requiring the use of expensive lock-in technique to measure the pick-up coil signals. Incorporating some Eu into the ferrite structure results in drop of μ_i from about 1900 down to about 400 and less. Observed behavior can be explained on the basis of a simple model describing the occupation of tetrahedral (A) and octahedral (B) sublattice as follows:

$$\left(Zn^{2+}_{0.7}Fe^{3+}_{0.3}\right)_{\rm A}\left[Ni^{2+}_{0.3}Eu^{3+}_{x}Fe^{3+}_{1.7-x}\right]_{\rm B}O^{2-}_{4}. \qquad (3.1)$$

Since the effective ionic radius of Eu^{3+} (94.7 pm) is significantly larger than that of Fe^{3+} (64.5 pm), europium prefers to occupy B sublattice where the ions have more room to settle. Assuming magnetic moments of the constituting ions (in the Bohr magnetons, $\mu_{\rm B}$) to be $m(Zn^{2+}) = 0\ \mu_{\rm B}$, $m(Ni^{2+}) = 2\ \mu_{\rm B}$, $m(Fe^{3+}) = 5\ \mu_{\rm B}$ and $m(Eu^{3+}) = 6\ \mu_{\rm B}$, respectively, the resulting values of total magnetic moment per formula unit calculated as the difference between the moments of B and A sublattices can be found easily as $n_{\rm B} = M_{\rm B} - M_{\rm A}$, see Table I.

TABLE I

Theoretical values of total magnetic moment per formula unit.

x [i./f.u.]	0.00	0.02	0.04	0.06	0.08	0.10
$n_{\rm B}$ [$\mu_{\rm B}$/f.u.]	7.60	7.62	7.64	7.66	7.68	7.70

This invokes the expectation that in ideal case the saturation magnetic polarization should increase linearly with x, since the magnetic moment of substituting Eu^{3+} ions is greater than that of original Fe^{3+} ions. However, the situation in real samples is much complicated. In fact, we can really observe the increase of the maximum flux density at the maximum exciting field of 1500 A/m (see Fig. 1), but on contrary to the above expectation the value of $B_{\rm max}$ reaches its maximum already for $x = 0.02$ and then slightly decreases (Fig. 1, Fig. 3). This can probably be explained by the hypothesis that due to large ionic radius not all Eu^{3+} ions are incorporated into the B sublattice (probably, the second phase is formed, see e.g. [9]) and thus they do not contribute to the increase of the total magnetic moment in expected manner. Moreover, one must take into account a mixture of other phenomena affecting the resulting properties, e.g. spin canting, etc. Again, $x = 0.08$ constitutes an exception that needs to undergo further analysis.

4. Conclusions

The experiments reported in this work revealed an important knowledge. It seems that the initial $Ni_{0.3}Zn_{0.7}Fe_2O_4$ ferrite, even if being one of the best within the tested family of NiZn ferrites from the point of view of the coercivity and initial permeability, is a too sensitive soft magnetic material that needs to be handled with extreme care. Any, even a slight, modification of the chemical composition by means of substituting iron by europium causes significant changes of magnetic properties comparing to the non-substituted ferrite, unfortunately within the tested range of x nearly independent of the europium contents and also with almost no benefit in the increase of the Curie temperature stated in other works. Thus, the compromise must be found between adding europium in an amount sufficient to increase the Curie temperature satisfactorily, while keeping the amount low enough to control magnetic parameters in a wider scale.

Acknowledgments

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