

Magnetic Capacitance of the $Gd_xBi_{1-x}FeO_3$ Thin Films

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Received March 14, 2016; in final form, June 27, 2016

Abstract—The capacitance, inductance, and dissipation factor of the $Gd_xBi_{1-x}FeO_3$ films were measured in the temperature range of $100\text{ K} < T < 800\text{ K}$ in magnetic fields of up to 8 kOe at frequencies of 0.1–100 kHz. The magnetic susceptibility maxima in the low-temperature region and dependences of the relaxation time and inductance on prehistory of the films cooled in zero and nonzero magnetic fields are established. The giant increase in magnetic capacitance in the external bias electric field is found. The results obtained are explained by the domain structure transformation in external electric and magnetic fields.

DOI: 10.1134/S1063783417040047

The $BiFeO_3$ -based multiferroics [1] have been widely used and intensively investigated as model objects for studying the interaction between the electric and magnetic subsystems and candidates for spintronic applications. The $BiFeO_3$ modulated magnetic structure (spin cycloid) disappears with decreasing film thickness in the 100-nm-thick films and weak ferromagnetism is observed in moderate fields with the linear magnetoelectric effect [2]. This can result in the formation of ferromagnetic domains due to the magnetostatic interaction.

The domain boundaries as fragments of magnetic spirals can induce electric polarization. This leads directly to the electric polarization of domain boundaries and makes it possible to control them by electric field [3]. The ferroelectric domain and magnetic domain walls in multiferroics appear coupled [4]. One of the possible mechanisms of this coupling in multiferroics is the flexomagnetoelectric effect [5]. Substitution of rare-earth elements for bismuth ions will lead to the variation in the magnetic and dielectric characteristics [6] and formation of localized electronic states in the band gap. Substitution of magnetically active rare-earth gadolinium ions for bismuth will lead to the displacement of oxygen ions in the octahedra containing iron ions and to the exchange coupling between gadolinium and iron ions, which will change the magnetic and ferroelectric structures.

The ferroelectric domain walls are charged and magnetic; their magnetic moment is determined by the wall width [7], which depends also on the density of impurity electrons localized near the walls. Substi-

tution of gadolinium for bismuth induces weakly coupled electrons near the domain wall. The external electric field induces electron hoppings near the wall and changes its shape. This model makes allowance for the spin-glass effects related to the degenerate states of domain walls and localized electronic states.

The aim of this study was to enhance the magnetic capacitance effect in the investigated films by changing their magnetic and electronic structures via substitution of gadolinium for bismuth ions over the value of this effect in bismuth ferrite.

The $Gd_xBi_{1-x}FeO_3$ ($x = 0.1$) bismuth ferrite solid solutions were formed by sputtering of the preliminary synthesized solid solutions onto quartz glass by a flash technique. Precursors were powders with a grain size from 0.1 to 0.3 μm . Sputtering was performed in a UVN-71R-2 vacuum facility. The pressure in a reaction chamber during sputtering was 10^{-2} – 10^{-3} Pa. The tantalum evaporator temperature was $\sim 2000^\circ\text{C}$. Substrates were placed at a distance of 10 cm from the evaporator. The substrate temperature was 250–300°C. The film thickness was 160 nm. According to the X-ray diffraction analysis (XRD) data, the $Gd_xBi_{1-x}FeO_3$ precursor has the rhombohedral crystal structure.

The permittivity and dissipation factor measurements were performed on the $Gd_xBi_{1-x}FeO_3$ ($x = 0.1$) film using an AM-3028 LCR meter in the temperature range of $100\text{ K} < T < 800\text{ K}$ and magnetic fields of up to 8 kOe at frequencies of 10 and 100 kHz. The magnetic field was directed parallel to the capacitor plates.

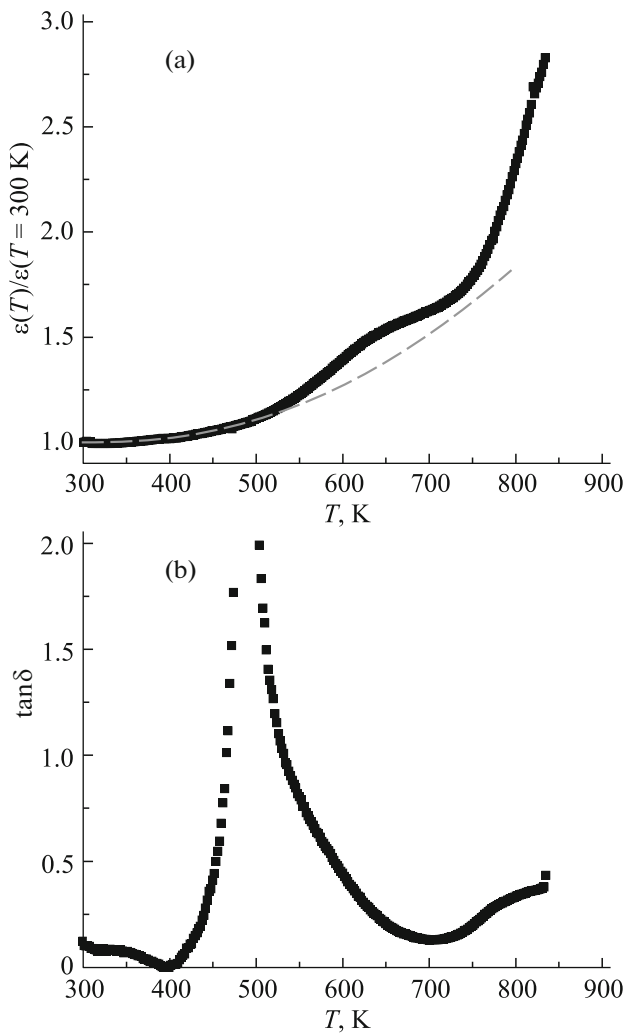


Fig. 1. (a) Permittivity normalized to its value at $T = 300$ K and (b) dissipation factor of $\text{Gd}_x\text{Bi}_{1-x}\text{FeO}_3$ ($x = 0.1$) at a frequency of 10^5 Hz as functions of temperature.

Figure 1 shows temperature dependences of the permittivity normalized to its value at $T = 300$ K and dissipation factor of the $\text{Gd}_x\text{Bi}_{1-x}\text{FeO}_3$ ($x = 0.1$) composition. The dielectric loss sharply increases at $T = 500$ K. For the bulk $\text{Gd}_x\text{Bi}_{1-x}\text{FeO}_3$ samples, we observed a kink in the temperature dependence of the imaginary part of the permittivity at this temperature [8]; for bismuth ferrite BiFeO_3 , below the Néel temperature $T_N = 646$ K ($x = 0$), the thermal expansion coefficient has a peak at $T = 533$ K [9], which is attributed to the structural transition. Possibly, substitution of gadolinium for manganese leads to the shift of the structural transition temperature by 30–40 K. In the vicinity of the Néel temperature, the permittivity grows. We determine the contribution of magnetic ordering to the permittivity using the approximation of the $\epsilon(T)$ dependence in the portion of 550–700 K by the power function (dashed line in Fig. 1a). The permittivity dif-

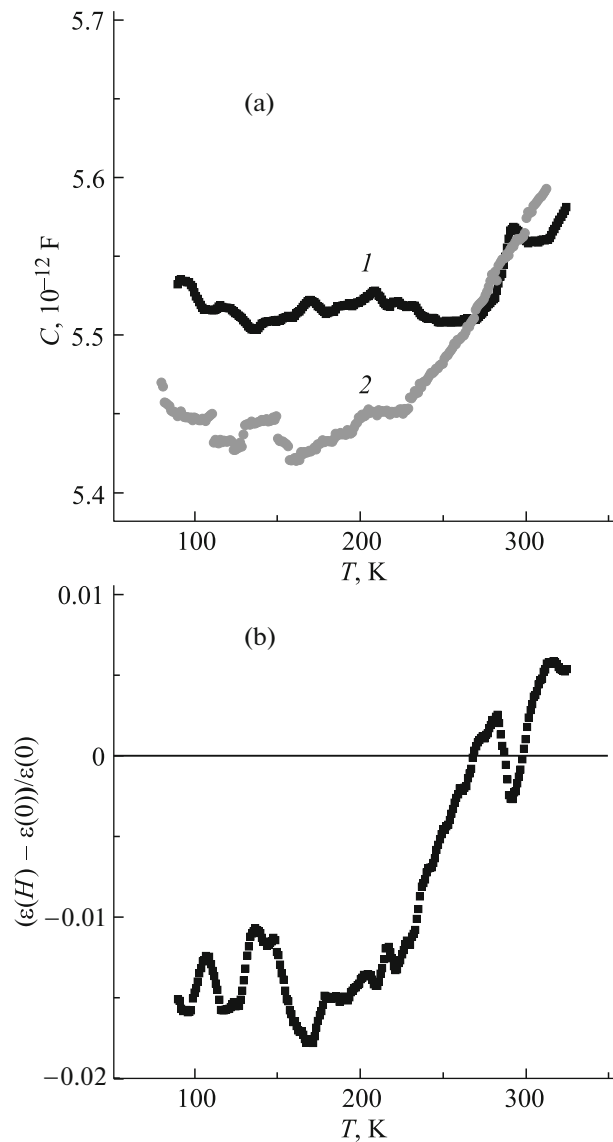


Fig. 2. (a) Electric capacitance of the $\text{Gd}_{0.1}\text{Bi}_{0.9}\text{FeO}_3$ film measured (1) in zero magnetic field and (2) in a magnetic field of 8 kOe at a frequency of 10^5 Hz as a function of temperature. (b) Relative permittivity variation in a magnetic field of 8 kOe with temperature.

ference ($\epsilon^{\text{ex}} - \epsilon^{\text{th}}$) is caused by the magnetoelectric contribution and is maximum near the temperature of the transition to the magnetically ordered state at $T_N = 632$ K. The contribution to the permittivity can be made by conduction electrons. The resistance of the BiFeO_3 films is over 10^{10} Ω cm and smoothly decreases with increasing temperature; at the Néel temperature, the activation energy changes twofold [7]. The contribution of conduction electrons to the dielectric loss near the Neel temperature is small against the background of the lattice strain induced by the magnetoelastic interactions.

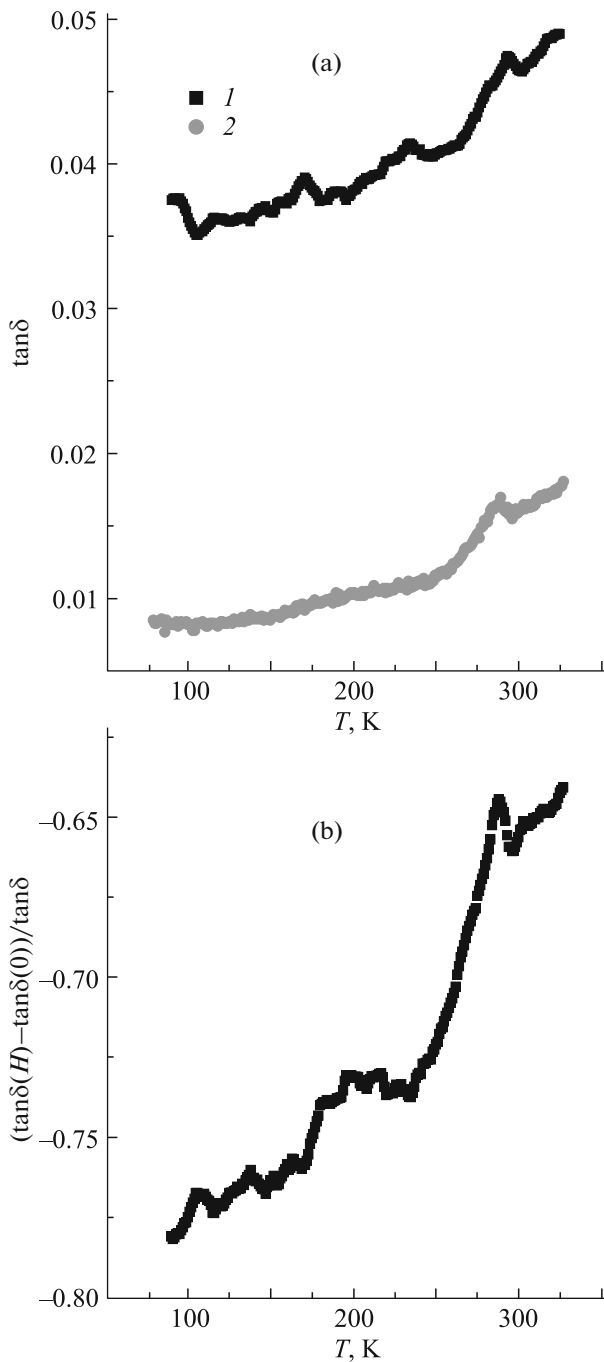


Fig. 3. (a) Dissipation factor of the $\text{Gd}_{0.1}\text{Bi}_{0.9}\text{FeO}_3$ film measured (1) in zero magnetic field and (2) in a magnetic field of 8 kOe at a frequency of 10^5 Hz as a function of temperature. (b) Relative variation in the dissipation factor in a magnetic field of 8 kOe with temperature.

As the temperature decreases, the permittivity sharply drops at $T = 290$ K (Fig. 2a). Below 270 K, the capacitance in a magnetic field becomes lower than in the sample in zero magnetic field and the relative magnetic capacitance decrease $(\epsilon(H) - \epsilon(0))/\epsilon(0)$ is 1.5% (Fig. 2b). The dielectric loss has a small maximum at

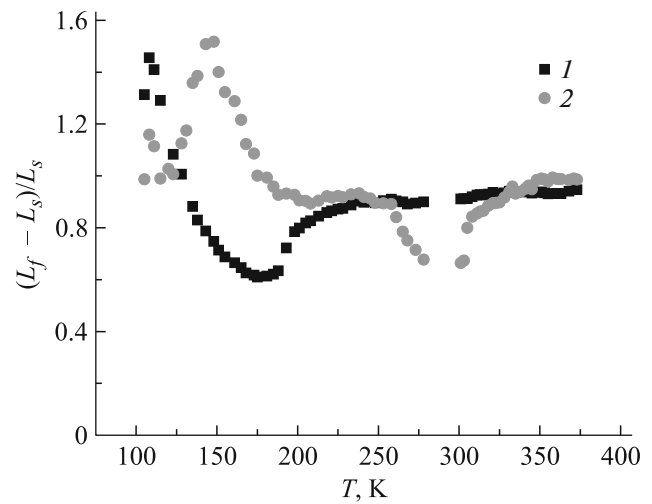


Fig. 4. Relative change $(L_f - L_s)/L_s$ in the inductance of the coil without film (L_s) and with the film (L_f) cooled in (2) zero magnetic field and (1) in a magnetic field of 2.5 kOe at a frequency of $\omega = 0.1$ kHz upon temperature variation.

a temperature of 286 K (Fig. 3a) and a decrease manifold in a magnetic field. The relative variation in the dissipation factor is illustrated in Fig. 3b, where one can clearly see a decrease in the dielectric loss in fields below 290 K.

We investigate the magnetic properties of the films using the measured inductances of a coil with the sample at different frequencies. For the bulk $\text{Gd}_x\text{Bi}_{1-x}\text{FeO}_3$ ($x = 0.1$) samples, we observed the hysteresis loop in the magnetic field dependences of magnetization with a coercive field of 3 kOe and a spontaneous magnetic moment of 0.2 emu/g [10]. The saturation magnetization is not attained in fields of up to 60 kOe, which distinguishes the substitution of magnetic ions for bismuth ones from the substitution of nonmagnetic (lanthanum or neodymium) ions [11]. The magnetic susceptibility growth in the fields weaker than the coercive field is mainly due to the translatory motion of domain walls under the action of heat fluctuations. Upon heating, the coercive field decreases and, when it is equal to the external magnetic field, the magnetic susceptibility sharply grows. Upon sample cooling in a magnetic field, the magnetic moment is induced, the density of domain walls decreases, and the magnetic susceptibility increases. As a result, the magnetic susceptibilities of the samples cooled in zero and nonzero magnetic fields should be different.

We measured the inductance of the solenoid with an inner diameter of $d = 2$ mm and a length of 10 mm with the $\text{Gd}_x\text{Bi}_{1-x}\text{FeO}_3$ ($x = 0.1$) film placed inside it. The inductances of the coil with and without the sample (L_f and L_s) were measured; since the inductance of the solenoid is related to the magnetic susceptibility

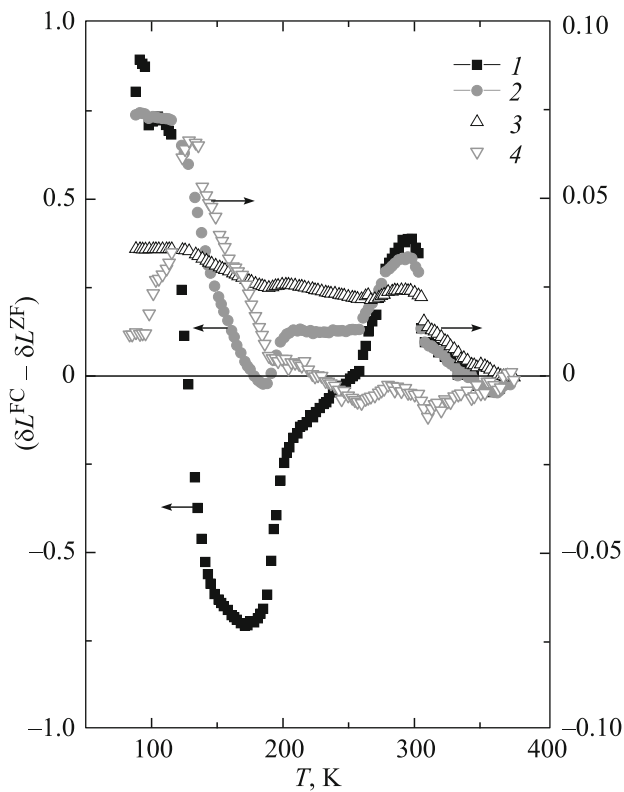


Fig. 5. Variation in the inductance $\delta L^{\text{FC}} - \delta L^{\text{ZF}}$ of the solenoid with the $\text{Gd}_x\text{Bi}_{1-x}\text{FeO}_3$ ($x = 0.1$) film cooled in zero field (ZF) and in a magnetic field of $H = 2.5$ kOe (FC) at frequencies of $\omega = (1)$ 0.1, (2) 1, (3) 10, and (4) 100 kHz.

as $L = n^2\mu\mu_0V$, then the magnetic susceptibility μ_r of the film with volume V_f is $\mu_r \sim \delta L = (L_f - L_s)/L_s$.

The inductance of the coil with the film cooled in zero field at frequencies of no higher than 10 kHz (Fig. 4) has a maximum near $T = 145$ K; the temperature of this maximum shifts toward lower temperatures to 109 K at a frequency of $\omega = 0.1$ kHz for the film cooled in a magnetic field of 2.5 kOe. The low-temperature anomalies in the dielectric and structural characteristics were observed in the bismuth ferrite BiFeO_3 nanotubes [12] and are missing in the bulk samples. In particular, the slope of the temperature dependence of the Raman phonon mode frequency changes at $T = 140$ K. The frequency of the E phonon mode increases by 14 cm^{-1} . The ultrasound dissipation increases, the impedance jump is observed, which is attributed to the capacitance growth, and the unit cell volume changes at $T = 150$ K. All these changes in the characteristics are related to the surface structural and magnetic phase transitions [13, 14]. The pyroelectric current has a sharp maximum at $T = 150$ K, whose temperature shifts toward lower temperatures upon sample cooling in a magnetic field.

The relative variation in the inductance of the solenoid with the film cooled in zero field has a small jump at $T = 300$ K (Fig. 4). Upon further cooling, the magnetic susceptibility sharply grows. The observed anomalies in the dynamic characteristics are explained by the change in the domain structure configuration.

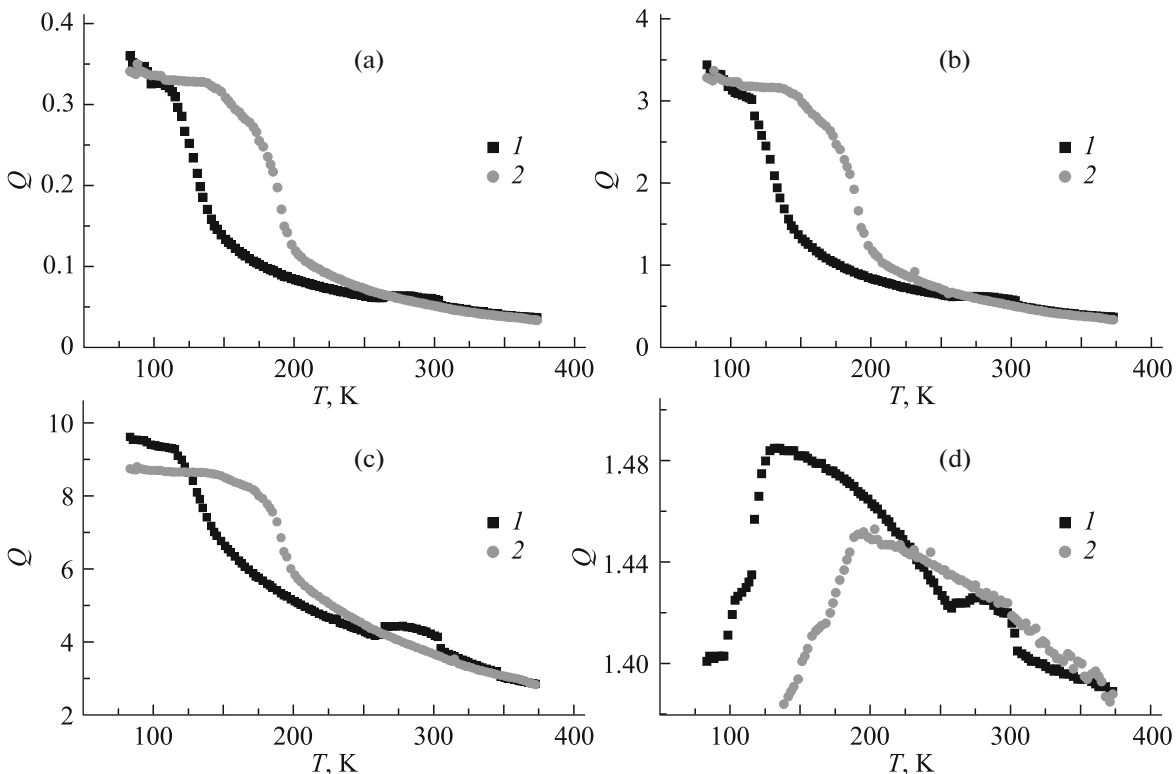


Fig. 6. Q factor of the electromagnetic oscillations of the solenoid with the $\text{Gd}_x\text{Bi}_{1-x}\text{FeO}_3$ ($x = 0.1$) film cooled (1) in zero field and (2) in a field of $H = 2.5$ kOe at frequencies of $\omega = (a)$ 0.1, (b) 1, (c) 10, and (d) 100 kHz.

Ferroelectric domain walls are charged; this charge is screened by electrons from the donor levels of gadolinium ions. At low temperatures, electrons are localized on the impurity levels and rigidly hold the domain wall. The domain wall motion in the external field at $T = 300$ K leads to the sharp growth of the magnetic susceptibility.

The variation in the inductance of the solenoid ($\delta L^{\text{FC}} - \delta L^{\text{ZF}}$) with the $\text{Gd}_x\text{Bi}_{1-x}\text{FeO}_3$ film cooled in the field (FC) and without it (ZF) is illustrated in Fig. 5. The negative value is related to the shift of the maximum of the relative change in the inductance of the solenoid with the film in a magnetic field from $T_m = 145$ K ($H = 0$) to $T_m = 109$ K ($H = 2.5$ kOe). These changes are indicative of the increase in the magnetic susceptibility of the film cooled in the magnetic field at frequencies of $\omega > 0.1$ kHz.

In nonequilibrium systems, the relaxation time is frequency-dependent. We determine the relaxation frequency from the Q factor $Q = \omega\tau/2$: $\tau = 2Q/\omega$. The Q factor of the electromagnetic oscillations of the coil with the sample is presented in Fig. 6. At low frequencies ($\omega = 0.1$ – 10 kHz), the relaxation time is frequency-independent. The relaxation time of the electromagnetic oscillations of the coil with the film cooled in zero field sharply increases with a decrease in temperature at $T = 140$ K (the derivative dQ/dT is maximum) and, with the films cooled in a magnetic field of $H = 2.5$ kOe, at $T = 190$ K. Below 190 K, the temperature dependence of the magnetic susceptibility changes (Fig. 4). At these temperatures, for the bulk samples we observed the intensity maxima in the magnon Raman spectrum with a small frequency shift at $T_1 = 140$ K and $T_2 = 201$ K [15], the ultrasound absorption maximum at $T = 200$ K [16], and the dependence of the susceptibility on prehistory of the sample cooled with and without field [17]. The temperature at which the susceptibilities χ^{FC} and χ^{ZF} are different, depends on the field and shifts from $T = 220$ K in a field of 0.5 kOe to $T = 80$ K in a field of 10 kOe [17]. These anomalies are caused by the orientational magnetic transitions. Upon cooling below 201 K, spins become orthogonal to the (111) plane and remain in this state below 140 K. Our films are characterized by the weak spontaneous moment and we may assume that the orientational magnetic transition occurs in a magnetic field at $T = 190$ K. As the temperature increases, the relaxation time decreases and the Q factor of the electromagnetic oscillations in the coil with the film has a small jump at $T = 300$ K, similar to the inductance of the coil with the film.

Thus, we can attribute the observed phenomena to domains and domain walls. Domains of three types have different coercive fields and oscillation frequencies. Switching of ferroelectric domains in the electric field by 109° in the BiFeO_3 films with a thickness of 600 nm was observed at $T > 300$ K by force piezoelectric spectroscopy with the rotation of antiferromag-

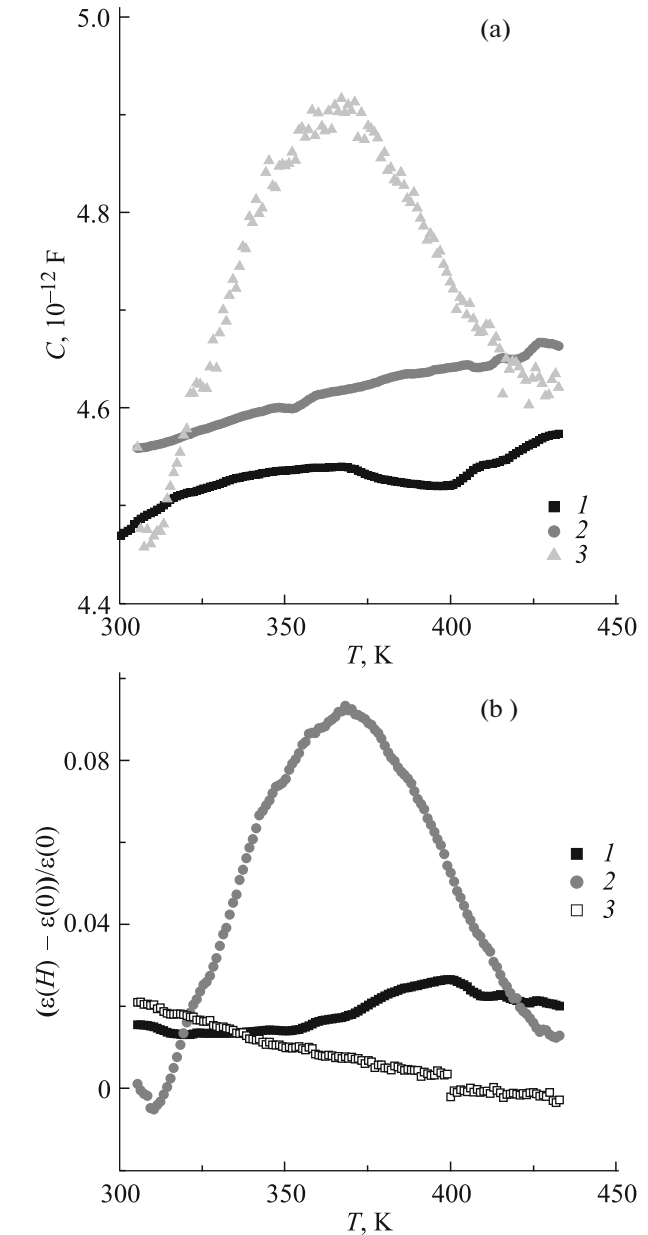


Fig. 7. (a) Temperature dependence of the electric capacitance of the film at a bias voltage of $U = 0.5$ V in magnetic fields of (1) $H = 0$, (2) 2.5, and (3) 8 kOe. (b) Relative permittivity variation $(\varepsilon(H) - \varepsilon(0))/\varepsilon(0)$ for the $\text{Gd}_x\text{Bi}_{1-x}\text{FeO}_3$ ($x = 0.1$) film at a frequency of $\omega = 100$ kHz in magnetic fields and at bias voltages of (1) $H = 2.5$ kOe and $U = 0.5$ V, (2) $H = 8$ kOe and $U = 0.5$ V, and (3) $H = 2.5$ kOe and $U = 1$ V.

netic domains by 90° , which was determined by photoemission electron microscopy with the linear X-ray dichroism, and the domain switching by 71° occurs at the higher temperature ($T = 380$ K) [18]. The switching time is 10^{-5} s [19].

The domain switching can be controlled by an external electric field. Let us investigate the permittiv-

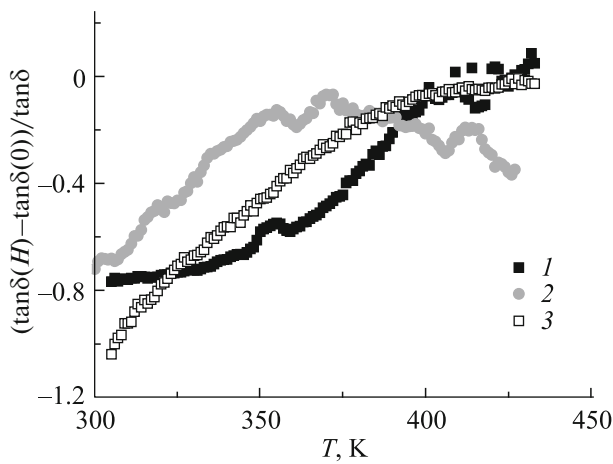


Fig. 8. Variation in the dissipation factor of the $\text{Gd}_x\text{Bi}_{1-x}\text{FeO}_3$ ($x = 0.1$) film at a frequency of $\omega = 100$ kHz in magnetic fields and at bias voltages of (1) $H = 2.5$ kOe and $U = 0.5$ V, (2) $H = 8$ kOe and $U = 0.5$ V, and (3) $H = 2.5$ kOe and $U = 1$ V.

ity of the film and dielectric loss at the simultaneous action of the electric and magnetic fields. Figure 7 shows plots of the electric capacitance in the electric fields with voltages of $U = 0.5$ and 1 V. The magnetic capacitance of the films increases in the external electric field at room temperatures in a magnetic field of 2.5 kOe due to the rotation of domains by 109° and the weak anomaly at 400 K is observed. A strong magnetic field (8 kOe) applied along the film reduces the activation energy of domain switching by 71° . In addition, the growth of permittivity in a magnetic field is related to the growth of the magnetic capacitance by an order of magnitude at $T = 370$ K with a voltage of $U = 0.5$ V.

The relative variation in the dissipation factor in a magnetic field is presented in Fig. 8. The permittivity increases in a magnetic field by 1–8% and the dielectric loss in the magnetic and electric fields at room temperature decrease by 70–100%. This is possibly due to the domain growth, a decrease in the number of domain walls, and enhancement of magnetic homogeneity of the film. In the temperature range of 370–400 K, the growth of the dielectric loss in a magnetic field has the same value as the permittivity growth. The permittivity growth in a magnetic field of $H = 8$ kOe was observed at a frequency of 10 kHz with a maximum value of 6% at $T = 420$ K (Fig. 9). The dielectric loss also decreases in a magnetic field and grows stepwise at $T = 390$ K.

Thus, the dielectric relaxation is caused by the motion of domain walls and switching of the ferroelectric domain orientation in the temperature range of 290–360 K under the action of the external electric field.

Thus, we obtained the following results.

In the low-temperature region, we found the maxima in the temperature dependence of the inductance

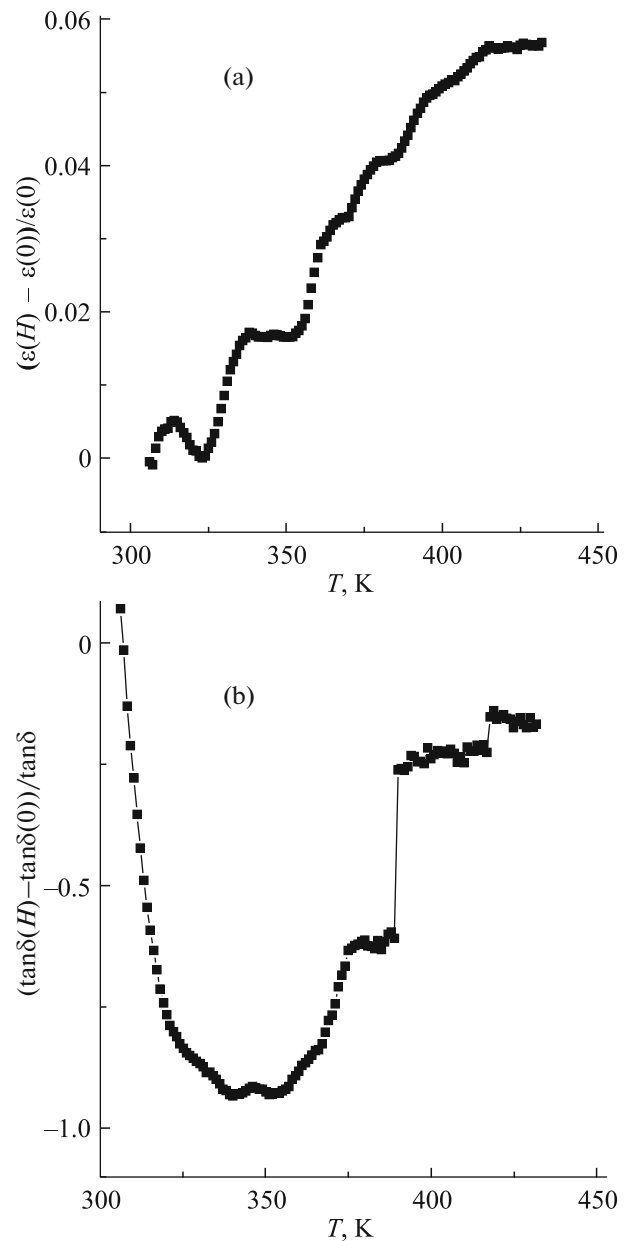


Fig. 9. Relative changes in (a) the permittivity and (b) dissipation factor in a magnetic field of 8 kOe for the $\text{Gd}_{0.1}\text{Bi}_{0.9}\text{FeO}_3$ film at a frequency of 10^4 Hz upon temperature variation.

of the solenoid with the film and the dependence of the inductance and Q factor of the electromagnetic oscillations of the prehistory of the film cooled with and without magnetic field as a result of the orientational magnetic phase transition. In the temperature range of 290–300 K, the temperature derivatives of inductance and permittivity attain their maximum values related to the switching of domains by 109° and the magnetic capacitance changes its sign from negative to positive. We established a decrease in the dielectric loss smaller by an order of magnitude than the mag-

netic capacitance in a magnetic field below 350 K. We observed the enhancement of the magnetic capacitance in the external electric field with the maximum in the temperature range of 370–400 K due to the switching of domains by 71° .

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, projects nos. 15-42-04099 r_sibir_a, 16-52-00045 Bel_a, and 16-42-240436 r_a and the state order no. 114090470016.

REFERENCES

1. A. P. Pyatakov and A. K. Zvezdin, *Phys.—Usp.* **55** (6), 557 (2012).
2. M. Fiebig, *J. Phys. D: Appl. Phys.* **38**, R123 (2005).
3. I. E. Dzyaloshinskii, *Eur. Lett.* **83**, 67001 (2008).
4. M. Fiebig, Th. Lottermoser, D. Fröhlich, A. V. Goltsev, and R. V. Pisarev, *Nature (London)* **419**, 818 (2002).
5. Z. V. Gareeva and A. K. Zvezdin, *Phys. Solid State* **52** (8), 1714 (2010).
6. S. S. Aplesnin, V. V. Kretinin, A. M. Panasevich, and K. I. Yanushkevich, *J. Exp. Theor. Phys.* **121** (3), 422 (2015).
7. G. Catalan and J. F. Scott, *Adv. Mater. (Weinheim)* **21**, 2463 (2009).
8. K. P. Andryushin, A. V. Turik, L. A. Shilkina, I. N. Andryushina, S. I. Dudkina, and L. A. Reznichenko, in *Proceedings of the International Scientific-Technical Conference “Fundamental Problems of Electronic Instrument Engineering” (INTERMATIC-2011), Moscow, November 14–17, 2011, Part 2.*
9. A. A. Amirov, A. B. Batdalov, S. N. Kallaev, Z. M. Omarov, I. A. Verbenko, O. N. Razumovskaya, L. A. Reznichenko, and L. A. Shilkina, *Phys. Solid State* **51** (6), 1189 (2009).
10. P. Suresh and S. Srinath, *Inst. Phys. Conf. Ser.: Mater. Sci. Eng.* **73**, 012082 (2015).
11. A. Ahlawat, S. Satapathy, V. G. Sathe, R. J. Choudhary, M. K. Singh, R. Kumar, T. K. Sharma, and P. K. Gupta, arXiv:RRCAT-SS-18-06-2013-6.
12. R. Jarrier, X. Marti, J. Herrero-Albillos, P. Ferrer, R. Haumont, P. Gemeiner, G. Geneste, P. Berthet, T. Schulli, P. Cevc, R. Blinc, Stanislaus S. Wong, Tae-Jin Park, M. Alexe, M.A. Carpenter, et al., *Phys. Rev. B: Condens. Matter* **85**, 184104 (2012).
13. M. K. Singh, R. S. Katiyar, and J. F. Scott, *J. Phys.: Condens. Matter* **20**, 252203 (2008).
14. M. K. Singh, W. Prellier, M. P. Singh, R. S. Katiyar, and J. F. Scott, *Phys. Rev. B: Condens. Matter* **77**, 144403 (2008).
15. J. F. Scott, M. K. Singh, and R. S. Katiya, *J. Phys.: Condens. Matter* **20**, 322203 (2008).
16. SAT Redfern, Can Wang, J. W. Hong, G. Catalan, and J. F. Scott, *J. Phys.: Condens. Matter* **20**, 452205 (2008).
17. T. J. Park, G. C. Papaefthymiou, A. J. Viescas, A. R. Moodenbaugh, and S. S. Wong, *Nano Lett.* **7**, 766 (2007).
18. T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M. P. Cruz, Y. H. Chu, C. Ederer, N. A. Spaldin, R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, and R. Ramesh, *Nat. Mater.* **5**, 823 (2006).
19. T. H. Kim, S. H. Baek, S. M. Yang, S. Y. Jang, D. Ortiz, T. K. Song, J. S. Chung, C. B. Eom, T. W. Noh, and J. G. Yoon, *Appl. Phys. Lett.* **95**, 262902 (2009).

Translated by E. Bondareva