Estimation of phase homogeneity of LiTiZn ferrites from the temperature dependence of the initial permeability near the Curie point

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Abstract. The estimation of the chemical homogeneity of lithium-substituted ferrite ceramics based on an analysis of the temperature dependences of the initial permeability near the Curie point was made. The transition of ferrite from ferrimagnetic to paramagnetic state at the Curie point is sensitive to the phase and chemical homogeneity of the material. It is shown that the best homogeneity is in ferrite products of the SL-187 brand compared with samples of ferrite ceramics, sintered in the laboratory conditions.

1. Introduction
Lithium-substituted ferrites have a wide range of applications in low-power microwave devices (phase shifters, switches, etc.). In addition, they have a low cost compared to other ferrites.

As is known, almost all the electromagnetic properties of ferrites are structurally sensitive, i.e. dependent on the content and volume distribution of defects in the microstructure.

It is known that ferrite ceramics obtained by classical ceramic technology has a number of structural defects and side phase inclusions [1, 2]. In a number of experimental works [3–6], the possibility of assessing the ferrite ceramics quality and its phase homogeneity according to the degree of decrease in the initial permeability on the temperature dependence near the Curie point is indicated.

Earlier, we proposed a method based on the mathematical processing of the experimental temperature dependences of $\mu_i$. It is shown that this method allows controlling the defects level affecting the processes of magnetization reversal in ferrites [7]. However, it was found that this method is not effective enough to estimate the chemical homogeneity of the magnetic phase of the initial powders and finished products. The transition of ferrites from the ferrimagnetic to the paramagnetic state is sensitive to the chemical homogeneity of the material. A characteristic of the transition is the rate of decline of the initial permeability on a temperature scale.

It is known that the Curie point $T_c$ of the material is highly sensitive to both chemical composition and the presence of controlled and uncontrolled impurities in the material. Consequently, any deviation of the chemical composition from the nominal level leads to a change in $T_c$, causing the blur of the curve $\mu_i(T)$ in the vicinity of $T_c$. Most clearly, this heterogeneity can be revealed by differentiating the $\mu_i(T)$ curve during the transition from the Hopkinson peak to the paramagnetic state of the material.

Therefore, to assess the chemical homogeneity of LiTiZn ferrites obtained under laboratory conditions, as well as industrial products of the SL-187 brand, in this work was used measurements of the initial permeability near the Curie point.
2. Experimental techniques
The synthesis of microwave ferrite was carried out on ceramic technology at the factory "Ferrite-Domen Co.", St. Petersburg. Industrial ferrite powder synthesized by oxide technology from a mechanical mixture of oxides and carbonates was used for the manufacture of samples.

The binder additive in the form of 10% aqueous solution of polyvinyl alcohol (PVA) in an amount of 12% by weight of the powder was introduced into the powder before pressing. Then the mixture was thoroughly mixed, sequentially rubbed through sieves and kept for 24 hours in the air at room temperature for more complete penetration of the binder solution into the powder particles. Compaction of samples in the form of disks and toroids was carried out using one-sided cold pressing using a PGr-10 hydraulic press. The pressure was 200 MPa. Exposure was three minutes.

Samples were sintered in laboratory conditions in the air in a resistance furnace with an integrated thermostat. Ferrite samples were sintered in 2 regimes: \( T_S = 1010 \, ^\circ C; \, t_S = 2 \, h; \, T_S = 1100 \, ^\circ C; \, t_S = 1 \, h \), where \( T_S \) is the sintering temperature, \( t_S \) is isothermal holding time. After sintering in the laboratory conditions, the samples had the form of toroids with dimensions: the outer diameter \( D = 18.5 \, mm \), the inner diameter, \( d = 14 \, mm \), thickness \( h = 2 \, mm \). Toroids from the examined ferrite were used as the cores of the inductor. Industrial ferrite products of the SL-187 grade were used for comparative studies. These ferrite products were made under the production conditions at the factory "Ferrite-Domen Co." at \( T_S = 960 \, ^\circ C; \, t_S = 8 \, h \). The dimensions of products: the outer diameter \( D = 20.5 \, mm \), the inner diameter \( d = 10.9 \, mm \), thickness \( h = 3.5 \, mm \).

The chemical formula: \( \text{Li}_{0.649}\text{Fe}_{1.598}\text{Ti}_{0.5}\text{Zn}_{0.2}\text{Mn}_{0.051}\text{Bi}_{0.002}\text{O}_4 \).

The phase composition of the samples was determined using an ARL X’TRA X-ray diffractometer (Switzerland) with a Peltier Si(Li) semiconductor detector and CuKα radiation. XRD patterns were measured for \( 2\theta = (10 – 80) \, ^\circ \) with a scan rate of 0.02 °/s. The phase compositions of the examined samples were determined using the PDF-4 powder data base of the International Centre for Diffraction Data (ICDD). The XRD patterns were processed by the full-profile Rietveld analysis using the Powder Cell 2.5 software.

The morphology of the sintered samples grains was investigated using a Hitachi TM-3000 scanning electron microscope (SEM). The average grain size was calculated using the intercept method.

The Curie point \( T_c \) was determined from the temperature dependence of \( \mu_i \) by drawing a tangent to the curve of the site of a rapid drop in \( \mu_i \) values. The intersection of this tangent with the temperature axis determined the value of \( T_c \). Also, this temperature was determined by the results of the mathematical processing of the temperature dependence of the initial permeability.

Measurement of inductance \( L \) of an inductor with a core of ferrite toroid was carried out by the bridge method [7].

3. Result and discussion
Figure 1 presents the X-ray diffraction pattern of samples sintered in laboratory conditions.

As can be seen from the Figure 1 obtained data confirmed the formation of single phase homogeneous cubic spinel structure.
Figure 1. The X-ray diffraction patterns of samples sintered in the laboratory conditions at $T_s = 1010 \, ^\circ C$, $t_s = 2 \, h$ (a) and $T_s = 1100 \, ^\circ C$, $t_s = 1 \, h$ (b).

Figure 2 presents a microstructure of the sintered ferrite ceramics. According to the data presented in Figure 2 sintered ferrite ceramics have well-formed grains. However, the grains are strongly agglomerated and have intragranular porosity. The average grain size showed similar values $(2.5 \pm 0.3) \, \mu m$ for both types of laboratory samples.

Figure 2. SEM micrographs of samples sintered in the laboratory conditions at $T_s = 1010 \, ^\circ C$, $t_s = 2 \, h$ (a) and $T_s = 1100 \, ^\circ C$, $t_s = 1 \, h$ (b).

At the same time, it was found the difference between the microstructure of laboratory samples and the microstructure of ferrite products of the SL-187 brand. Such materials are characterized by higher porosity and an average grain size of 50-100 microns (Figure 3).

Figure 3. SEM micrographs of industrial ferrite product SL-187.
Magnetic hysteresis loops are a traditional method for magnetic materials control. Comparing the parameters of the hysteresis loop allows estimating the irregularity and the presence of non-magnetic inclusions of ferrite ceramics. Figure 4 shows magnetic hysteresis loops obtained by the traditional oscillographic method.

Figure 4. Magnetic hysteresis loops of samples sintered in the laboratory conditions at $T_s = 1010 \, ^\circ\text{C}, t_s = 2 \, \text{h}$ (a), $T_s = 1100 \, ^\circ\text{C}, t_s = 1 \, \text{h}$ (b), and industrial ferrite product SL-187 (c).

From a comparison of the parameters of the hysteresis loops, it can be seen that similar parameters of the hysteresis loop are characteristic of laboratory samples, while for an industrial product there are lower values of the coercive force (Table 1).

| Samples type          | $B_s$ (mT) | $B_r$ (mT) | $H_c$ (A/m) |
|-----------------------|------------|------------|-------------|
| $T_s=1010 \, ^\circ\text{C}, t_s=2 \, \text{h}$ | 170        | 127        | 95          |
| $T_s=1100 \, ^\circ\text{C}, t_s=1 \, \text{h}$ | 168        | 129        | 98          |
| Industrial product SL-187 | 160        | 143        | 81          |

From Table 1 it can be seen that, according to the value of the coercive force $H_c$, industrial products are characterized by the smallest defectiveness due to smaller internal stresses affecting the magnetic reversal of ferrite magnetic domains according to the Neel theory [2].

Figure 5 shows the temperature dependences of the initial permeability near the Curie point. A sharp decrease in the initial permeability near the Curie point suggests the formation of a single-phase and chemically homogeneous structure of ferrite ceramics. There are sharp decreases of initial permeability near the Curie point. This behavior assumes the formation of a single-phase and chemically homogeneous ferrite structure.

According to the temperature dependences of the initial permeability in our work [7], the parameters of the phenomenological expression and the defects level were calculated. It was shown that the defects level in industrial products is lower compared with samples sintered in laboratory conditions. For samples manufactured under laboratory conditions, the optimal defects level was obtained for the sintering regime $T_S = 1010 \, ^\circ\text{C}, t_s = 2 \, \text{h}$. 

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III International Conference "Cognitive Robotics"  
IOP Conf. Series: Materials Science and Engineering 516 (2019) 012034  
doi:10.1088/1757-899X/516/1/012034
Figure 5. Comparison of the temperature dependencies of initial permeability for the samples sintered in industrial (1) and laboratory (2) conditions (2 – at 1010 °C for 2 h; 3 – at 1100 °C for 1 h) in the vicinity of the Curie point.

Figure 5 shows temperature dependencies of initial permeability of industrial products and the samples sintered in laboratory conditions. From a comparison of obtained experimental data, it follows that the greatest homogeneity is characteristic of the industrial products and slightly worse in the samples sintered in laboratory conditions.

4. Conclusion
In this work, the analysis of the experimental data showed that the transition of ferrite from ferrimagnetic to paramagnetic state at the Curie point is sensitive to phase and chemical homogeneity (homogeneity) of the material.

It is shown that the rate of decrease of the temperature dependence of initial permeability in the vicinity of the Curie point can be a quantitative characteristic of homogeneity [1]

Acknowledgements
This research was supported by the Ministry of Education and Science of the Russian Federation in part of the “Science” program, Project 3.4937.2017.

References
[1] Verma A., Chatterjee R. 2006 J. Magn. Magn. Mater. 306 313–320
[2] Smith J. and Wijn H. P. J. 1959 Ferrites: Physical Properties of Ferromagnetic Oxides in Relation to their Technical Applications (Phillips Technical Library: Eindhoven)
[3] Khan Z. H. et al 2013 J. of Alloys and Comp. 548 2018–215
[4] Parvin R. et al 2016 J. Magn. Magn. Mater. 401 760–769
[5] Ghodake J. S. et al 2015 J. Magn. Magn. Mater 378 436–439
[6] Hu J. et al 2007 Physica B: Cond. Mat. 400 119–123
[7] Malyshev A. V. et al 2018 J. Magn. Magn. Mater. 456 186–193