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Negative dynamic dielectric permittivity of a ceramic multiferroic $LuFe_2O_4$ with oxygen nonstoichiometry under the combined influence of temperature and electric field

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The temperature dependences $(100-380\,K)$ of the dielectric constant and conductivity of a ceramic multiferroic $LuFe_2O_4$ with oxygen nonstoichiometry, measured at alternating current (1, 10, 100 kHz, 1 MHz) and in a static electric field $(0-7.1\,V/mm)$, are presented. The regularity of the sign inversion of the dynamic permittivity caused by the appearance of solid-state inductance in the samples is discussed.

Keywords: negative permittivity, solid-state inductance, multiferroic.

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High requirements for high-density data recording and storage devices have initiated an interest in the scientific community in the search and study of functional materials in which the magnetization can be changed by a static electric field and vice versa. Such materials include the multiferroic compound $LuFe_2O_4$. Numerous experimental data indicate that at a temperature of $\sim 340\,K$, charge ordering (CO) appears in these compounds, and at $T \approx 240\,K$ — magnetic ordering (appearance of magnetization due to ordering magnetic moments of iron cations in the compound) [1–6]. The $LuFe_2O_4$ compound attracts the attention of researchers due to an unusual mechanism for the occurrence of electric polarization due to electron correlation processes and geometric frustration of charges (Fe^{2+}/Fe^{3+}) in the temperature range between 350 and 500 K [1]. The closeness of the charge and magnetic ordering temperatures to room temperature makes the multiferroic $LuFe_2O_4$ a promising material for the above applications.

There is no complete agreement in the literature regarding the multiferroic properties of $LuFe_2O_4$ [7–10] despite the large amount of experimental facts indicating the relationship between charge and magnetic ordering in this connection [3,11,12]. In the introductory part of the work [13], a review of recent studies is presented, which reveals topical problems in the physics of multiferroism in $LuFe_2O_4$ compounds. For a brief introduction to the circumstances in this area, we refer the reader to this article. The dielectric properties of $LuFe_2O_4$ are determined by the balance between polarization and conductivity due to the double charge exchange between iron cations of different valences (Fe^{2+}/Fe^{3+}) [14]. Deviation from oxygen stoichiometry δ, temperature T, electric field E and measuring field frequency ω are the factors that disturb this balance, and hence the very multiferroicity of $LuFe_2O_4$ [11,15]. To establish the impact of external influences on the parameters of materials based on the $LuFe_2O_4$ compound, it is important to study their permittivity ε and electrical conductivity as functions of the above parameters.

It is known that the dynamic permittivity, in contrast to the static one $(\omega \to 0)$, can have not only positive, but also negative values [16,17]. At the moment, in the works devoted to studying the dependence ε $(T, E = \text{const}, \omega = \text{const})$ of the $LuFe_2O_4$ of both polycrystalline and single crystal species, nothing has been reported about a negative dielectric constant in certain parameter ranges. Probably the authors [8], who studied samples prepared using a technology similar to ours, did not find sign inversion on the temperature-frequency dependence ε due to lower values of the measuring alternating and constant electric fields. It is important to note that they do not consider the temperature area above room temperature.

In this article, we report on the regularities of the inversion of the sign of the dynamic dielectric constant of ceramic $LuFe_2O_{4\pm\delta}$ with oxygen nonstoichiometry under the combined effect of temperature $(T = 100-380\,K)$ and electric field $(E = 0-7.1\,V/mm)$.

$LuFe_2O_4$ ceramic samples, prepared according to the so-called „paper synthesis“ technique, were used in the work. At the initial stage of synthesis, solution homogenization occurs — we prepare a stoichiometric solution of nitrates of all cations that are part of the sample. Next, quantitative filter papers were impregnated with this solution. After that, they are dried and burned. The resulting ash is annealed in air at a temperature of 600°C. Then the ash is ground and pressed into tablets with a diameter of ~ 6 mm and a thickness of about 1.5 mm [18]. Silver contacts with a diameter of 3 mm were deposited on opposite faces of a circular cross section by magnetron sputtering. Measurements were made on LCR-meters AM-3001 (AKTAKOM) and E7-12. The sample heating rate was ~ 2 K/min. The temperature was controlled by a copper-constantan thermocouple, the temperature measurement error in the range of $100-350$ K did not exceed 1 K. The amplitude of the testing sinusoidal voltage was 0.25 V. The real part of the complex permittivity of the objects of study was determined as the ratio of the measured electrical capacitance C of the sample to the geometric capacitance of the contacts to it C_0, and the imaginary part — through the specific electrical conductivity ($\sigma = \varepsilon_0 \varepsilon'' \omega$, ε_0 — dielectric constant, ε'' — imaginary part of permittivity). Samples of $LuFe_2O_{4+\delta}$ with different oxygen nonstoichiometry indices ($\delta = 0.07$ and -0.05), further denoted as KL-1 and KL-2, respectively. A positive value δ means a more oxidized state of $LuFe_2O_{4+\delta}$, i.e. relation $Fe^{3+}/Fe^{2+} > 1$; a negative value δ means a more reduced state of $LuFe_2O_{4+\delta}$, i.e. $Fe^{3+}/Fe^{2+} < 1$.

Figures 1, 2 show the temperature-frequency dependences of the permittivity and specific electrical conductivity KL-1 and KL-2 measured in a constant electric field and without a field at different frequencies of the test signal. Dependences $\varepsilon(T)$ for KL-1 and KL-2 at all frequencies of the measuring alternating voltage without an external field pass through a pronounced maximum with increasing temperature in the region $\sim 200-380$ K. The half-width of the maxima $\varepsilon(T)$ of the oxygen-deficient KL-2 sample is noticeably wider than that of the oxygen-rich KL-1 sample. A distinctive feature of the measurement results is the detection of a large negative permittivity and its frequency dispersion in the ω range used. Positions of maxima ($T_{\max} \approx 308$ K) and sign inversions ($T_{inv} \approx 330$ K) of $\varepsilon(T)$ temperature spectra at frequencies less than 1 MHz without field (Fig. 1) do not undergo noticeable changes with an increase ω. The application of a constant electric field over a measuring sinusoidal one leads to a shift in the position of the maximum and the sign inversion point ε towards low temperatures on the dependence $\varepsilon(T)$ for $\omega < 1$ MHz (Fig. 1).

For the oxygen-deficient sample KL-2 (Fig. 2), a similar picture is observed, the displacement of T_{inv} with increasing electric field occurs according to the law $T_{inv} = T_0 - 34.3U + 2.1U^2$ ($T_0 = T_{inv}$ at $U = 0$) at frequencies less than 1 MHz. The characteristics of the $\varepsilon(T, E = \text{const}, \omega = \text{const})$ curves for KL-1 and KL-2 are given in the table. Attention should be paid to the dependences $\varepsilon(T, E, \omega)$ at $E = 5.7$ V/mm (which corresponds to a voltage of 8 V applied to the sample) at frequencies 1 and 10 kHz (Fig. 2): with an increase in temperature in the region of $\sim 239-300$ K, the permittivity becomes negative and sharply increases in absolute value, passing through a sharp maximum at $T = 243$ K (the temperature of the magnetic ordering) for frequencies 1 and 10 kHz. At a frequency of 1 MHz, the inclusion of a constant electric field leads to an insignificant decrease in the value of $\varepsilon(T)$ for KL-1 and KL-2 in the area of the maximum. On the whole, the nature of the $\varepsilon(T)$ dependence for KL-1 and KL-2 is intermediate between $\varepsilon(T)$ for ferroelectrics with a smeared phase transition and ferroelectric relaxors.

Characteristics of the temperature spectra of the permittivity of $LuFe_2O_4$ with excess (KL-1) and deficiency (KL-2) oxygen

Sample	ω, kHz	$T_{\max}$, K $U = 0$ V	$T_{\max}$, K $U = 5$ V	T_{inv}, K $U = 0$ V	T_{inv}, K $U = 5$ V	T_{inv}, K $U = 8$ V
KL-1	1	308	164	335	267	–
	10	304	251	325	261	–
	100	310	254	328	260	–
	1000	270	268	289	289	–
KL-2	1	328	–	379	260	239
	10	334	–	380	266	239
	100	334	–	373	268	239
	1000	310293	312	310	310	

The temperature-frequency dependences σ for KL-1 and KL-2 at $U = 0$ have a typical semiconductor character [16]. At low temperatures ($T < 250$ K), σ does not depend on temperature, and at $T > 250$ K σ is practically not affected by the measurement voltage frequency less than 1 MHz. At a frequency of 1 MHz, $\sigma(T)$ for KL-1 and KL-2 tends to form a pronounced peak. The imposition of an electric field leads to a significant modification of $\sigma(T)$, except for the case $\omega = 1$ MHz.

Negative capacitance manifests itself in structures with inertial-relaxation conduction provided that the reactive component of the total conductance exceeds the Maxwellian displacement current [17]. Since the conductivity in dielectrics has a polaron character, it can „lag" behind the applied field at a lower frequency $E(t)$ than in semiconductors [16]. Such conductivity is typical for samples with an inductive type of impedance (phase lag of the current from $E(t)$). Therefore, in such structures, inductance data can be derived from negative capacitance values. When replacing a parallel chain of R and C elements (equivalent to a sample with a capacitive impedance type) by a series circuit with R and L elements (simulating the inductive properties of the sample), one can show [19] such that $L = R^2(-C)/(1 + \omega^2 R^2 C^2)$. For $\omega RC \ll 1$ the inductance can be approximated by the function $L = R^2(-C)$, and for $\omega RC \gg 1$ we obtain the estimate $L = 1/\omega^2(-C)$.

The inductance, in addition to the size and shape of the sample, also depends on the magnetic permeability of the material $\mu = B/B_0$ (B, B_0 — magnetic induction in matter and vacuum, respectively), which characterizes the magnetic properties environment. Therefore, a mechanism in which the formation of a sharp (in absolute value) maximum $\varepsilon(T)$ for frequencies 1 and 10 kHz at $U = 8$ V (Fig. 2) cannot be ruled out, among other reasons, it also occurs due to the development of magnetic ordering in

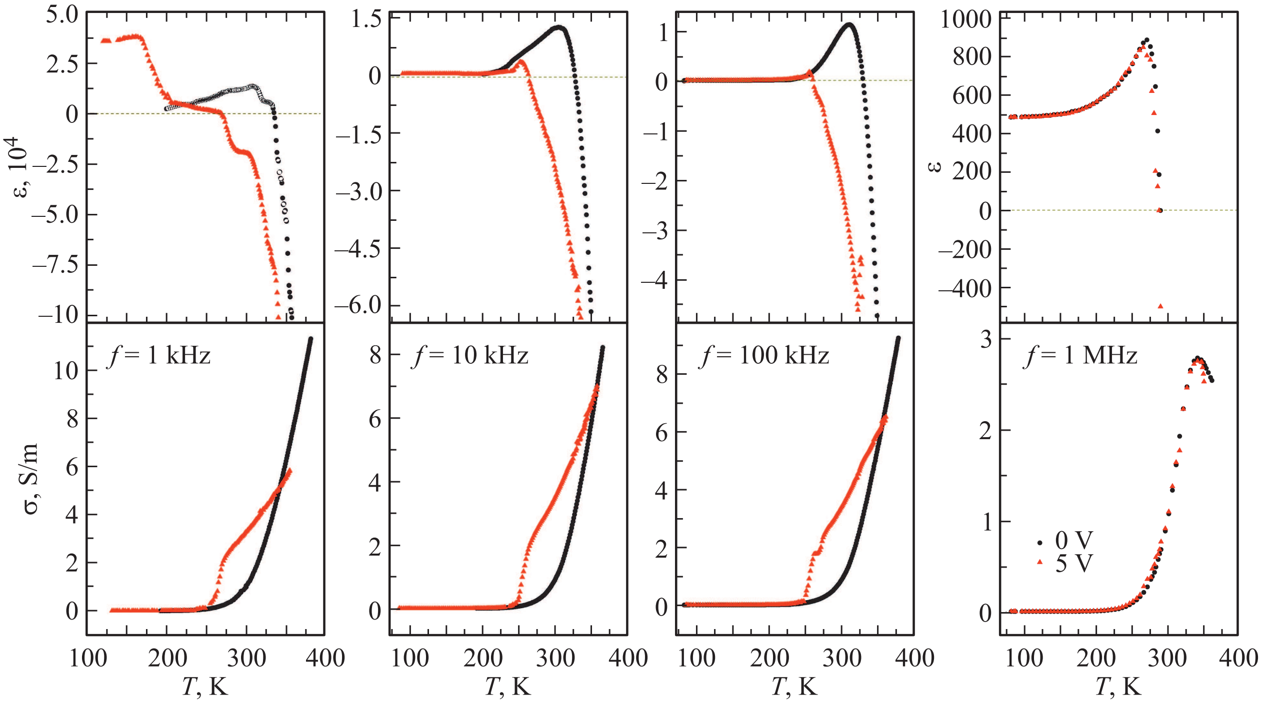

Figure 1. Temperature dependences of the permittivity and specific electrical conductivity of $LuFe_2O_{4+\delta}$. The frequencies of the measuring sinusoidal voltage f and the values of the constant voltage are indicated (in the field of the last graph).

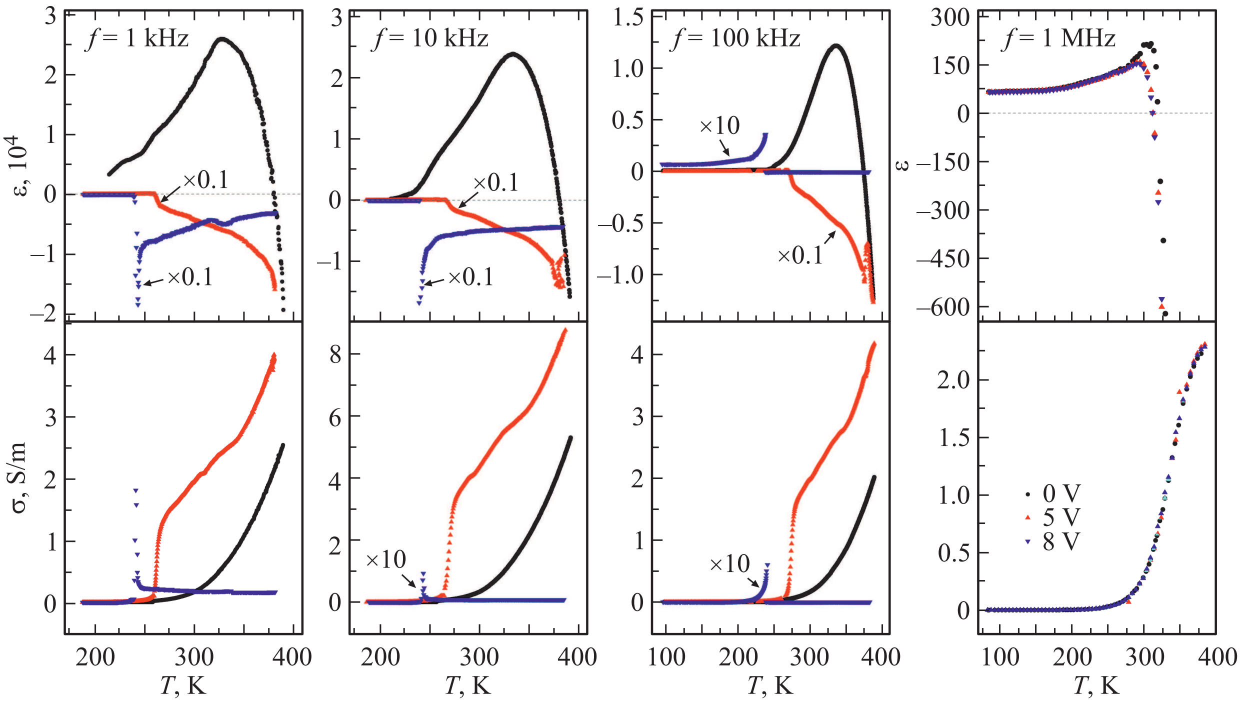

Figure 2. Temperature dependences of the permittivity and specific electrical conductivity of $LuFe_2O_{4-\delta}$. The frequencies of the measuring sinusoidal voltage f and the values of the constant voltage are indicated (in the field of the last graph).

the sample. This idea is suggested by the coincidence of the temperature of this maximum $T = 243$ K with the temperature of magnetic ordering and the proportionality of $(-C) \propto L \propto B$. Then it is appropriate to assume that the $\varepsilon(T)$ bursts (for $\omega = 1$ and 10 kHz, $U = 8$ V) observed at $T \approx 240$ K (Fig. 2) are due to the motion of the boundaries of the electric polarization domains with a characteristic relaxation time commensurate with the half-cycle of the test signal [8]. It is clear that when a quarter of the period of the measuring voltage at a frequency of 100 kHz is much less than the relaxation time of this conductivity mechanism, then it (conductivity) will contribute to the polarization, as can be seen in Fig. 2 for $\varepsilon(T)$ in the vicinity of the temperature 240 K.

Thus, the data obtained indicate an indirect relationship between the static electric field and the magnetic properties of the multiferroic $\mathrm{LuFe_2O_{4+\delta}}$ ($\delta = -0.05$). Selection of electric field values (from 0 to ~ 7.1 V/mm, which corresponds to the voltage applied to the sample 0−10 V), temperature ($\sim 250-400$ K) and frequency of the measuring voltage, the inductive properties of ceramics and thin $\mathrm{LuFe_2O_4}$ films can be changed in a controlled way. The results obtained create the prerequisites for the use of these materials in memory elements, as well as their use as solid-state inductors in planar technology for the production of integrated circuits.

Conflict of interest

The authors declare that they have no conflict of interest.

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