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The study of the ferroelectric properties of lithium-titanium ferrite

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Abstract. Loop-shaped dependences of the electric polarization on the electric field strength (the dielectric hysteresis) are registered for the first time for polycrystalline Li-Ti ferrite. Temperature evolution of the hysteresis loop parameters is investigated for ferrite samples. A thermal Barkhausen effect is detected during heating and cooling of ferrite specimens prepolarized in an electric field. The results obtained can be interpreted from the viewpoint of the Maxwell-Wagner relaxation polarization or induced ferroelectric-like state in the electric ferrite subsystem.

Keywords: Ferrite; Relaxation polarization; Residual polarization; Coercive field; Barkhausen pulse.

1. Introduction

Ferrite ceramics of the lithium group are the materials with well-established magnetic properties [1-3]. On the other hand, in [5, 6] it was shown that a ceramic material of the following composition $Li_{0.649}Fe_{1.598}Ti_{0.5}Zn_{0.2}Mn_{0.051}O_4$ under certain conditions exhibits dielectric behavior peculiar to ferroelectric materials.

It was shown that the experimental temperature dependences of the complex dielectric permittivity at the frequencies 10^2, 10^3, 10^4 and 10^6 Hz demonstrate a number of anomalies when measured at a high-level of the test signal (E_{test}=120 V/cm) at the frequency 10^2 Hz [2]. The anomalous behavior consisted in a sharp drop of the values of the real part of the permittivity ε' in the vicinity of the magnetic Curie temperature (575 K). When these dependences are measured at a low level of the test signal (E_{test}=2.3 V/cm) with a continuous voltage bias, the anomalies are manifested as sudden variations in the values of ε' and ε'' within narrow temperature intervals. Based on the analysis of the data obtained, the authors put forward a hypothesis that an additional relaxation polarization process induced by the electric field might occur in the ferrite, which is characterized by ferroelectric behavior [5, 6].

The present work reports the results of investigations of the feasibility and conditions of formation of properties similar to those of ferroelectric materials; in particular, the results on non-linearity and hysteresis of the electric-field-induced relaxation polarization dependences $P = f(E_p)$, where E_p is the polarizing electric field strength, applied to the specimen.

2. Experimental techniques

The sintering process and specimen preparation method were the same as reported in [3, 4]. The specimens were manufactured using a standard ceramic production process from an industrially synthesized mixture (Russian designation of the grade “3ZSC-18”) by thermal sintering of the compacts in air in a laboratory resistance furnace at the temperature 1283 K for two hours. The mode of sintering was selected to follow that used in the industrial production of the 3ZSC-18 ferrite. In order to remove the sub-surface layers having non-uniform distribution of electric properties over the depth, the surfaces of two sides of the specimens were ground using powdered Al_2O_3 (with different grain size) and a polishing paste.

The specimens were shaped as tablets measuring 13 mm in diameter and 0.24 mm in thickness, with silver electrodes deposited onto their surface using a PVD technique. The diagnostic electrode diameter was 5 mm.

The main phases and structural parameters of the examined ferrite were determined at room temperature by the x-ray phase analysis method (using an X'TRA diffractometer). The crystal lattice was cubic (with the lattice parameter a = 8.367 Å) and had Fd3m type spatial symmetry group. The method of differential scanning calorimetry (using an STA 449C Jupiter Netzsch thermal analyzer) did not show any noticeable exo- or endothermic reactions of the sintered ferrite ceramics at temperatures in the range 300-525 K which would be indicative of any phase structural transitions in the ferrite ceramics. In this case, the magnetocaloric effect with magnetic Curie temperature of 550 K was registered.

Experimental investigations of the temperature-field dependence of the ferrite ceramics polarization were performed using the classical Sawyer-Tower circuit [7].

Measurements of the polarization field dependences were performed at the electric field frequency changing from 20 Hz to 3 kHz and the electric field strength in the range 0-8300 V/cm with the ferrite samples whose temperatures changed in the range 300-600 K. The field dependences were registered with a Tektronix TDS-2012B electron storage oscillograph.

Repolarization current pulses (Barkhausen pulses) were monitored using a setup whose block diagram is given in Figure 1. The measurements were carried out during slow heating of (2 deg/min) of specimens in the temperature interval *T*=300-600 K. A DC voltage bias was applied to the specimens. Electric pulses were detected using a Velleman PCS-500 computer-automated oscilloscope.

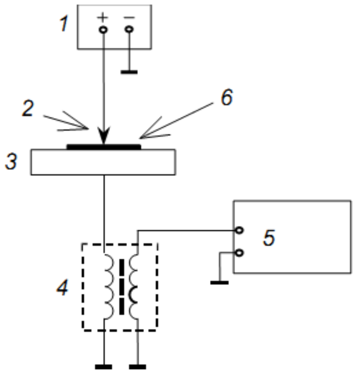

Figure 1. Layout of the Barkhausen pulses experiment: DC power supply (1), upper electrode (2), lower electrode with heater (3), transformer (4), oscilloscope (5), and specimen under study (6).

3. Result and discussion

Figure 2 presents a selection of electric field induced dependences of ferrite relaxation polarization at the temperatures 410 K.

Our investigations demonstrated the presence of dielectric hysteresis loops of classical shape for temperatures in the range 300-450 K and electric field frequencies f = 300-800 Hz (Figure 2). The hysteresis loop shapes indicate the possibility of the induced ferroelectric character of the ferrite polarization under the given conditions. It should be noted that similar hysteresis loops were observed only for the ferrite ceramic samples subjected to cooling from 600 K to room temperature in a constant electric field with strength higher than 500 V/cm. In this case, the heating degree was limited by the probability of thermal breakdown. It was believed that upon cooling of the ferrite samples in the electric field, the polarization was induced due to the orientation of electrical domains in each crystallite along the field direction, and that the residual polarization remained after the field removal. Similar processes were observed for dielectrics with the metastable electric polarization [9]. It is well known that the hysteresis loops of similar shapes are observed for a number of ferrohard materials in which internal fields are a serious obstacle to the efficient polarization [10].

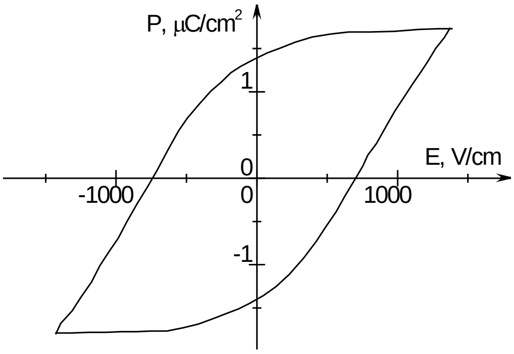

Figure 2. Dependence of the dielectric polarization P on the electric field strength E for the ferrite sample having a temperature of 410 K in the electric field having the frequency f = 300 Hz.

Beyond the indicated electric field frequency range for samples whose temperature is higher than 450 K, the loop-shaped field dependences are transformed into oval-shaped or linear dependences. It seems likely that in this case, the dielectric losses on the through conductivity are much greater than the losses on the relaxation polarization, thereby masking loops.

On the other hand, the similar hysteresis loops could be observed for nonlinear dielectrics with losses (the Maxwell-Wagner type relaxation polarization) [11]. The narrow frequency range f = 300-800 Hz in which the hysteresis loops are similar to those of ferrites testify to the Maxwell-Wagner polarization. However, a consideration of the given polarization mechanism demonstrates that processes of electron transfer and relaxation polarization are identical. Hence, the corresponding activation energies of these processes must be close in values. However, in [2] it was demonstrated that the activation energy of the process of electron transfer calculated from the temperature dependences of the conductivity for alternating current was approximately twice as great as the activation energy of the polarization process calculated from the temperature dependences of the parameter ε'.

Figure 3 shows the temperature dependences of the polarization loop parameters (the coercive field strength E_c and the residual polarization P_r) measured for an electric field frequency of 300 Hz. We note that their character is similar to the corresponding characteristics of the ceramic ferroelectric materials in which the smooth decrease in the P_r value with increasing ferrite sample temperature is caused by the nonuniformity and imperfection of the crystal structure.

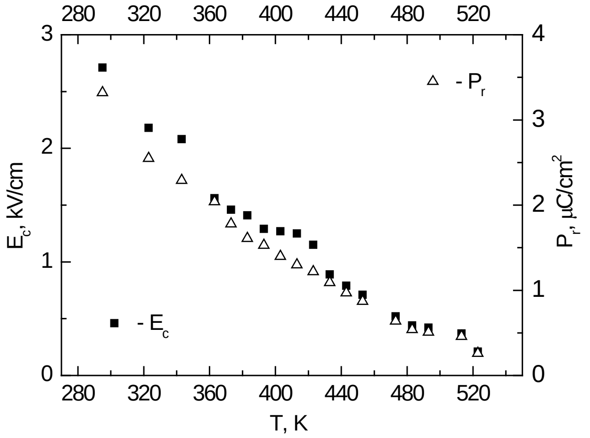

Figure 3. Temperature dependence of the coercive field strength E_c and residual polarization P_r at f = 300 Hz.

The E_c value decreases with increasing temperature due to the increased mobility of electric domains. Some special features of the E_c temperature dependence at T=410 K can be due to the influence of the heterogeneous microstructure of the ferrite ceramics on the mobility of electric domains. Thus, the character of the obtained temperature dependences is in agreement with the existing concepts about the ferroelectric materials [8].

Together with this, in the literature there are no experimental data on the temperature dependences of the hysteresis loop parameters of heterogeneous materials in the case of treatment of the results in the context of the Maxwell–Wagner model of the relaxation polarization.

Typical Barkhausen pulseforms are shown in Figure 4. Depicted in Figure 5 is the temperature dependence of the maximum Barkhausen pulse height U_m for ferrite specimens pre-polarized by an electric field. The figure implies that Barkhausen pulses are observed in the temperature interval T=465-575 K at the polarizing field strength $E_p > 80$ V/cm.

For $E_p<80$ V/cm, only electromagnetic noise is detected with a pulse height lower than 100 mV.

A sharp drop in re-polarization current pulses at 575 K might have been caused by a structural transition from ferroelectric to paraphrase state [8].

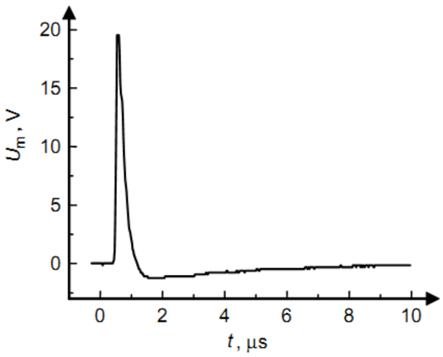

Figure 4. Typical electric pulse waveform: T=510 K, E_p=125 V/cm.

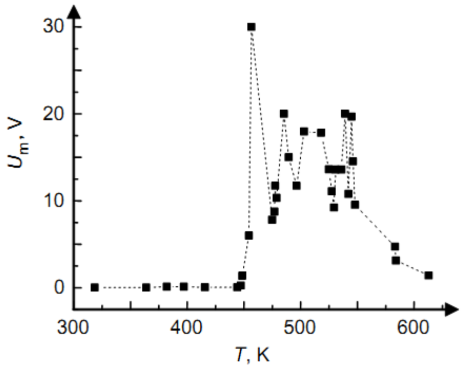

Figure 5. Temperature dependence of the maximum Barkhausen pulse height U_m for ferrite specimens pre-polarized by an electric field.

The ambiguity of treatment of the results obtained does not allow us to identify the relaxation polarization mechanism in ferrite ceramics and calls for further research in the field of relaxation phenomena in solid bodies including, for example, piezoelectric effect, temperature dependences of the lattice parameter [8]. The results obtained will allow the field of technical application of the lithium-titanium ferrite in modern electronics to be expanded together with the field of experimental and theoretical studies of multiferroics.

4. Conclusions

For the first time, the dielectric hysteresis loops have been established for the lithium-titanium ferrite ceramics, and the temperature dependences of the polarization loop parameters have been obtained.

The results obtained can be treated both as the mechanism of the Maxwell-Wagner relaxation polarization and as the mechanism that under definite conditions gives rise to the induced ferroelectric state in ferrite ceramics.

5. Acknowledgements

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References

[1] Venevtsev Yu N, Gagulin V V and Lyubimov V N 1982 Ferromagnets [in Russian] (Moscow: Nauka) p 130
[2] Malyshev A V, Peshev V V and Pritulov A M 2004 *Fiz. Tverd. Tela [in Russian]* **46** No 1 185-188
[3] Malyshev A V and Peshev V V 2007 *Russ. Phys. J.* **50** No 2 161-164
[4] Surzhikov A P, Lysenko E N, Malyshev A V et al 2013 *Russ. Phys. J.* **56** No 6 681-685
[5] Belov K P, Goryaga A M and Sheremetev V V 1986 *Fiz. Tverd. Tela [in Russian]* **30** 314-320
[6] Danil’kevich M. I. and Al-Sharr D 1992 *Bull. Byelorussian Univ. [in Russian]* **3** 71-78
[7] Lines M and Glass A Principles and Applications of Ferroelectrics and Related Materials 1979 (Oxford: Clarendon Press) p 736
[8] Zheludev I S 1968 Physics of Crystalline Dielectrics [in Russian] (Moscow: Nauka) p 464
[9] Gridnev S A 1997 *Soros. Obshcheobraz. Zh. [in Russian]* **5** 105-115
[10] Panich A E and Kupryanov M F 1989 Physics and Technology of Ferroceramics [in Russian] (Rostov-on-Don: Publishing House of Rostov-on-Don State University) p 389
[11] Ioffe A F 1957 Physics of Semiconductors [in Russian]. (Moscow: Academic Press) p 758