Effects of Iron Deficiency on Magnetic Properties of NiZn Ferrites

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Selected magnetic properties of (Ni0.33Zn0.67)1−xFe2−xFexO4 ferrite (where x = 0, 0.08, 0.12, 0.2) are investigated. The Curie temperature and the maximum flux density of Ni0.33Zn0.67 ferrites with Fe deficiency increases due to the increase in super-exchange interactions between A-B sites of spinel structure. Deficiency of Fe results in a decrease of grain size, susceptibility and permeability, meanwhile the coercivity and resonant frequency increase. The physical characteristics of the resulting products were investigated by X-ray diffraction, Mössbauer spectroscopy and thermomagnetic analysis. Deficiency of Fe in the studied composition extends temperature scale of the ferrite applicability, as well as enhances a temperature stability of ferrite.

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1. Introduction

NiZn ferrites are the widely used soft magnetic materials for high-frequency applications thanks to their high electrical resistivity, permeability, low losses and cost. As it is known, the deficiency of Fe affects the magnetic properties of NiZn ferrites, and results in the variation of the chemical composition and structure of NiZn ferrites. A systematic study of Fe-deficient NiZn ferrite is an interesting problem and changing the iron content in the composition is one of the ways to determine the magnetic properties of such materials [1–5]. When evaluating the effects of Fe deficit in such system to modify its final properties, one should find a suitable type of the initial composition of NiZn ferrite. In our case, as the initial composition to study the Fe deficiency effect on magnetic properties of ferrite, the Ni0.33Zn0.67Fe2O4 was chosen. Thus the influence of non-stoichiometry on the magnetic properties of (Ni0.33Zn0.67)1−xFe2−xFexO4 for x = 0.00 up to x = 0.20 was investigated.

2. Experimental methods used

The ferrites were prepared by wet method from an organo-metallic precursor with glycine, using low-temperature auto-combustion. Samples were prepared at various sintering temperatures (Ts). The thermomagnetic analysis was performed on the basis of magnetic susceptibility measured with automated balancing bridge Kappabridge KLY-2 at frequency 960 Hz. The phase compositions observed by thermomagnetic curves were compared with the Mössbauer spectroscopy results using the spectrometer with 57Co(Rh) source, and with PAN analytical X’PertPRO diffractometer using CoKα source.

The average grain size was calculated by the Scherrer equation. The magnetic properties at low frequencies were evaluated by means of computer-controlled hysteresisgraph built-up from commercially available measuring instruments. The experimental set-up allows usage of hardware as well as software feedback to control the waveform shape of either exciting field H(t), or flux density B(t). High-frequency magnetic properties were measured by automated equipment using network and/or impedance analyzer. The ferrite samples prepared with composition (Ni0.33Zn0.67)1−xFe2−xFexO4, where x = 0.00, 0.08, 0.12, and 0.20, were used for the experiments.

3. Results and discussion

XRD patterns of ferrites for samples with particular substitutions x = 0.00, . . . , 0.20 were measured. Rietveld method as implemented in the DiffracPlusTopas program (Bruker AXS, version 4.2) was used for determining crystallographic parameters and estimation of weight fractions of as-identified oxides. In the ferrite with initial composition Ni0.33Zn0.67Fe2O4 (sample with x = 0) sintered at 1200°C/6 h, two crystalline phases were identified. The first one was a spinel-type NiZn ferrite having the lattice parameter a = 8.4146 Å, the crystallite size D = 417 nm, and the weight fraction w = 99.4%. The second phase was identified as traces of ZnO (zincite) with the crystallite size D = 126 nm, and weight fraction w = 0.6%. In the case of samples with substitutions x = 0.08, 0.12, and 0.20 sintered at 1200°C/6 h, also two crystalline phases were identified. In Fig. 1 an example of the XRD patterns of Ni0.396Zn0.804Fe1.8O4 ferrites (with Fe-deficient content x = 0.2) sintered at 1200°C/6 h is shown. The first phase was identified as a spinel-type NiZn ferrite having the lattice parameter a = 8.4035 Å, the crystallite size D = 315 nm, and weight fraction w = 93.3%. The second phase was identified again as the ZnO having the crystallite size D = 131 nm, and the weight fraction w = 6.7%.

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Fig. 1. X-ray diffraction patterns made for \( \text{Ni}_{0.396}\text{Zn}_{0.804}\text{Fe}_{1.8}\text{O}_4 \) ferrite samples.

The selected properties of prepared materials are shown in Table I.

<table>
<thead>
<tr>
<th>Material</th>
<th>Fe\text{−}O, mg/m ²</th>
<th>Hc, A/m</th>
<th>µs</th>
<th>TC, °C</th>
<th>ZnO [%]</th>
<th>Size [nm]</th>
<th>Tc, °C</th>
<th>µ′</th>
<th>fc, MHz</th>
<th>Δf, MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni}<em>{0.33}\text{Zn}</em>{0.67}\text{Fe}_2\text{O}_4 )</td>
<td>0.178</td>
<td>0.226</td>
<td>0.185</td>
<td>0.209</td>
<td>110</td>
<td>1006</td>
<td>67</td>
<td>90</td>
<td>40</td>
<td>36</td>
</tr>
<tr>
<td>( \text{Ni}<em>{0.33}\text{Zn}</em>{0.67}\text{Fe}_2\text{O}_4 )</td>
<td>0.12</td>
<td>0.2</td>
<td>0.12</td>
<td>0.2</td>
<td>314.8</td>
<td>396</td>
<td>0.804</td>
<td>1</td>
<td>49</td>
<td>49</td>
</tr>
<tr>
<td>( \text{Ni}<em>{0.33}\text{Zn}</em>{0.67}\text{Fe}_2\text{O}_4 )</td>
<td>0.185</td>
<td>206.7</td>
<td>7.415</td>
<td>0.12</td>
<td>55</td>
<td>367</td>
<td>( 0.0−1.2 )</td>
<td>( 0.0−9 )</td>
<td>( 0.0−13 )</td>
<td>( 0.0−47 )</td>
</tr>
</tbody>
</table>

The weight fractions of ZnO and the crystallite sizes of NiZn ferrite for other two samples with \( x = 0.08 \) and \( 0.12 \) can be found in Table I. In the case of ZnO, its phase increases while the crystallite size \( D \) decreases due to Fe deficiency. On the other hand, \( D \) increases with \( T_s \).

Mössbauer spectra of the samples were measured at room temperature. Results for initial samples \( \text{Ni}_{0.33}\text{Zn}_{0.67}\text{Fe}_2\text{O}_4 \) and \( \text{Ni}_{0.396}\text{Zn}_{0.804}\text{Fe}_{1.8}\text{O}_4 \), sintered at 1200 °C/6 h, are shown in Fig. 2. The fitting model of spectra exhibits two components: one distribution corresponding to the magnetic phase of the sample, and other one corresponding to the non-magnetic phase of the sample. Mössbauer spectrum of initial \( \text{Ni}_{0.33}\text{Zn}_{0.67}\text{Fe}_2\text{O}_4 \) ferrite, shown in Fig. 2a, has the hyperfine field distribution area of 96%, and quadrupole splitting distribution area of 4%. Mössbauer spectrum of a sample with Fe-deficient content \( x = 0 \), is relaxation spectra rather than normal Zeeman spectra. Exceptionally it exhibits broad magnetic and quadrupole inhomogeneity [6]. Mössbauer spectrum of \( \text{Ni}_{0.396}\text{Zn}_{0.804}\text{Fe}_{1.8}\text{O}_4 \) ferrite, shown in Fig. 2b, has the hyperfine field distribution of 99%, and quadrupole splitting distribution area of 1%. Note that the distribution of magnetic component in the spectrum increases with decreasing contribution of Fe\(^{3+}\) in the sample. This is clearly seen in the case of those spectra that already display a Zeeman pattern [6]. Moreover, it is in line with the increase of super-exchange interactions between A-B sites of spinel, and also with the increase of \( T_C \).

As example, Fig. 3 shows the temperature dependencies of magnetic susceptibility \( \chi(T) \) of \( \text{Ni}_{0.33}\text{Zn}_{0.67}\text{Fe}_2\text{O}_4 \),\( \text{Ni}_{0.396}\text{Zn}_{0.804}\text{Fe}_{1.8}\text{O}_4 \),\( \text{Ni}_{0.33}\text{Zn}_{0.67}\text{Fe}_2\text{O}_4 \) samples, they all came from the same batch sintered at three selected temperature values (from 850 °C/6 h to 1050 °C/6 h with linear step of 100 °C). The Curie temperatures of these samples were \( T_C = 106 \) °C. Figure 3 shows also \( \chi(T) \) of \( \text{Ni}_{0.396}\text{Zn}_{0.804}\text{Fe}_{1.8}\text{O}_4 \) ferrite samples for which \( T_C = 220 \) °C. The Curie temperature increased roughly twice, from 106 up to 220 °C when Fe-deficient content \( x \) in the composition varied from 0 to 0.2. The values of \( \chi(T) \) increased with the sintering temperature \( T_s \). When \( T_s < 1050 °C \), there were no pronounced changes of \( T_C \) for all Fe-deficient samples observed in the \( \chi(T) \) curves behaviour. The crystal structure was found to be a magnetic monophasic. For \( T_s > 1200 °C \), the increase of ZnO phase with the amount of Fe deficiency and \( T_s \) was found. The \( \chi(T) \) dependencies for samples sintered at lower temperatures \( T_s \) exhibited a Hopkinson peak close to \( T_C \). This fact confirms the phase purity and particle size homogeneity of ferrite powders [5].
In case of Ni$_{0.33}$Zn$_{0.67}$Fe$_2$O$_4$ ferrite a mixed structure was detected. The part of Ni$^{2+}$ ions was substituted by Zn$^{2+}$ ions, the 0.67 of Zn$^{2+}$ ions took the A site and the equivalent number of 0.67 Fe$^{3+}$ ions was moved from A site to B site. Consequently, the magnetic moment $m_T$ has raised, according to the theoretical model

$$m_T = -m_A + m_B = -(1.65)\mu_B + [0.726 + 8.35]\mu_B,$$

where the magnetic moment of Fe$^{3+}$ ions is equal 5 $\mu_B$, the magnetic moment of Ni$^{2+}$ ions is equal 2.2 $\mu_B$, and $\mu_B$ is Bohr magneton. The ( ) parentheses in above equation denote the ions localization in A sites, while the square brackets [ ] show the localization of ions in B sites. According to that, the theoretical total magnetic moment $m_T$ at right side of (1) is expressed. However, the B lattice should be divided to sublattices B$_1$ and B$_2$ due to Yafet-Kittel canting. The measured moment $m_E = 4.25\mu_B$ turns out to be smaller than theoretical value, $m_E < m_T$ [7]. Since the B-B super exchange interactions are getting stronger, the effective moment $m_{BE}$ in B sites given by the sum of the projections of moments of both (B$_1$, B$_2$) sublattices to ferrimagnetic axis, becomes smaller than $m_B$, i.e., $m_{BE} < m_B$. In connection with it, the A–B super-exchange interactions become small. This might explain the low value $T_C = 106^\circ$C in Ni$_{0.33}$Zn$_{0.67}$Fe$_2$O$_4$ sample.

In Ni$_{0.396}$Zn$_{0.604}$Fe$_{1.8}$O$_4$ ferrite we can assume that Fe deficiency of the initial composition may affect the change of the theoretical $m_T$, according to the model

$$m_T = -(1.98)\mu_B + [0.8712 + 7.02]\mu_B = -m_A + m_B.$$  

By the reduction of Fe$^{3+}$ ions in B sites and rise of Fe$^{3+}$ in A sites the A-B interactions strengthen, which results in the increase of $T_C$ to approximately 220$^\circ$C. Consequently, the B–B interactions are reduced, the canting angle decreases and the projections of partial moments of both sublattices (B$_1$, B$_2$) increase together with the real $m_E$ value and the value of maximum induction $B_{max}$. Nevertheless, theoretical calculations of $m_T$ still indicate lower values, see (2). Thus, deficiency of Fe causes that the canting angle decreases while the effective magnetic moment $m_{BE}$ in B sites increases. In general, it means an increase $B_{max}$ at $H_{max} = 2000$ A/m, despite the fact that the $H_{C}$ values continue their increasing trend (see Table I). The maximum flux density $B_{max}$ values are characteristic when approaching the saturation regime, which is structurally-sensitive process.

The influence of insufficiency of the Fe ions on the relative amplitude permeability $\mu_r$ is clearly visible in Fig. 4. The dependencies of $\mu_r$ are shown upon the exciting field amplitude at sinusoidal field waveform of the ferrite samples sintered at 1200$^\circ$C. Note that the maximum amplitude permeability substantially decreases with the Fe ions deficiency. Extrapolating the curves in Fig. 4 to zero field, one can also find the initial permeabilities $\mu_i$. Results are given in Table I. The observed decrease of $\mu_i$ with increasing Fe deficiency can be attributed to increasing contribution of Ni, as well as, to the variation of grain size and porosity.

4. Conclusions

As can be seen from the experiments presented here, the level of Fe deficiency strongly affects the Curie temperature, structural and magnetic properties of substituted initial Ni$_{0.33}$Zn$_{0.67}$ ferrites. The increase of $T_C$ with Fe deficiency can be attributed to the decrease of the amount of Fe ions in B-sites, and increase of Fe ions in A-sites, consequently increasing A–B super-exchange interactions. Further, due to the reduction of the canting angle such increase is responsible for the increase of effective magnetic moment in B sites, and the increase of $B_{max}$. However, the decrease of susceptibility, initial and
amplitude permeability, the increase of coercivity and resonant frequency with Fe deficiency are probably due to increasing contribution of Ni, as well as, to the variation of grain size and porosity. The $\text{Ni}_{0.33}\text{Zn}_{0.67}$ ferrite powders with appropriate level of iron deficiency can also be used as magnetic fillers, for example, in the ferrite polymers composites for various microwave applications at a higher frequency range.

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**References**