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Effect of dopant on piezoelectric and dielectric properties of thin films $Bi_{3.25}La_{0.75}Ti_{3-x}A_xO_{12}$ (A — Mn, Zr, Nb)

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It is shown that microstructure, dielectric and piezoelectric properties change in films based on lanthanum-substituted bismuth titanate (BLT) depending on the alloying impurity material, which leads to changes in coercive voltage, internal displacement field and control coefficient.

Keywords: lead-free ferroelectric films, bismuth titanate, electrophysical properties, capacitance-voltage characteristics, piezoresponse force microscopy.

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1. Introduction

Bismuth titanate compound $Bi_4Ti_3O_{12}$ is a three-layer ($n = 3$) phase of Aurivillius ($Bi_2A_{n-1}B_nO_{3n+3}$) and is a lead-free ferroelectric with a high Curie temperature ($T_C = 675°C$) [1]. To control the dielectric and ferroelectric properties of bismuth titanate, various options for A- and B-cationic substitutions of a perovskite-like sublattice with corresponding ionic radii and valence are considered. Thus, lanthanum-substituted bismuth titanate $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) is considered as a material for FeRAM memory, which in some respects (in particular: the number of switching cycles) is superior to traditional ferroelectrics based on lead zirconate-tinatan (PZT) [2]. The authors of the study [3] showed that the replacement of bismuth with lanthanum in $Bi_4Ti_3O_{12}$ leads to a decrease in the T_C, while improving the dielectric properties of bismuth titanate-based ceramics, since bismuth volatility decreases and the number of oxygen vacancies decreases. In addition to cationic substitution, methods for obtaining thin films are the dominant factors affecting the microstructure and ferroelectric properties of films based on bismuth titanate. Thus, the microstructure of BLT films has several types of grains, but basically these are rods and plates that are formed by sol-gel method [4], pulsed laser deposition [5] or high-frequency magnetron spraying [6]. It was also found that the shape of the grains and the orientation of films based on $Bi_4Ti_3O_{12}$, synthesized by chemical precipitation from the solution, can be controlled using the heating rate and annealing temperature [7].

The present paper presents the results of a study of the microstructure, piezoelectric and dielectric properties of thin films based on lanthanum-substituted bismuth titanate doped with manganese, niobium and zirconium ions.

2. Samples and experimental procedure

Thin-film samples of lanthanum-substituted bismuth titanate of compositions $Bi_{3.25}La_{0.75}Ti_3O_{12}$, $Bi_{3.25}La_{0.75}Ti_{2.97}Mn_{0.03}O_{12}$ (BLT : Mn), $Bi_{3.25}La_{0.75}Ti_{2.975}Nb_{0.025}O_{12}$ (BLT : Nb) and $Bi_{3.25}La_{0.75}Ti_{2.975}Zr_{0.025}O_{12}$ (BLT : Zr) with a thickness of 200 nm obtained by chemical precipitation from a solution and applied to $Pt/Ti/SiO_2/Si(100)$ substrates using the centrifugation technology. High-temperature treatment (annealing) was performed at 750°C for 30 min. The topography of the films and the processes of „macroscopic“ polarization were carried out using the Ntegra Prima nanolaboratory (NT-MDT SI, Russia) in the mode of power microscopy of piezoresponce. The vertical component of the piezoresponce signal (Mag×Cos channel) was recorded by the application on the conductive probe NSG10/TiN (Tipsnano, Tallinn, Estonia) of alternating voltage with an amplitude of 5 V and a frequency of 150 kHz, the scanning speed was 0.5 Hz. Residual loops of piezoelectric hysteresis were obtained on a multifunctional scanning probe microscope MFP-3D™ Stand Alone (Oxford Instruments Asylum Research, USA) in DART mode near the contact resonance „cantilever−sample“ (∼ 1.1 MHz), after which they were corrected using the model of a simple harmonic oscillator [8]. To measure the capacitance-voltage characteristics, contact pads made of platinum with a thickness of 100 nm and a diameter of 100 μm were applied to the surface of films by magnetron sputtering through a shadow mask. The

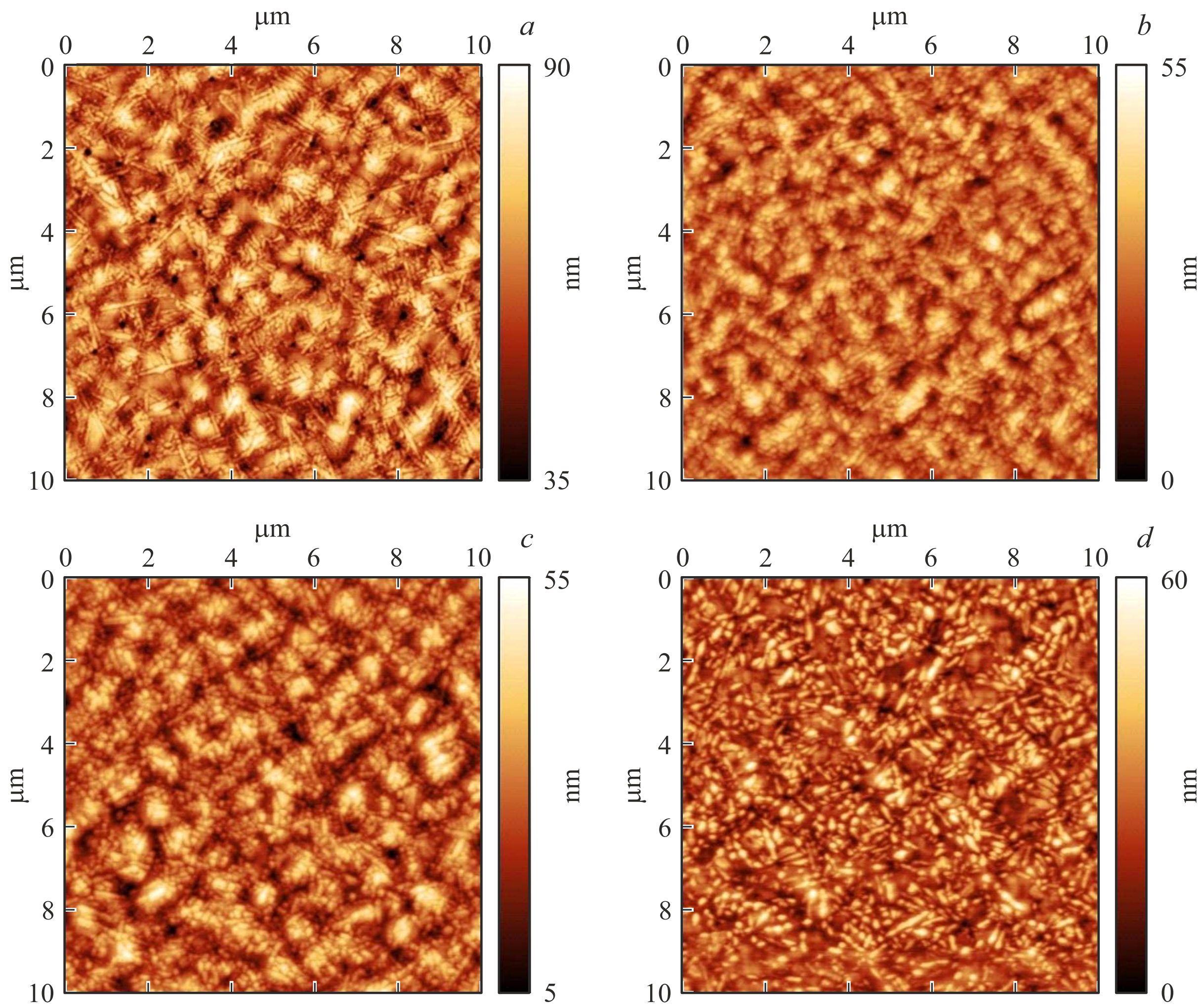

Figure 1. Images of the surface of thin BLT films (*a*), BLT : Mn (*b*), BLT : Nb (*c*) and BLT : Zr (*d*).

study of the electrophysical properties of the obtained capacitors was carried out on the measuring automated stand [9] using the precision meter LCR E4980A from Agilent. All measurements were performed at room temperature.

3. Results and discussion

Figure 1 shows images of the surface of BLT films. These film structures are characterized by the presence of two types of grains: rod-shaped (up to 1.5 μm and width 100 nm) and plate-shaped (up to 500 nm in diameter). In [10,11] it is reported that the rod grains have an orientation along the direction (117), while the plate grains are oriented along the axis c. This combination of grains is most clearly observed in BLT films (Fig. 1, a) and BLT doped with zirconium (Fig. 1, d), which are characterized by large surface roughness values compared to films doped with manganese and niobium. Table 1 presents the parameters of the root mean square (Rms) and the average (Ra) roughness of the surface of the studied films, as well as the average grain radius (r), calculated according to the procedure described in [12].

Table 1. Statistical parameters of BLT-based films based on scanning probe microscopy data

Sample	Rms, nm	Ra, nm	r, nm
BLT	8.6	6.9	228
BLT : Mn	6.7	5.3	231
BLT : Nb	7.2	5.8	267
BLT : Zr	8.3	6.6	157

Experiments were conducted on the polarization of the studied films in the mode of force microscopy of the piezoresponce. For example, the results of repolarization of pure BLT film (Fig. 2, a) and niobium-doped BLT : Nb (Fig. 2, b, c) are given. The studied area was divided into 2 squares, which were subjected to local polarization by applying a negative (-30 V — „dark" area of $15 \times 15\,\mu\text{m}^2$) and a positive ($+30$ V — „light" area of $7.5 \times 7.5\,\mu\text{m}^2$)

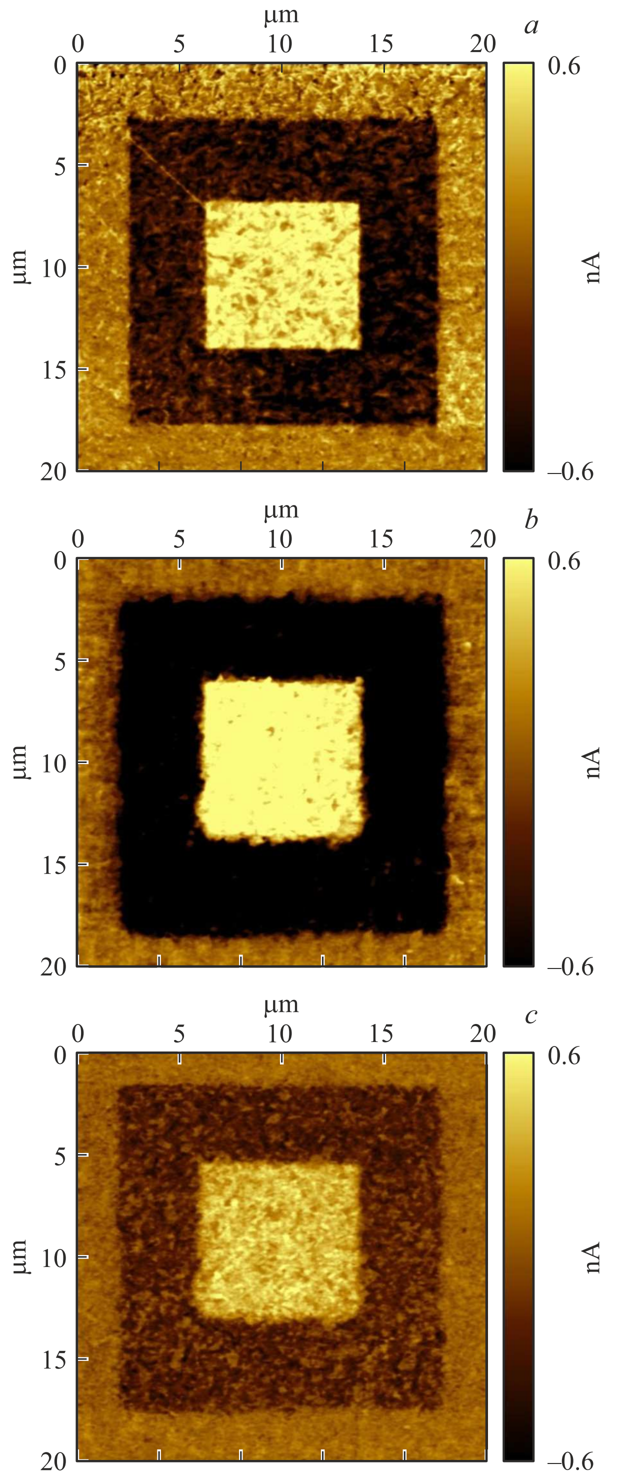

Figure 2. Images of the piezoresponce signal after applying -30 V to the external and $+30$ V to the inner square for the film BLT (*a*) and BLT:Nb (*b* — immediately after polarization, *c* — after 4 days).

voltage. Then the region $20 \times 20\,\mu m^2$, containing a polarized region of the films, was investigated. The image of the residual piezoresponce signal clearly visualizes square regions with a polarization orientation from the substrate to the film surface (dark square) and in the direction of the lower electrode (light square). Such polarized regions proved to be stable over time. Thus, for a film of lanthanum-substituted bismuth titanate doped with niobium, the contrast of polarized regions can be observed 4 days after polarization (Fig. 2, *c*).

Table 2. Parameters of BLT-based films calculated from piezoelectric hysteresis loops

Sample	S, arb. units	k	$PR_{+30\,V}$, pm/V	V_C, V	V_B, V
BLT	183	0.87	4.9	9.3	−0.6
BLT:Mn	256	0.83	6.5	11.2	1.4
BLT:Nb	212	0.75	6.5	8.7	0.6
BLT:Zr	67	0.6	4.4	4.7	0.4

In the polarization switching spectroscopy mode, residual loops of piezoelectric hysteresis were obtained (Fig. 3), which also confirm the switching of polarization in the nanoscale region. The following parameters are calculated from the obtained dependencies (Table 2): loop area (S), loop squareness coefficient (k), piezoresponse at maximum voltage ($PR_{+30\,V}$), switching voltage (or coercive voltage) (V_C) and offset voltage (*build-in* or internal electric field) (V_B). The last two parameters were calculated using the formulas presented in the work [13].

It has been experimentally established that doping bismuth titanate with zirconium leads to a decrease in all calculated parameters obtained from the piezoelectric hysteresis loop (Fig. 3, curve *4*). On the other hand, since the film BLT:Zr has a minimum grain size (Table 1), it becomes easier to initiate a polarization switch (dimensional effect), which affects the lowest value of the coercive stress of the entire series of films under study, i.e. the addition of zirconium makes the BLT film more soft. So for the film BLZ:Nb having an average grain size $r = 267$ nm more and a coercive voltage of 8.7 V against 4.7 V for a film of BLT:Zr composition with a grain size of 157 nm.

Attention is also drawn to the sign change (from negative to positive) of the internal electric field (V_B) when doping a film of lanthanum-substituted bismuth titanate with Mn, Nb and Zr elements, which should also be reflected in the sign of the piezoresponce signal when scanning the *as-grown* surface of the film [14]. More detailed studies, including the presence of unipolarity (the effect of self-polarization) in films based on bismuth titanate will be presented in further works.

Figure 4 shows the capacitance-voltage characteristics (C–V characteristics) of film capacitors based on BLT films, measured at room temperature at a frequency of 100 kHz. The sample was supplied with a bias voltage of V_g from V_{min} to V_{max} and back again with a step of 0.25 V and an amplitude of the measuring signal of 25 mV with a data reading speed of 3 points/s. The curves of the dependence of the capacitance on the bias voltage have a bell mouth shape.

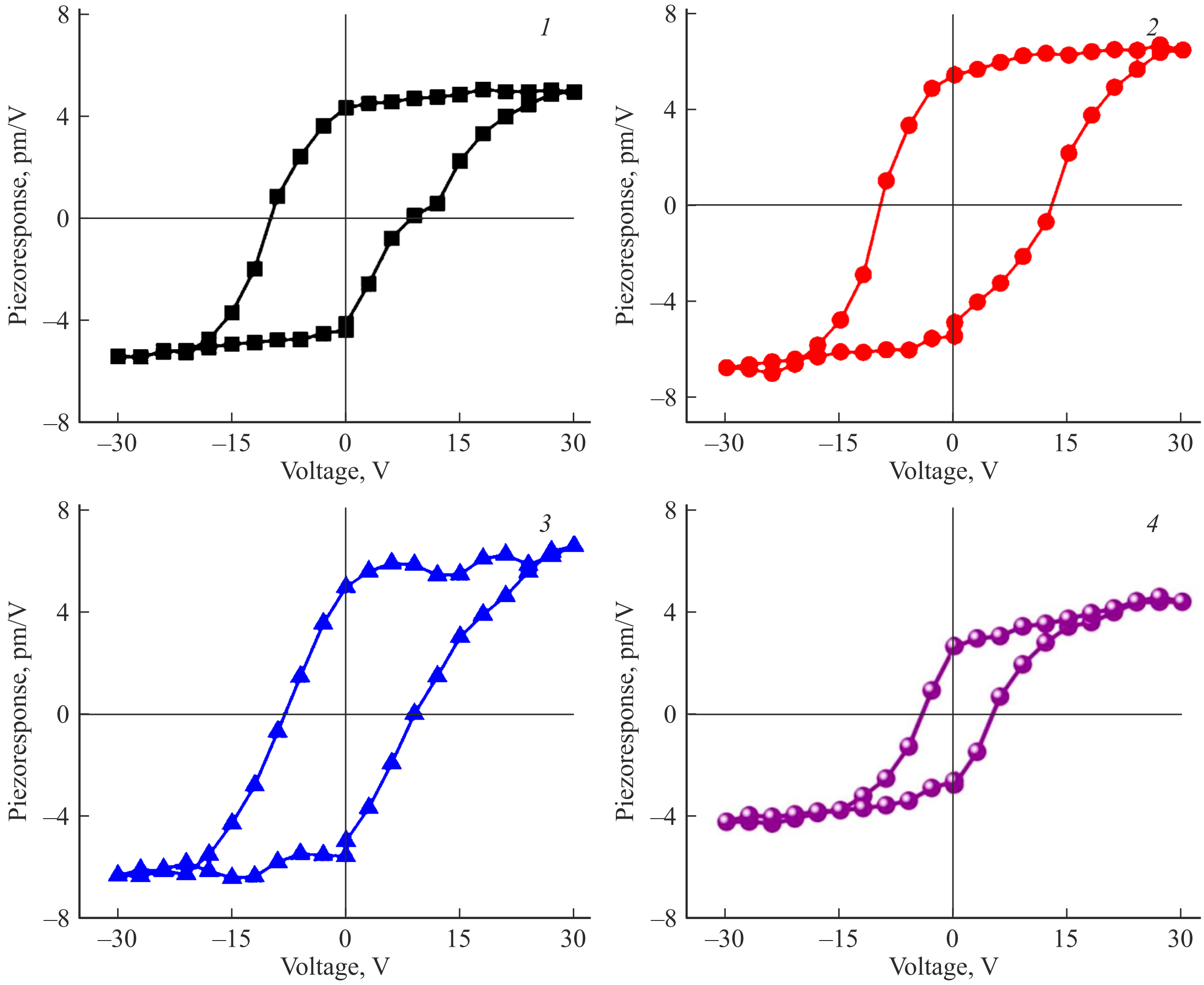

Figure 3. Residual piezoelectric hysteresis loop of the film BLT (curve 1), BLT : Mn (curve 2), BLT : Nb (curve 3) and BLT : Zr (curve 4).

Table 3. BLT-based film parameters calculated from C–V characteristics

Sample	n	V_C, V	V_B, V
BLT	1.19	1.8	−0.61
BLT : Mn	1.19	2	0.3
BLT : Nb	1.72	1.3	0
BLT : Zr	1.29	1.03	0.23

As in the case of calculating the parameters from the local loops of piezoelectric hysteresis, a general trend is observed in the parameters calculated from the C–V characteristics for the films studied in the work (Table 3). So, for a pure film of lanthanum-substituted bismuth titanate, the internal displacement field also has negative values. The control coefficient (n), calculated as the ratio of the maximum capacitance value to the minimum, reaches a maximum value of 1.72 for a capacitor based on BLT : Nb film.

For the same sample, there is no internal electric field. As noted in [15], from a practical point of view, when using thin ferroelectric films in non-destructive memory (FeRAM) devices, the presence of an internal electric field is a parasitic effect, leading to a preferred orientation of spontaneous polarization (its normal component) in the direction of either the lower or upper electrode of the ferroelectric capacitor. In microelectromechanics (MEMS), by contrast, the presence of an internal field in a thin film is a condition for increased reliability of MEMS devices [16]. And in the case of BLT film doping with zirconium, the switching voltage (or coercive voltage) also has the lowest values of all compositions.

4. Conclusion

Studies by scanning probe microscopy, as well as the electrophysical characteristics of thin films based on lanthanum-substituted bismuth titanate presented in the work, showed the effect of the alloying impurity on the microstructure,

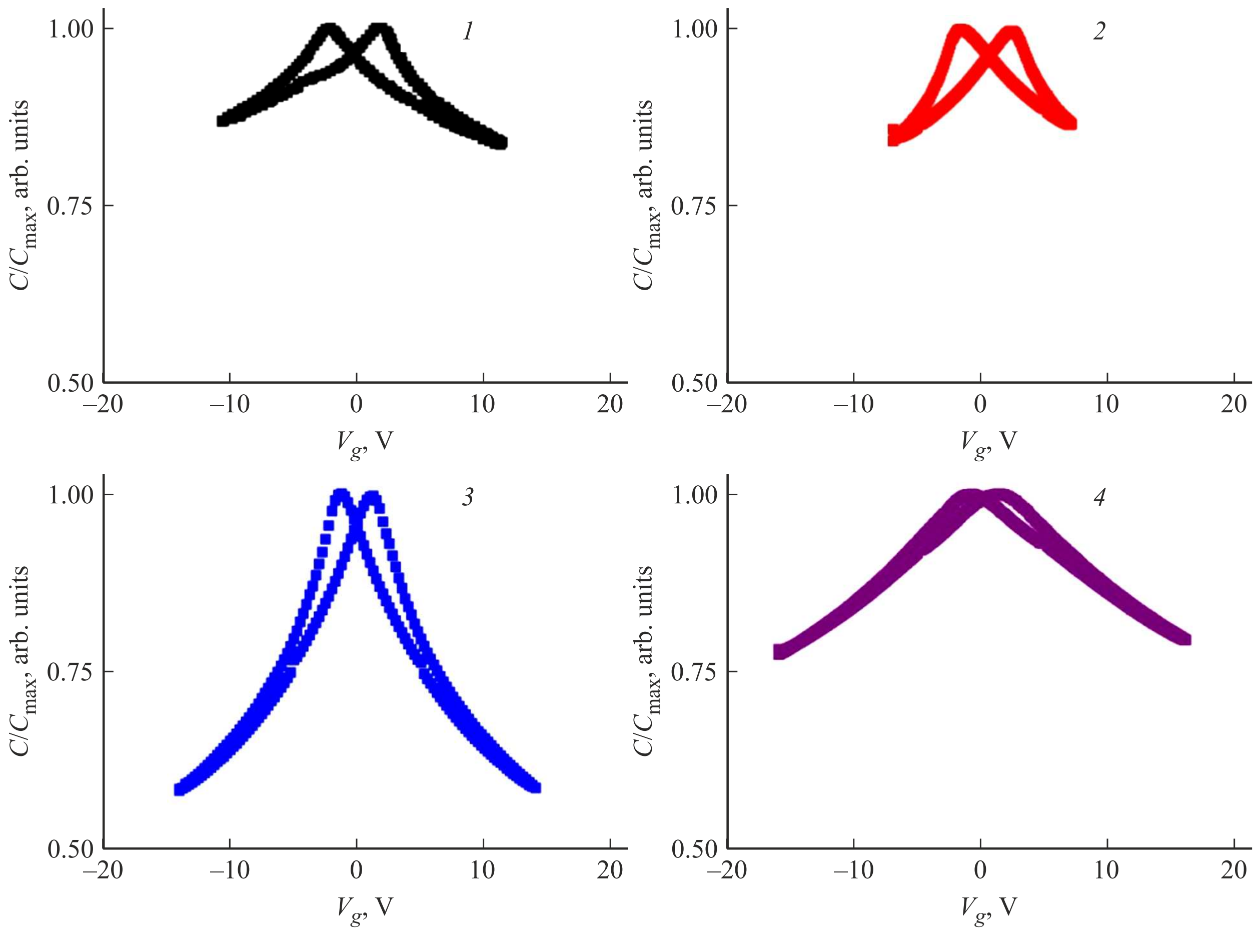

Figure 4. Capacitance-voltage characteristics of BLT film-based capacitors (curve *1*), BLT:Mn (curve *2*), BLT:Nb (curve *3*) and BLT:Zr (curve *4*).

dielectric and local piezoelectric properties. The residual piezoresponce is stable in time, and for a film of lanthanum-substituted bismuth titanate doped with niobium, it persists for 4 days after preliminary polarization. This composition is also characterized by the highest control coefficient (1.72) and the absence of an internal electric field based on the results of capacitance-voltage characteristics. A film of lanthanum-substituted bismuth titanate doped with Zr is the most ferrous soft compared to other compositions. The results obtained in the work show that BLT thin films can be used in non-volatile memory technology based on lead-free ferroelectric.

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Conflict of interest

The authors declare that they have no conflict of interest.

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