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Nickel/Zinc Ratio and Lanthanum Substitution Effect on Structural and Magnetic Properties of Nickel Zinc Ferrites

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Improvement of NiZn ferrites properties by means on Ni/Zn content ratio modification and by partial substitution of Fe^{3+} ions by La^{3+} ions is presented. $Ni_xZn_{1-x}Fe_2O_4$ and $Ni_xZn_{1-x}La_{0.02}Fe_{1.98}O_4$ samples of small particles were prepared by self-propagated combustion method. X-ray spectroscopy was used for structural analysis, temperature dependence of magnetic susceptibility was used for evaluation of chemical and phase composition. Analysis showed that pure spinel structure without secondary phase caused by La ions for all values of Ni/Zn content was present. Noticeable growth of the magnetic susceptibility at room temperature was observed with rising of Zn^{2+} ions content.

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1. Introduction

Nowadays, attention is still focused on soft magnetic spinel ferrites. They are important and extensively used in several applications due to their good magnetic parameters, high resistivity together with relatively cheap production. There are several approaches to improve their parameters by modification of preparation procedure as well as by definition of an optimal chemical composition. Substitution of Fe^{3+} ions by rare-earth ions is one of them [1]. Due to chemical composition changes, magneto-crystalline anisotropy and therefore magnetic properties (e.g. resistivity, power losses) of ferrites are influenced [2]. Beside other rare-earth ions, influence of La^{3+} substitution on ferrite properties has been investigated [3, 4], $Ni_{0.5}Zn_{0.5}La_yFe_{2-y}O_4$ (fixed Ni/Zn ratio), where $y = 0$–0.3 ferrite composition was deeply analyzed [5].

The aim of presented work is to study the effect Ni^{2+}/Zn^{2+} ratio as well as the influence of partial substitution of Fe^{3+} ions by La^{3+} ions on structural and magnetic parameters of ferrites at various values of Ni^{2+}/Zn^{2+} ratio.

Several procedures of NiZn ferrite preparation are used yielding different particle size and morphology, and therefore the anisotropy, as ceramic technique [6], nitrate-citrate autocombustion method [7], high-energy ball milling [8] and sol–gel technique [9]. Most magnetic parameters are influenced by the particles anisotropy and size. X-ray spectroscopy was used for structural analysis, temperature dependence of magnetic susceptibility was used for evaluation of chemical and phase composition.

2. Specimen preparation and experiment

The ferrite powders were prepared by means of glycine–nitrate–acetate autocombustion synthesis. An advantage of this synthesis is the wet process of preparation allowing mixing of raw soluble salts in solution on the atomic scale. Thus, better homogeneity of prepared samples is achieved. The ferrite samples with chemical composition $Ni_xZn_{1-x}Fe_2O_4$ and $Ni_xZn_{1-x}La_{0.02}Fe_{1.98}O_4$ ($x = 0.3$, 0.36, 0.42, 0.5, 0.7, and 1.0) were synthesized from raw salts of analytical grade purity. The nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$, zinc acetate $Zn(CH_3COO)_2 \cdot 2H_2O$, lanthanum nitrate $La(NO_3)_3$ and iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$, as well as glycine NH_2CH_2COOH acting as the organic precursor in required stoichiometric amount were solved in deionized water. Raw solutions were mixed and heated until the gel consistence was reached. Further, the gel was consecutively heated until the self-propagating combustion process started. Obtained fluffy powder was sintered in the kanthal furnace at the temperature of 850 °C for 6 h. Prepared ferrite powder samples were analysed by measurement of temperature dependences of magnetic susceptibility. The NiZnLa ferrite structure was investigated and analysed by XRD (Co K_α radiation, $\lambda = 0.179020$ nm).

Magnetic susceptibility temperature dependences were measured by an AC bridge method at magnetic field intensity 760 A/m [10]. It represents and effective way of indicating phase composition and purity of powder ferrite samples. The $\chi(T)$ dependence is very sensitive to chemical and phase composition of ferrite. Compared with other method as SEM microscopy or XRD, it gives no such detailed information, but it is relatively cheap and quick.

3. Results and discussion

Structure of La-substituted NiZn ferrite was characterized by XRD for various NiZn ratio. The phase analysis confirmed single-phase cubic spinel structure for all the prepared ferrite samples. The presence of second phase $LaFeO_3$ was not found since the amount of La ions ($x = 0.02$) was very small. It appears at higher La ion content ($x = 0.025$), besides major spinel struc-

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ture also the minor orthorhombic structure of the $LaFeO_3$ appears [11].

XRD patterns of $Ni_xZn_{1-x}La_{0.02}Fe_{1.98}O_4$ (Fig. 1) show a small drift of the peak due to increase of Ni^{2+} concentration in the ferrite composition. This fact was confirmed by structural results, the value of the lattice parameter a slightly decreased with growing content of Ni^{2+}; for the composition $Ni_{0.3}Zn_{0.7}La_{0.02}Fe_{1.98}O_4$ ($x = 0.3$) with the lowest Ni contents achieved the higher value ($a = 8.41868$ Å) and for the maximal amount of Ni ($x = 1$, the composition $NiLa_{0.02}Fe_{1.98}O_4$, without Zn^{2+} ions in structure) the value of lattice parameter was the lowest ($a = 8.3419$ Å).

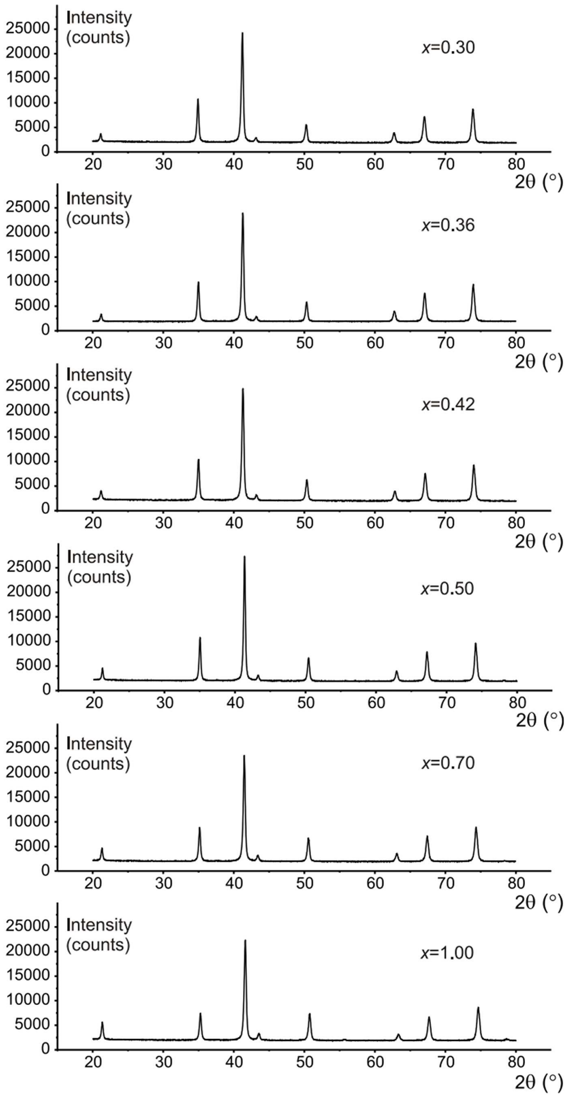

Fig. 1. XRD patterns of $Ni_xZn_{1-x}La_{0.02}Fe_{1.98}O_4$.

The decrease of the values of lattice parameter a is caused by increasing concentration of Ni^{2+} ions with the ionic radius of 0.69 Å, which is slightly lower than that of Zn^{2+} (0.74 Å). The dependence of lattice parameters on the Ni contents in NiZnLa ferrite samples is plotted in Fig. 2.

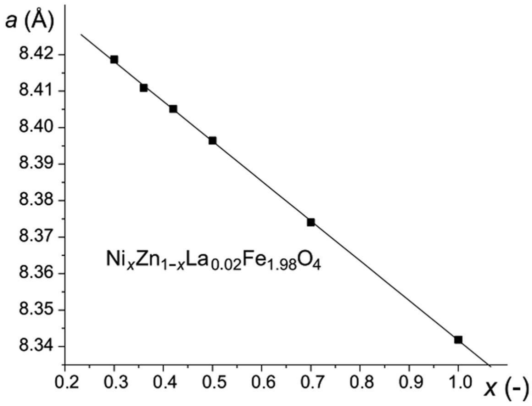

Fig. 2. Dependence of lattice parameter a on the Ni content x.

Temperature dependence of magnetic susceptibility was taken both on pure NiZn ferrite as well as on La-substituted samples. Dependences without any partial drops indicating presence of secondary phases were found on all samples; excessive Hopkinson peak reveals small-sized ferrite particles [10] (Fig. 3). Such result is in agreement with the self-combustion preparation method.

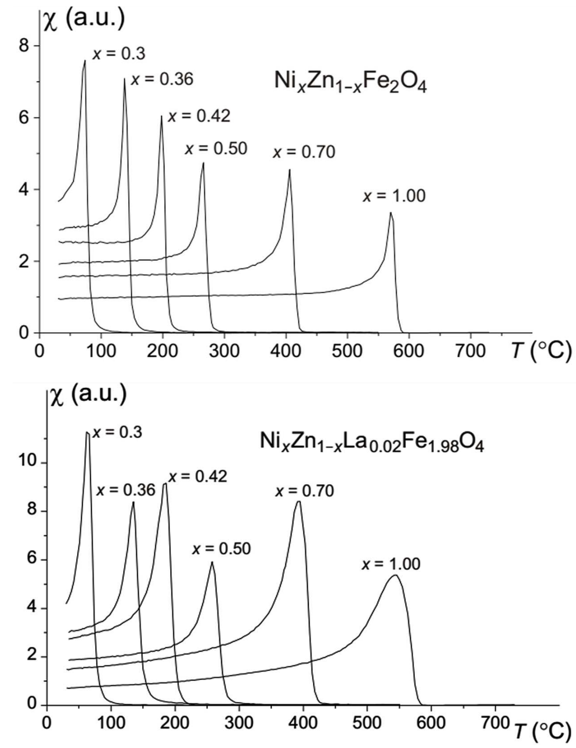

Fig. 3. (top) Temperature dependence of magnetic susceptibility of NiZn ferrite. (bottom) Temperature dependence of magnetic susceptibility of La-substituted NiZn ferrite.

The Curie temperature T_C was evaluated of both pure and La substituted NiZn ferrite samples for all values of Ni content x. It was determined numerically by a point of inflexion on Hopkinson's peak falling edge. The results, shown in Table I, reveal increase of T_C, with the addition of Ni^{2+} ions, and slight decrease of T_C, with the addition of La^{3+} ions. Both phenomena can be attributed to the variation of the Fe–Fe interaction number. In the first case, enter of Zn^{2+} ions into the A sites causes replacement of corresponding amount of Fe^{3+} ions from A to B sites, and in the second case, enter of La^{3+} ions into the B sites causes decrement of corresponding amount of Fe^{3+} ions in B sites and its paramagnetic character may violate coupling between magnetic ions. All described processes result in variation of A–B exchange interactions and affect the value of the T_C [12].

TABLE I

Curie temperature of pure and La-substituted NiZn ferrite on Ni content x.

	T_C [°C]	
x	$Ni_xZn_{1-x}Fe_2O_4$	$Ni_xZn_{1-x}La_{0.02}Fe_{1.98}O_4$
0.3	77.6	71.1
0.36	145.2	141.7
0.42	204.2	193.8
0.5	271.3	268
0.7	412.7	407.8

In Fig. 4, there are values of magnetic susceptibility at room temperature. The magnetic susceptibility values of pure NiZn ferrite powders are declining with rising of x and change only a slightly with La-substitution at low Ni content. It is in accordance with noticed an increase of coercive field [13] associated with growth of the demagnetizing field, and with the magnetocrystalline anisotropy changes, related to the strong spin–orbit coupling of rare-earth ions. In addition, we can conclude from these dependences that Fe–Fe interaction dominates also in the substituted ferrites regardless on Ni content [14].

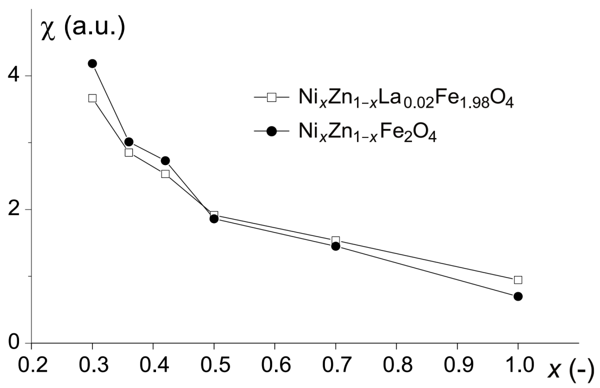

Fig. 4. Dependence of magnetic susceptibility of pure and La-substituted NiZn ferrite on Ni content x at room temperature.

4. Conclusions

La-substituted ferrite samples were prepared with fixed substituent content and of various Ni/Zn content. X-ray diffraction analysis shows the pure spinel structure without secondary phase caused by La ions for all values of Ni/Zn content. It is proved by the temperature dependences of magnetic susceptibility without multiple drops indicating presence of secondary phases. Strong Hopkinson's peak reveals small particle size typical for ferrites prepared by auto-combustion technology. The Curie temperature of pure NiZn ferrite increase with the addition of Ni^{2+} ions, and slight decrease with the addition of La^{3+} ions in substituted NiZn ferrite. Moreover, noticeable growth of the magnetic susceptibility at room temperature was observed with rising of Zn^{2+} ions content.

Acknowledgments

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References

[1] S.E. Jacobo, S. Duhalde, H.R. Bertorello, *J. Magn. Magn. Mater.* **272-276**, 2253 (2004).

[2] Y.C. Yang, L.S. Kong, S.H. Sun, D.M. Gu, B.P. Cheng, *J. Appl. Phys.* **63**, 3702 (1988).

[3] M.A. Gabal, A.M. Asiri, Y.M. AlAngari, *Ceram. Int.* **37**, 2625 (2011).

[4] Y. Liu, S. Wei, B. Xu, Y. Wang, H. Tian, H. Tong, *J. Magn. Magn. Mater.* **349**, 57 (2014).

[5] X. Wu, W. Wu, L. Qin, K. Wang, S. Ou, K. Zhou, Y. Fan, *J. Magn. Magn. Mater.* **379**, 232 (2015).

[6] S.E. Shirsath, S.M. Patange, R.H. Kadam, M.L. Mane, K.M. Jadhav, *J. Mol. Struct.* **1024**, 77 (2012).

[7] P.K. Roy, B.B. Nayak, J. Bera, *J. Magn. Magn. Mater.* **320**, 1128 (2008).

[8] S. Gao, S. Song, Q. Song, *J. Mater. Sci. Chem. Eng.* **3**, 50 (2015).

[9] N. Chen, M. Gu, *Open J. Met.* **2**, 37 (2012).

[10] V. Jančárik, E. Ušák, *J. Electr. Eng.* **50**, 63 (1999).

[11] P.K. Roy, J. Bera, *Mater. Res. Bull.* **42**, 77 (2007).

[12] G. Aravind, A. Gaffoor, D. Ravinder, V. Nathanial, *Adv. Mater. Letters* **6**, 179 (2015).

[13] A. Verma, T.C. Goel, R.G. Mendiratta, P. Kishan, *J. Magn. Magn. Mater.* **208**, 13 (2000).

[14] N. Rezlescu, E. Rezlescu, *Solid State Commun.* **88**, 139 (1993).