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Impurity Phases in Polycrystalline Films of Ferroelectric Oxides of the Perovskite-Type on the Basis of $Bi_2SrTa_2O_9$ and $Pb(Zr,Ti)O_3$

D. S. Agafonova[a, b], A. B. Kozyrev[b], N. V. Mukhin[b, *], D. N. Red'ka[b], K. G. Elanskaya[b], M. V. Rudenko[c], A. Oseev[d], and S. Hirsch[d, e]

[a] *Dagestan State University, Makhachkala, Republic of Dagestan, 367000 Russia*
[b] *St. Petersburg State Electrotechnical University LETI, St. Petersburg, 197376 Russia*
[c] *Belorussian State University of Informatics and Radioelectronics, Minsk, 220013 Republic of Belarus*
[d] *Otto-von-Guericke-University Magdeburg, Magdeburg, 39106 Germany*
[e] *University of Applied Sciences Brandenburg, Brandenburg an der Havel, 14770 Germany*
**e-mail: MuhinNV_LETI@mail.ru*

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Abstract—Processes of the formation of inclusions of impurity phases in lead zirconate titanate and strontium bismuth tantalate (SBT) films by changing the excess concentration of the most volatile cation component and temperature-time regimes of their formation are studied. The conditions in which the introduction of an excess Pb content does not lead to the formation of impurity phases are selected.

Keywords: complex oxides, perovskites, heterophase films, nonstoichiometry

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INTRODUCTION

Triple ferroelectric oxides with a perovskite structure and solid solutions based on them are often used in modern technologies, in particular, for memory devices [1], piezoelectric microelectromechanical systems [2], devices on surface and bulk acoustic waves [3, 4], sensor devices [5], and biocompatible systems [6]. The compounds most in demand are solid solutions of strontium bismuth titanate, strontium bismuth tantalate (SBT), and lead zirconate titanate. Methods for the formation of ferroelectrics of the oxygen-octahedral type for studying thin-film structures are widely studied [1, 7].

During the formation of defect-free solid solutions of perovskites, it is necessary to take into account the balance and compatibility of the valencies, as well as the ion radii of the elements [8, 9]. However, a deviation from the stoichiometric composition is characteristic for complex ferroelectric oxides [10].

During the preparation of polycrystalline ferroelectric oxides, the inclusions of the impurity phases on the interfaces of the studied materials are described in [11–19]. The authors [11] in the study of the structural properties of the film of barium-strontium titanate as a function of the technological conditions of the preparation of films by the high-frequency magnetron sputtering of the ceramic target $Ba_{0.4}Sr_{0.6}TiO_3$ found that the studied films contain the impurity phases of polytitanates: Sr_2TiO_4, $Sr_4Ti_3O_{10}$ and $Sr_3Ti_2O_7$. In [12] when studying the processes of the formation of ceramics based on $BaTiO_3$ and $Bi(Zn_{1/2}Ti_{1/2})O_3$ powders, the authors observed the inclusions of the $BaTiO_3$:TiO_2, $BaTi_2O_5$, $BaTiO_4$, Ba_2TiO_4, Bi_2O_3, $Bi_4Ti_3O_{12}$, and $BaBiO_3$ phases. In [13] in the study of the phase transformations in $MgSiO_3$, inclusions of phases of simple oxides MgO, SiO_2 were observed in the composition of samples. In [14] the phase Fe_2O_3 was observed in the formation of $BiFeO_3/La_{0.67}Sr_{0.33}MnO_3$ heterostructures at the interface of the layers. The authors [15] in the study of processes of the formation of ceramic samples $Pb_{1.86}Mg_{0.24}Nb_{1.76}O_{6.5}$ found that the increase in the PbO content leads not only to an increase in the fraction of the perovskite phase but also to an increase in the number and size of the inclusions of the impurity $Pb_{1.5}Nb_2O_{6.5}$ phase. The inclusions of side phases of bismuth silicides were found in the composition of the formed films in [16] when studying the thin $Bi_2SrTa_2O_9$ films deposited on the platinized silicon substrate. The inclusions of the side phase of lead oxide in the $Pb(Zr,Ti)O_3$ films were studied in [7, 17–19]. As a rule, they are dispersed discharges of the oxide phase on the grain boundaries [1, 19].

The presence of inclusions affects the electrophysical characteristics of the film structures. The presence of the impurity phase can lead to the significant long-term aging of the active ferroelectric layers and, as a consequence, a reduction in the operational lifetimes

of the instruments built based on them. However, the problem of separating the impurity phases requires basic research in the field of the application of the considered ferroelectric layers in the composition of multilayered structures.

This work aims to study the processes of the formation of inclusions of impurity phases in ferroelectric oxides by changing the concentration of the most volatile component and the temperature–time regimes of the formation of films. This work is a continuation of the studies [20–25].

EXPERIMENTAL

Studied samples and the technology used to prepare them. Thin-film structures based on $Bi_2SrTa_2O_9$ and $Pb(Zr,Ti)O_3$ were formed according to the sol-gel technology.

SBT films were prepared by the sol-gel method from acetic acid sols. Tantalum ethoxide ($Ta(OC_2H_5)_5$) and acetic salts of strontium ($SrCH_3COO)_2$ and monobasic bismuth ($BiOCH_3COO$) were used to synthesize the sols. Acetic acid served as the solvent. Using acetone as a stabilizer of sol makes it possible to control the gel formation rate by changing the stabilizer's concentration and provides good adhesion to the surface of the substrate. The sol is usable for a period of one week, after which the gel formation process starts, and as a result a white gel is formed. The sols were deposited on single-crystal silicon substrates and silicon/TiO_2/Pt structures by centrifugation. The centrifugation rate was 2700 rpm. For manufacturing the lower electrode of the capacitor silicon/TiO_2/Pt structure, platinum and titanium oxide layers were formed on silicon substrates with the subsequent heat treatment in an oxygen atmosphere at a temperature of 450°C for 30 min. After the deposition of each layer, the samples were subjected to heat treatment at a temperature of 200°C for 10–20 min. The final high-temperature heat treatment was carried out during 40 min at a temperature of 700°C or 800°C. For manufacturing a capacitor structure, the upper nickel electrodes of the square shape with a face of 0.8 mm were formed. The finally formed SBT was locally subjected to chemical etching in a solution based on hydrochloric acid using photolithographs for the formation of the contact to the lower electrode for carrying out electrical measurements.

The film-forming solutions of lead zirconate titanate (PZT) were prepared according to the sol-gel technology by mixing the components when there was an excess of lead. The ratio of components Zr/Ti in the solution was 48/52. In this method, lead acetate $Pb(CH_3COO)_2$ was prepared by the solid-phase synthesis at room temperature with the application of absolute reagents: PbO, acetic anhydride, and a seed amount of acetic acid; moreover, the final concentration of the film-forming solution in the calculation of the sum of the alcoholates Ti and Zr was 0.25 M. The PZT films were formed on substrates with the following structure: Pt/Ti/SiO_2/Si. The film-forming PZT solution was deposited on the lower electrode by layered (six layers were used) centrifugation at a rate of 3000 rpm with intermediate drying at a temperature of 400°C. The final heat treatment was performed at a temperature of 600°C.

The X-ray phase analysis was carried out using a Rigaku diffractometer on monochromatized CuK_α radiation and a Bruker AXS D8 ADVANCE diffractometer. The transmission electron microscopy was carried out on a Philips EM430 ST device and, the scanning electron microscopy was carried out on Helios Nanolab D449 FEI Company and HITACHI S4800 devices. The electrophysical characteristics of the ferroelectric films were measured using the modified Sawyer-Tower and Merz schemes [1, 7]. The processes of dynamic fatigue of PZT films were studied at the impact of the bipolar pulses of the electric field.

RESULTS AND DISCUSSION

The images of SBT films with an excess concentration of bismuth 15% prepared on a Pt/TiO_2/Si substrate after heat treatment at a temperature of 700°C are given in Fig. 1. The film contains 10 layers of xerogel. The thickness of the TiO_2 layer is 110 nm, the thickness of the platinum layer is 75 nm, and the thickness of the SBT films is 240 nm.

The results of the X-ray phase analysis of the SBT films formed on the silicon substrates are presented in Fig. 2. The sample is single-phase and the $Bi_2SrTa_2O_9$ peaks are observed. It has an orthorhombic structure with the unit cell parameters a = 5.51415 Å, b = 5.51415 Å, and c = 25.0322 Å. The SBT films prepared at the temperature of 700°C from sols with an excess bismuth concentration of 5 and 15% (Figs. 2a, 2d) contain compounds of bismuth with silicon, and in particular, bismuth silicide. The conditions were chosen such that the formation of impurity phases was not observed: an increase in the temperature of the heat treatment to 800°C and a decrease in the excess bismuth concentration to 5% (Fig. 2b).

The prepared PZT films with a thickness of 230 nm had a polycrystalline structure. The results of the X-ray phase analysis (Fig. 3) showed that the main volume in the PZT films is occupied by the ferroelectric phase of the perovskite of the tetragonal syngony with the unit cell parameters a = 4.028 Å and c = 4.066 Å. At an excess of lead of 0 and 5 mol % in the original film-forming solution, the intensity of the 111 reflection significantly exceeded the intensity of the other PZT reflections, which indicates the high degree of the texture of the resulting PZT films in the $\langle 111 \rangle$ direction. This result indicates the orienting action of the lower Pt electrode on the PZT film. With an increase in the excess of lead in the film-forming solution to 15 mol %,

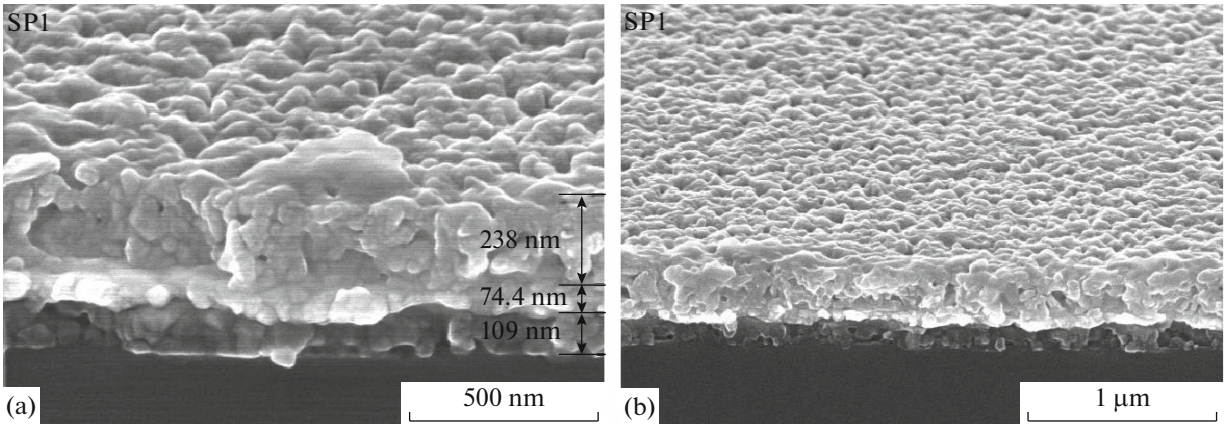

Fig. 1. SEM images of surface and cleavage of SBT film formed on $Pt/TiO_2/Si$ substrate.

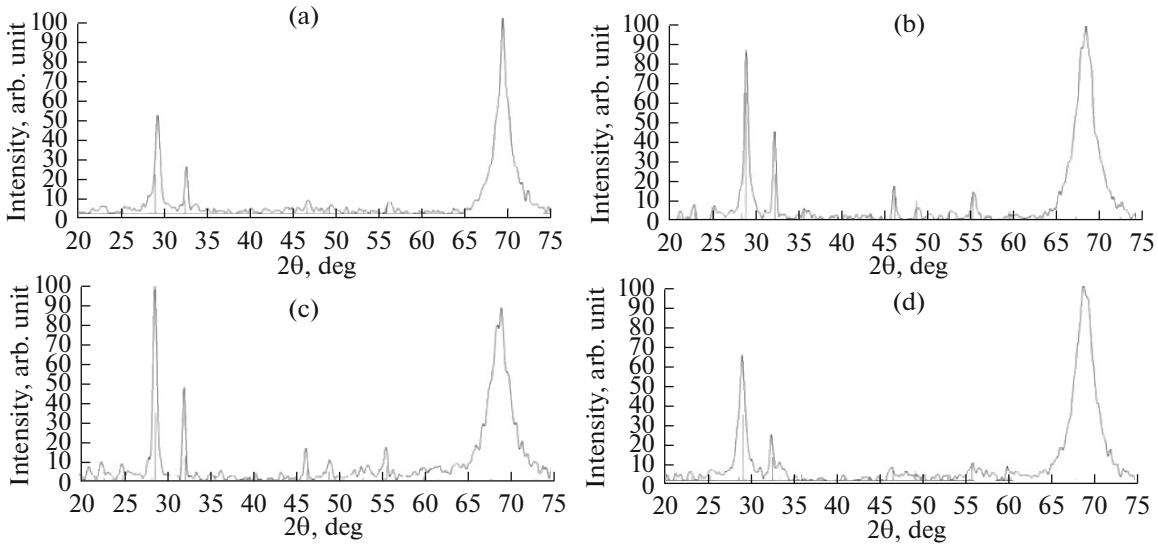

Fig. 2. Diffraction patterns of SBT films prepared from sols with excess bismuth concentration of 15 mol % at temperature of 700°C (a), with excess concentration of 5 mol % at temperature of 800°C (b), with excess concentration of 15 mol % at temperature of 800°C (c), with excess concentration of 5 mol % at temperature of 700°C (d).

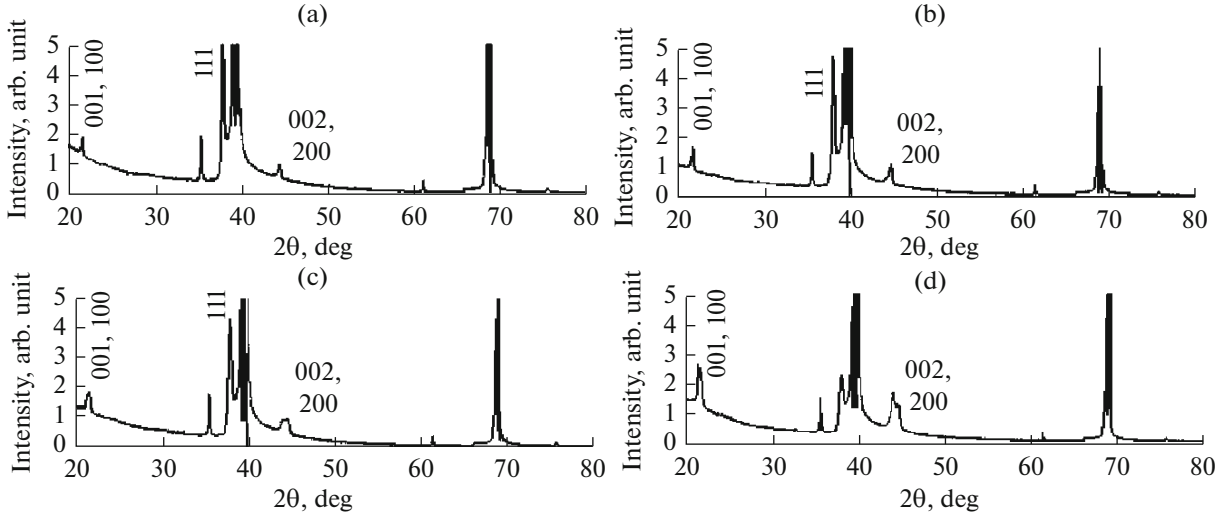

Fig. 3. Radiographs of PZT films prepared from film-forming solutions with excess lead content: 0 (a), 5 (b), 15 (c), and 30 mol % (d).

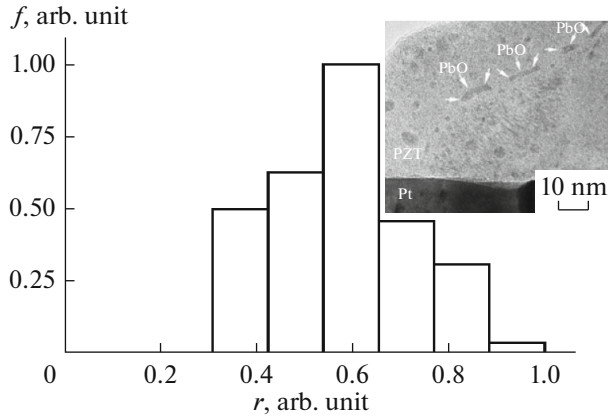

Fig. 4. Experimental histogram of size distribution function of dispersed lead oxide inclusions. Inset shows image of films obtained by transmission electron microscopy TEM image of PZT film with PbO inclusions.

the size of the grains decreases. The tetragonal lattice parameters *a* and *c* increase. In the study of multilayered structures with the PZT films prepared from a solution with a 30 mol % lead excess, there was also a further decrease in the average grain size. The comparative analysis of the intensities of the peaks of the perovskite phase also showed the presence of texture in the ⟨100⟩ direction. The intensity of the 111 reflection decreased significantly. At the excess of the lead content of more than 30% in the film-forming solution, the dispersed precipitates of the lead oxide phase were found in the PZT films using transmission electron microscopy.

Figure 4 shows the experimental histogram of the size distribution function of the dispersed lead oxide inclusions. The inset to the graph shows the images of the films obtained by transmission electron microscopy [1, 19, 25], where the lead oxide nanoinclusions are seen. The size of the inclusions ranged from 3 to 10 nm.

Additional studies of the ferroelectric properties of the PZT films are presented in Figs. 5 and 6, which clearly demonstrate the effect of the amount of lead in the film on the residual polarization (P) and coercive field (E_c), and also on the susceptibility of the PZT films to dynamic fatigue. The P and E_c values were determined from the hysteresis loops of capacitor Pt/PZT/Pt structures measured according to the Sawyer–Tower scheme [7]. The dynamic fatigue processes were studied under the action of the bipolar pulses of the electric field with a strength of 100 kV/cm on the Pt/PZT/Pt structures.

The results show that the PZT films prepared by chemical precipitation from solutions with the addition of an excess of 5 mol % of stoichiometric lead in the initial film-forming solution annealed at a temperature of 600°C for 40 min have the best ferroelectric properties and resistance to dynamic fatigue processes. The deterioration of the ferroelectric properties of the PZT films (a decrease in P and an increase in E_c) during the decrease in the excess lead in the initial film-forming solution is associated with the the cation depletion of the formed films; and during the increase in the excess of lead, with the formation of grain-boundary inclusions of the impurity lead oxide phase.

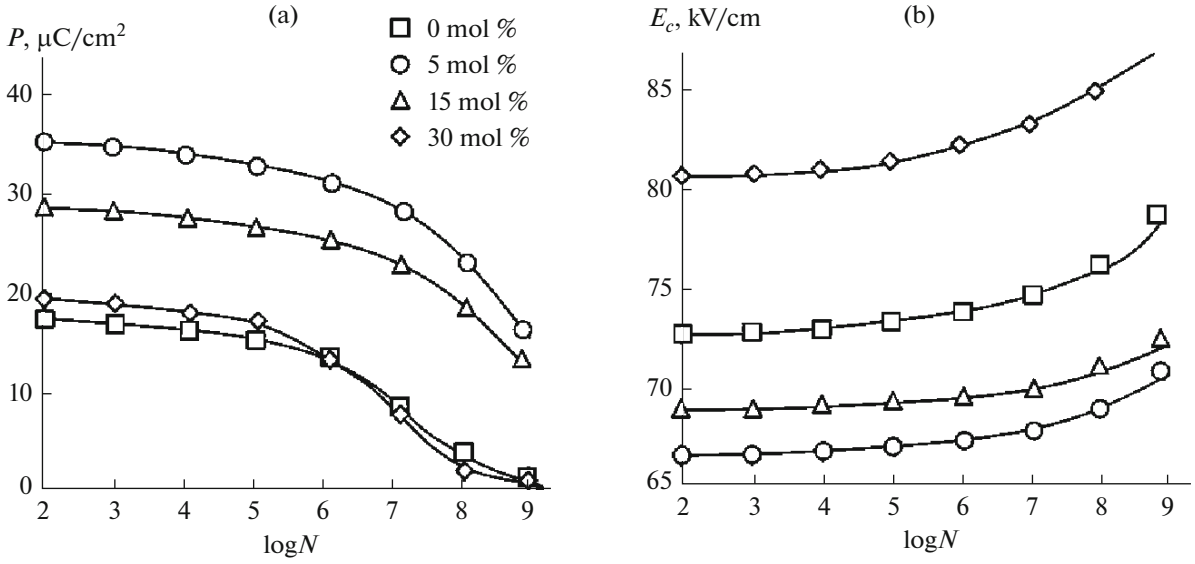

Fig. 5. Dependence of values of switchable polarization and coercive field on logarithm of number of switching cycles for PZT films with different degrees of excess lead (0, 5, 15, and 30 mol %) in the initial film-forming solution after treatment at 600°C for 40 min.

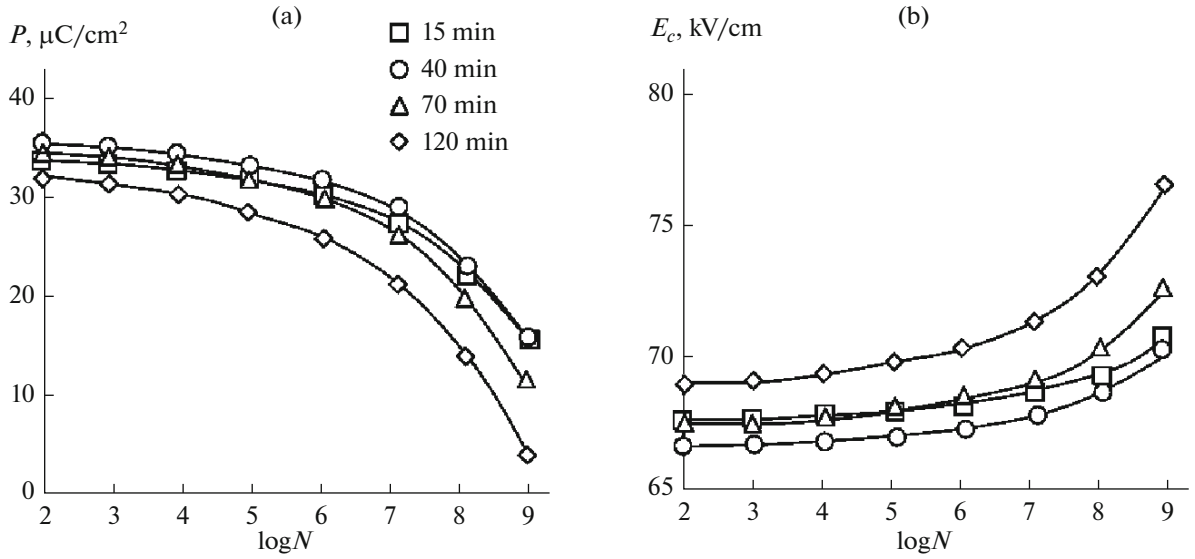

Fig. 6. Dependence of values of switchable polarization and coercive field on logarithm of number of switching cycles for PZT films with excess lead of 5 mol % in initial film-forming solution after treatment at 600°C for 15, 40, 70, and 120 min.

CONCLUSIONS

The processes of the formation of polycrystalline PZT and SBT films were experimentally studied by varying the excess concentration of the most volatile cation component in the composition of the films and the temperature–time regimes of their formation. The relatively high volatility of bismuth and lead oxides, leading to a deficiency of these components in the composition of the formed ferroelectric films, is a general feature of these compositions. To avoid losses of bismuth and lead in the solution, they are added in excess in the synthesis process. This, in turn, can lead to another problem: hetero-phase films.

The conditions are chosen such that the introduction of an excess content of Pb into PZT and Bi into SBT does not lead to the formation of impurity phases. The best results for the SBT films were obtained at an excess bismuth concentration of 5% and heat treatment at 800°C for 40 min; and for the PZT films, at an excess lead concentration of 5% and heat treatment at 600°C for 40 min.

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