ROLE OF THERMOMAGNETIC CURVES AT PREPARATION OF NiZn FERRITES WITH Fe IONS DEFICIENCY

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The temperature dependence of magnetic susceptibility $\chi(T)$ is very suitable tool for the identification of magnetic phases into the ferrites and their Curie temperatures T_C. The initial susceptibility measured data offer qualitative and partly quantitative analysis of different types of magnetic materials. It is possible to determine the oxidation state, morphological and chemical features of materials.

Keywords: susceptibility, magnetic moment, Curie temperature, ferrites, annealing temperature

1 INTRODUCTION

The characteristic features of some thermomagnetic curves $\chi(T)$ can exhibit the existence of a well expressed maximum, namely the Hopkinson peak just below the Curie temperature T_C. It is known, that the maximum low temperature value of permeability can be reached by zinc content nearly over 0.7 ions per formula units in NiZn ferrite. The low value of Curie temperature should be modified (T_C = 70 °C), because it is very close to operating temperature. The one way of solving this problem presents iron deficiency variation in ferrite [1-6]. The influence of the non-stoichiometry of the NiZn ferrite on the magnetic properties has been investigated for compositions given by the chemical formula of $(Ni_{0.33}Zn_{0.67})_{1-x}Fe_{2-x}O_4$. There were values of x from 0.0 up to 0.20. The thermomagnetic analysis was mainly used to select a convenient substitution and appropriate Fe^{3+}/ Me^{2+} ions ratio in substituted ferrite and to estimate the annealing temperature of prepared ferrite sample (T_A). The phase compositions observed by thermomagnetic curves were compared with Mössbauer spectroscopy analysis results. In the presented work, attention was paid to NiZn ferrites, which were prepared by the wet method from an organo-metallic precursor with glycine, using the low-temperature autocombustion.

2 EVALUATION CHANGES OF INTRINSIC AND EXTRINSIC PROPERTIES

Fig. 1 shows $\chi(T)$ dependencies of $Ni_{0.33}Zn_{0.67}Fe_2O_4$ and $Ni_{0.396}Zn_{0.804}Fe_{1.8}O_4$ ferrite samples where were (the ratio of divalent ions Me^{2+} to trivalent ions Fe^{3+}, Me^{2+}: Fe^{3+} = 1: 2 and 1 : 1.5), annealed at various temperatures. In case of ferrite with 1: 2 ion ratio, it is a mixed structure, where the part of Ni^{2+} ions in the original inversed ferrite

$$\left(Fe^{3+}\right)\left[Ni^{2+}Fe^{3+}\right]O_4^{2-} \qquad (1)$$

is substituted by Zn^{2+} ions. Whilst 0.67 of Zn^{2+} ions occupy the A sites (Zn^{2+} always tends to take the position of tetrahedral coordination) and the equivalent amount of 0.67 Fe^{3+} ions shifts from A site to B site. Thereby, it reaches the theoretical magnetic moment according to the model

$$\left(Zn_{0.67}^{2+}Fe_{0.33}^{3+}\right)\left[Ni_{0.33}^{2+}Fe_{1.67}^{3+}\right]O_4^{2-} \qquad (2)$$

consequently

$$\overrightarrow{(0\times 0.67+5\times 0.33)}\overleftarrow{[2.2\times 0.33+5\times 1.67]}\mu_B \qquad (3)$$

where the magnetic moment of Fe^{3+} ions is $5\mu_B$ and the one of Ni^{2+} ions is 2.2 μ_B (Bohr´s magnetons). The () parenthesis brackets in the relation (3) express the placement of the ions in A sites and [] parentheses express the placement of the ions in B sites. According to the relation (3), the theoretical resulting magnetic moment equals to

$$m_T = (-1.65+[0.726+8.35])\mu_B = 7.426\mu_B \qquad (4)$$

Experimentally measured magnetic moment is $m_E = 4.25\mu_B$ [7]. This difference can be explained by Yafet-Kittel´s canting, *ie* the disintegration of B site to 2 sublattices B_1 a B_2, whilst their magnetic moments hold an angle. More Fe^{3+} ions switch from A site to B site more the angle increases. The disintegration is the result of the B-B super exchange interaction getting stronger, which, in this case, tends to direct the magnetic moments in B site antiparallel, and consequently the m_B effective magnetic moment in B site is given by the sum of projections of partial moments of both sublattices (B_1, B_2) into the antiparallel axis of the ferrite and it is smaller than the theoretically given moment in the B state, *ie* $m_B < (0.726 + 8.35)\mu_B$. Because of this the real m_E is significantly smaller than m_T.

Curie´s temperature is primarily determined by the strongest interaction, *ie* A-B super exchange interaction that predominates the A-A or B-B interaction. The dominant role in A-B interaction is that of Fe^{3+} ions, occurring in both sites. Therefore, the T_C will decline in the number of A-B interactions, *ie* with the increase of Zn^{2+} ions in A site in expense of Fe^{3+} ions. It is obvious, that the angles between the Fe^{3+} ions in B sites weaken the A-B interaction, and therefore also the T_C value even more. Therefore the $Ni_{0.33}Zn_{0.67}Fe_2O_4$ ferrite sample has a

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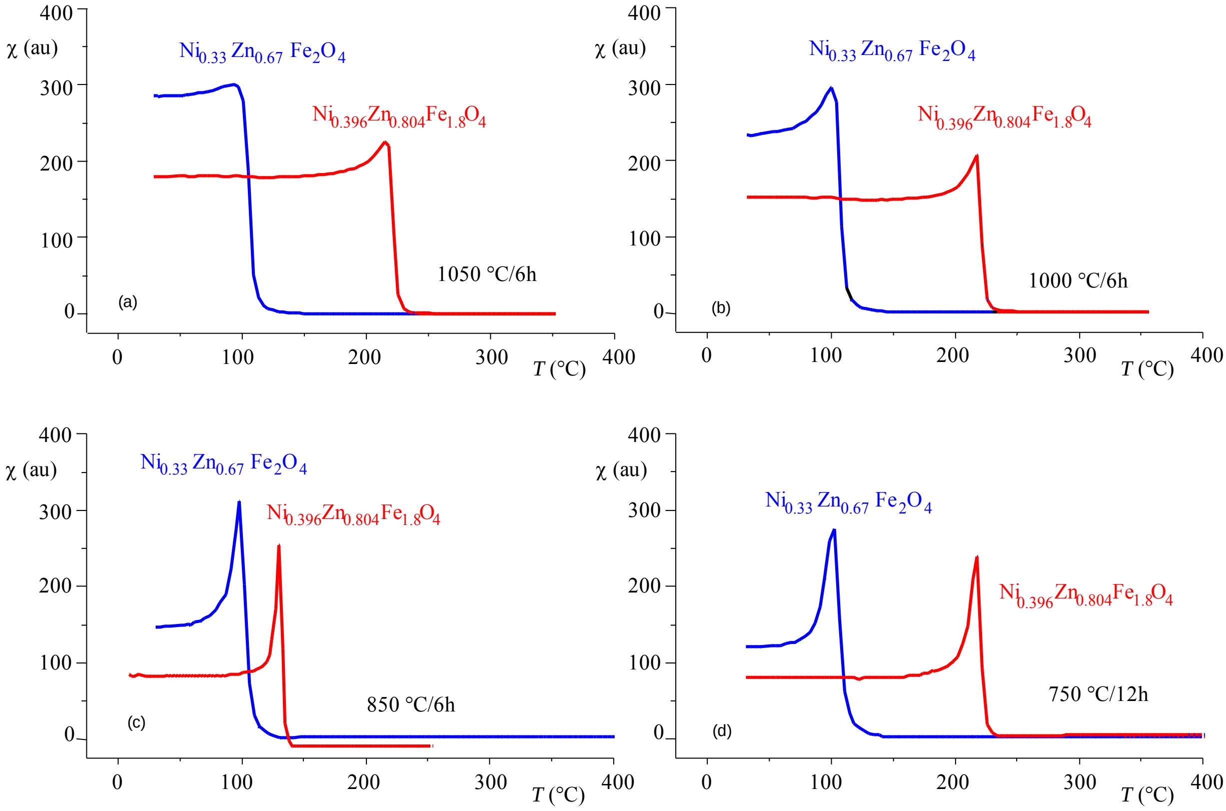

Fig. 1. Temperature dependencies of the susceptibility $\chi(T)$ of $Ni_{0.33}Zn_{0.67}Fe_2O_4$ and $Ni_{0.396}Zn_{0.804}Fe_{1.8}O_4$ ferrite samples annealed at different temperatures

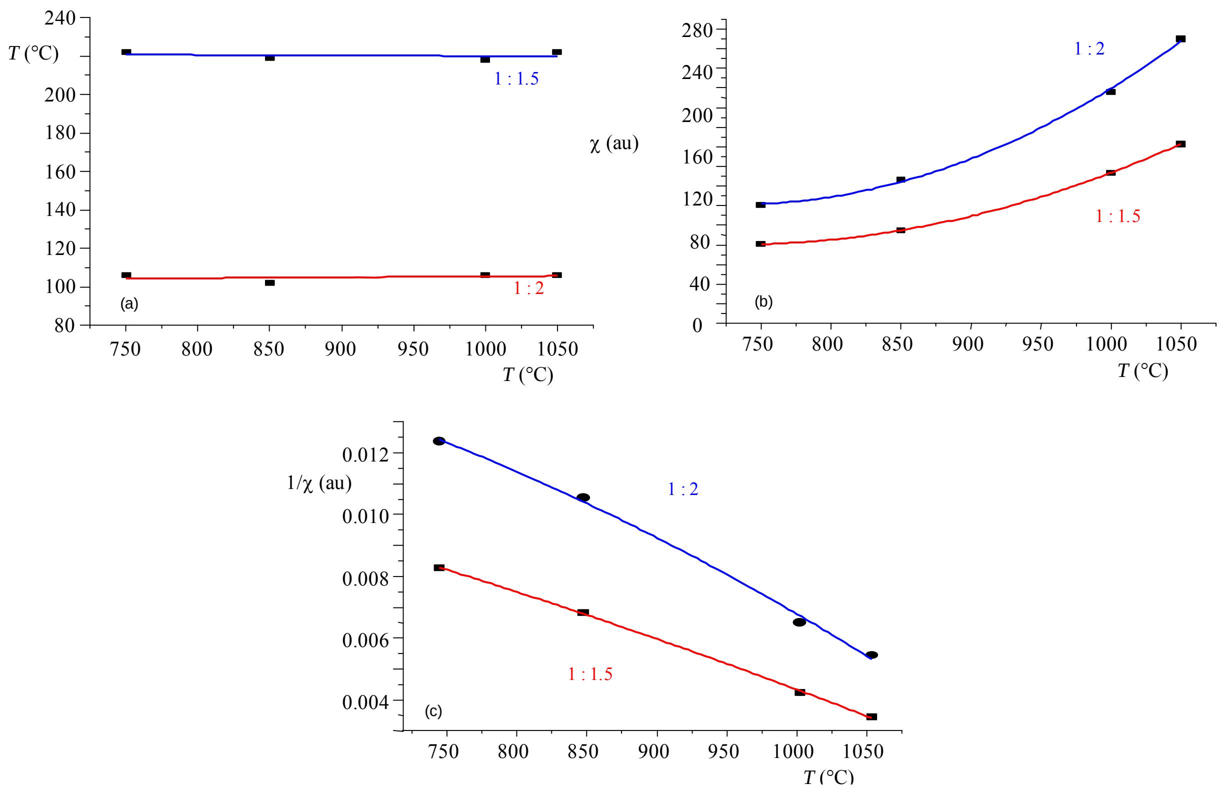

Fig. 2. (a) – Curie temperature, (b) - initial susceptibility and (c) – inverted value of the initial susceptibility of $Ni_{0.33}Zn_{0.67}Fe_2O_4$ and $Ni_{0.396}Zn_{0.804}Fe_{1.8}O_4$ ferrite samples as functions of the annealing temperature

low T_C value (T_C = 112°C). If the ratio of ions in this ferrite changes to Me^{2+} : Fe^{3+} = 1: 1.5, we can assume that the deficiency of Fe^{3+} ions will be only in B sites and results in partial reduction of spinel ferrite phase and creating the secondary phase ZnO zinc oxide on the grain boundary of the ferrite. Calculated value m_T of the magnetic moment of the composition

$$\left(Zn^{2+}_{0.603}Fe^{3+}_{0.396}\right)\left[Ni^{2+}_{0.297}Ni^{3+}_{0.099}Fe^{3+}_{1.404}\right]O^{2-}_{4-y} + xZnO \tag{5}$$

will be

$$(0\times 0.603 + 5\times 0.396)[2.2\times 0.396 + 5\times 1.404]\mu_B \tag{6}$$

and then

$$m_T = (-1.98 + [0.8712 + 7.02])\mu_B = 5.9112\mu_B \tag{7}$$

By the reduction of 0.267 Fe^{3+} ions in B sites, the B-B interaction weakens and consequentially the A-B interaction strengthens which results in the increase of T_C to approximately 220°C. The change of T_C resulting from the reduction of Fe^{3+} ions is obviously not only from Fig. 1 but also from Fig. 2a. However, in this case (when lacking Fe^{3+} ions in B sites) the rule, that with the increase of the content of Zn^{2+} ions T_C decreases, doesn´t apply. The stated knowledge, except the decrease in the χ can be considered as an indirect confirmation of the correctness of the assumed model expressed in formulae (5) and (6). The decrease of the initial susceptibility resulting from the deficit of Fe^{3+} ions can be explained using the equation

$$\chi(T) = \frac{J_S{}^2(T)}{A_{eff}(T)} \approx \frac{J_S(T)}{H_a(T)} \tag{8}$$

(where J_S is saturation polarization, A_{eff} is the effective energy of anisotropy and H_a is the anisotropy field) in the way that the decrease of the total magnetic moment probably causes the decrease of the J_S and thus the decrease of χ value.

In the both series of samples the ion ratio 1: 2 and also 1 : 1.5 susceptibility depends on the annealing temperature T_A. The $\chi(T_A)$ grows with T_A (Fig. 2b). Since T_C and the chemical consistency doesn´t depend on T_A, neither does the saturation polarization J_S. Then, according to the equation (8), the $\chi(T_A)$ can grow as a consequence of the decrease of the value of effective anisotropy $A_{eff} = (A_a + A_d)$ and it is done by the decrease of the value of the energy of demagnetisation A_d and therefore the value of the demagnetisation field. The energy of magnetocrystalic anisotropy A_a will not change under the influence of T_A, because in the given interval of temperatures, the temperature of annealing does not change the microstructure of the samples. The decrease of A_d can be in the first place caused by the increasing of the average size D of grain, as the consequence of the increase of T_A. The decrease of A_d can mostly be caused by the decrease of (primarily intragranular) porosity.

The value of H_c, or better its change as a result of the increase of T_A can be estimated from the dependency $1/\chi$ (T_A) (Fig. 2c). If the grains are formations with more domains, then the values H_c and $1/\mu$ tend to decrease according to the well known law $1/D$. In case of the dependencies in Fig. 2c the $1/\chi$ dependencies don´t work according to the $1/T_A$ law. We can therefore assume, that the growth of the D isn´t directly dependent on the annealing temperature.

In case of emergence of Hopkinson peak in $\chi(T)$ dependencies, we can assume that the grains (particles) at the temperatures T just below T_C get into a superparamagnetic state. All particles are magnetically stable (blocked) at temperature $T < T_k$. The dependence of the temperature $\chi(T)$ near T_C temperature will change according to the equation

$$\chi_P(T) = J_S^2 / A_a \tag{9}$$

whilst J_S (T) and $A_a(T)$ approach zero, but A_a decreases more quickly in its temperature. The main reason of the emergence of Hopkinson peak is the rapid decrease of $A_a(T)$. The anisotropy of the demagnetisation field A_d is in this case zero (or almost zero), since the particles are in superparamagnetic state. The high value of χ_p refers to a large number of particles (grains) which are at the temperature of $T \in < T_K, T_C >$ in a superparamagnetic state. By disappearance of Hopkinson peak, as a result of increasing temperature of annealing, the number of grains in superparamagnetic state decreases. It can be caused by the increase of the size of a growing number of particles, which don´t get to superparamagnetic state.

5 CONCLUSIONS

Iron deficiency variation in NiZn ferrite was used as a tool for the modification of the value of Curie temperature while preserve the required magnetic parameters. The thermomagnetic analysis was mainly used for the evaluation of T_C. The results were verified by SEM, Mössbauer spectroscopy and X-ray diffraction.

NiZn ferrite powders can be used as magnetic fillers in ferrite polymer composite materials for microwave applications. Ferrites and ferrite polymer composites can be utilised in a great variety of technical fields such as electric chokes, cores for LF and RF transformers, magnetic recording media, magneto-optical readers, rod antennas, and more recently radar absorbing materials (RAM).

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