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UDC 537.226.4   https://www.doi.org/10.33910/2687-153X-2021-2-3-101-109

Microstructure and properties of polycrystalline PZT films obtained by RF magnetron sputtering with fine variation of the composition near morphotropic phase boundary

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Abstract. The article discusses the possibilities of fine composition variation of polycrystalline PZT films at the morphotropic phase boundary. The composition of thin films prepared by RF magnetron sputtering of a ceramic target of stoichiometric composition $PbZr_{0.54}Ti_{0.46}O_3$ was varied by changing the distance from the target to the substrate in the range of 30–70 mm. This made it possible to change the composition by ∼1.5%. The study focused on the dielectric properties of the formed self-polarized films. The study found that the resistance to external electric fields depends on the conditions of film preparation.

Keywords: method of fine composition variation, PZT, thin films, morphotropic phase boundary, scanning electron microscopy.

Introduction

A popular and highly efficient piezoelectric ceramic based on $PbZr_{1-x}Ti_xO_3$ (PZT) solid solutions was developed in the 1960s. It is still widely used in technical applications. Numerous studies of pre-polarized ceramic PZT samples have shown that high piezoelectric coefficients are observed only in a very narrow range of changes in the Zr/Ti ratio corresponding to the concentration phase transition from the tetragonal to rhombohedral modification of the ferroelectric phase (Fig. 1) (Jaffe et al. 1971).

This region of concentration is usually called the morphotropic phase boundary (MPB). The reasons for the abnormal changes in physical characteristics at the MPB are still a point of controversy, and there are at least several approaches to their explanation (Isupov 1983; Jaffe et al. 1971; Noheda et al. 1999; Sergienko et al. 2002; Wada et al. 2006; Xu 1991). The width of this region is estimated from fractions of a percent to several percent and depends on the ceramic technology, including the temperature and atmosphere of synthesis (and sintering), the presence of excess lead, the purity of the reagents used, grain size, and mechanical stress (Isupov 1983; Jaffe et al. 1971; Xu 1991). In this case, the broadening of the MPB region leads to a decrease in the dielectric and electromechanical parameters.
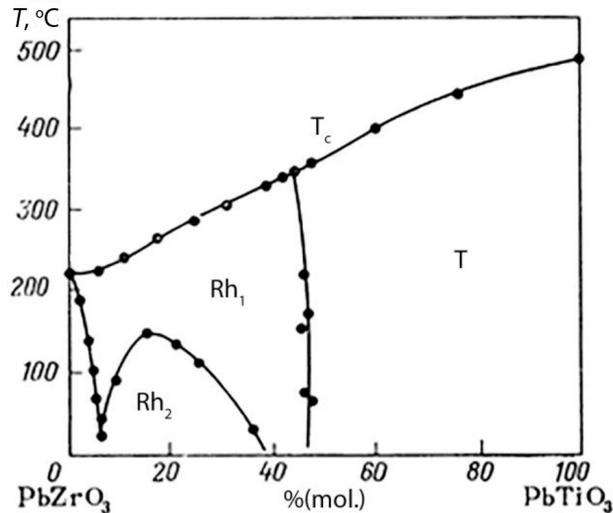
Fig. 1. Phase diagram of ferroelectric $Pb(Zr_{1-x}Ti_x)O_3$ solid solutions. The line separating the T and Rh_1 phases corresponds to the region of the morphotropic phase boundary (Jaffe et al. 1971)

The end of the 20th century witnessed the development of thin-film technologies (both physical and chemical) resulting in rigorous studies of PZT-based thin-film structures. It has been shown that the range of their possible application is much wider than that of ceramics, and covers such areas as non-destructible random-access memory (FRAM) (Izyumskaya et al. 2007; Scott, Paz de Araujo 1989; Scott 1998; Vorotilov et al. 2011), microelectromechanics (MEMS) (Kang et al. 2016; Muralt 2008; Polla 1995; Whatmore 1999), IR technic (Bruchhaus, Pitzer, Schreiter 1999; Whatmore 1999); multiferroics, etc. (Eerenstein et al. 2006; Scott 2007).

For MEMS applications, PZT compositions belonging to MPB are optimal. One of the advantages, is that the produced (virgin) films have macroscopic polarization (self-polarization) and require no additional polarization. In addition, experiments have shown that such films are more resistant to external (electrical, mechanical and thermal) influences (Afanasjev et al. 2001; Bruchhaus et al. 1999; Kholkin et al. 1998; Sviridov et al. 1994).

Finding the compositions with the best properties necessitates fine variation of composition within the MPB range. It is relatively easy to achieve variation with chemical methods of film formation through a simple change in the composition of the precursors. When using physical methods of deposition, for example, the method of magnetron sputtering, a variation may be achieved in the presence of individual targets of metals included in the composition. However, this method is not very reliable for reproducing the composition of the films. When sputtering a ceramic target, changing the composition of the deposited film requires replacing one ceramic target with another.

Nevertheless, in the latter case, it is possible to vary the composition of the films within certain limits by changing the deposition parameters. Thus, it has been shown that by varying the working gas pressure (in the range of 2–60 Pa) during RF magnetron sputtering of a ceramic target of barium-strontium titanate ($Ba_{1-x}Sr_xTiO_3$ or BST), it is possible to change the composition within a fairly wide range ($x = 0.3 - 0.65$) (Volpyas et al. 2016). The physical reason for this is a change in the length of the thermalization zone. In this case, with an increase in the working gas pressure, the ratio of atoms deposited under directional and diffuse sputtering regimes changes (Volpyas, Kozyrev 2011; Volpyas et al. 2016).

Experiments similar to the studies mentioned above were carried out with RF magnetron sputtering of a ceramic PZT target of composition $x = 0.46$, where the length of the thermalization zone of the metal atoms of the target also changed. These experiments showed the possibility of changing the composition of the deposited films by ~ 2.5% with a variation in the pressure of the working gas mixture ($Ar + O_2$) in the range of 2–8 Pa (Fig. 2) (Osipov et al. 2018; Pronin et al. 2017). A drawback of the obtained results was the formation of two-phase (perovskite-pyrochlore) films when the working gas pressure dropped below 6 Pa. The reason was the decrease in the lead content in the deposited films below the stoichiometric value.
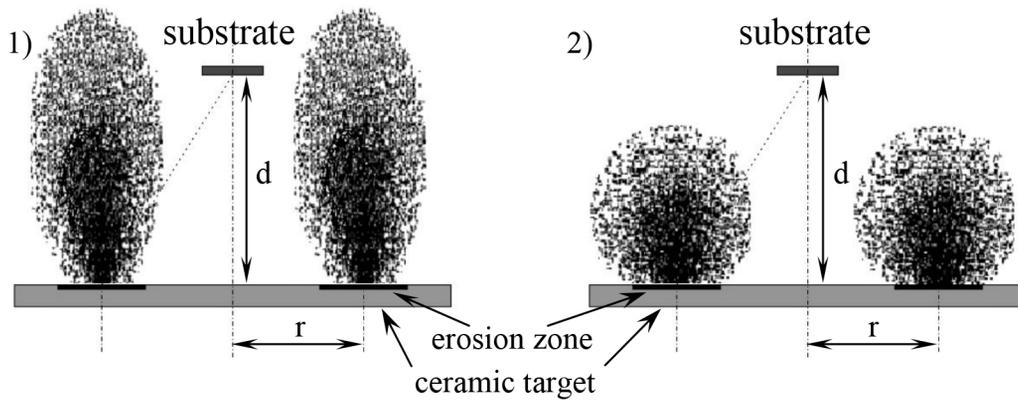
Fig. 2. Sputtering system geometry of the of RF magnetron deposition and the thermalization zone of lead atoms in the working gas plasma at different pressures: 1) 2 Pa; 2) 8 Pa. d = 50 mm, r = 30 mm (Vol'pyas et al. 2019)

The aim of this work was to study the possibility of a fine change in the composition, microstructure, and physical properties of thin films by varying the target-substrate distance ("d") in an RF magnetron sputtering chamber.

Thin film preparation

The films deposition was carried out using divided ceramic PZT target 100 mm in diameter of a stoichiometric composition. The composition of the ceramic target corresponded to the morphotropic phase boundary. The target was sputtered at a gas mixture (80% Ar + 20% O_2) pressure of 8 Pa. At this pressure, the heaviest lead atoms were deposited on the substrate mainly in the diffusion mode. The power supplied to the magnetron (200 W) was kept constant. The distance from the target to the substrate varied in the range of 30–70 mm, while the temperature of the substrate, due to heating in the plasma, varied from 160 to 90 °C. A platinized silicon wafer was used as a substrate. The thickness of the deposited layers was ~500 nm. The deposited films were characterized by an amorphous structure. The mutual geometry of the target and substrate is shown in Fig. 2.

At the second stage of preparation, the samples were annealed in air in a furnace at temperature of T_{ann} = 580 °C (1 hour) to form single-phase perovskite films. To study the electrophysical properties, platinum contact pads with a size of 200 × 200 μm were formed on the surface of the films by the method of RF magnetron sputtering.

Study of composition and microstructure

The composition of thin films was studied using an EVO-40 scanning electron microscope (Carl Zeiss) equipped with an INCA energy dispersive attachment. The incident electron energy was 12 keV, at which the near-surface region of the PZT layer ~300 nm deep was probed.

The composition analysis of the deposited (amorphous) films showed that the elemental ratio of Zr and Ti atoms monotonically changed towards a decrease in the number of titanium atoms with an increase in the target-substrate distance (Fig. 3.1, curve 1). It can be seen from the figure that the range of variation of the composition in the deposited films was ~1.5% from x = 0.485 to x = 0.47. High-temperature annealing led to a change in the elemental ratio of Zr and Ti by ~1.5% (Fig. 3.1, curve 2). The reasons for such changes are not associated with the loss of titanium atoms (the volatility of its oxide vapor is low, in contrast to the anomalously high volatility of lead oxide vapor). Rather, the changes are caused by the segregation of titanium (zirconium) atoms during the crystallization of the perovskite phase. The segregation process is associated with the difference (by more than 100 °C) in the crystallization temperatures of the perovskite phase in lead zirconate and lead titanate (Calame, Muralt 2007). This means that the probability of nucleation of the perovskite phase will be higher in that part of thin layer volume where the local titanium content is higher. The growth of the island is caused by the migration of titanium atoms to the phase boundary of the island and the reverse migration of zirconium atoms.
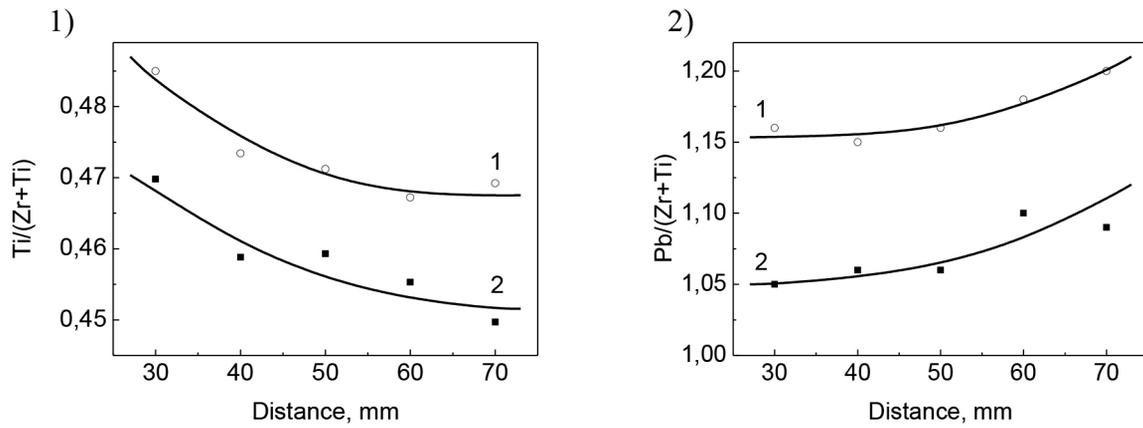
Fig. 3. Changes in the relative content of titanium (1) and lead (2) atoms in PZT films
with a change in the target-substrate distance.
The curves correspond to: 1—amorphous phase, 2—perovskite phase. Annealing temperature—580 °C

The location of the predominant nucleation (and growth) of perovskite islands over the polycrystalline layer thickness (near interfaces or in the bulk of the layer, Fig. 4) is determined by a number of competing factors. These include the local presence of lead excess, the presence of sublayers that facilitate the nucleation of the perovskite phase, and the difference in mechanical conditions at the upper and lower interfaces and in the bulk of the thin film. For the predominant nucleation of the perovskite phase near the lower interface (near the boundary of the PZT layer and the lower platinum electrode), nanolayers of titanium dioxide or metallic titanium are often used, previously deposited on the surface of the lower electrode. These nanolayers also determine the orientation of the growth texture of a thin film with a predominant "100" or "111" orientation (Pronin et al. 2013; Willems et al. 1997). In the absence of such nanolayers, the minimization of the formation energy of perovskite islands will be determined by the presence of excess lead.
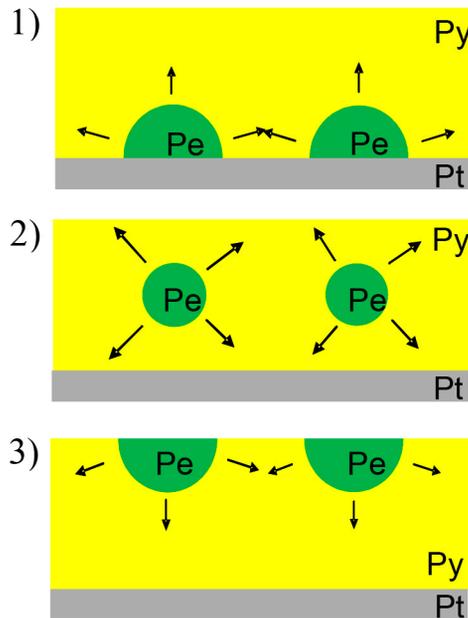

Fig. 4. Schematic models of the perovskite (Pe) phase nucleation in the matrix of the pyrochlore (Py) phase:
near the lower interface (1), in the bulk (2) and near the upper interface of the PZT layer (3).
The arrows show the direction of Pe islands growth

In our case, in the presence of a predominant <110> growth texture of the formed films (Pronin et al. 2010), a decrease in the titanium content in the upper part of the film indicates that the nucleation and growth of perovskite islands occurs mainly near the lower PZT layer interface. Judging by the monotonic change in the Zr/Ti ratio, this mechanism works during the formation of the perovskite phase in all the films under study, i.e., for all values of "d".

Fig. 3.2 shows the change in the lead content with a variation in the target-substrate distance in amorphous and annealed films. An increase in the lead content in amorphous films (curve 1) with an increase in "d", as noted earlier, is associated with a change in the thermalization zone length of the heaviest atoms (lead) (Fig. 2). The relatively low excess of lead over the stoichiometric content and its loss during annealing also indicates that the nucleation of islands of the perovskite phase and their growth occurs in the lower part of the thin layer, or in its bulk, Fig. 4.1 and 4.2. In this case, there will be a directed migration of titanium atoms from the surface into the depth of the film, and zirconium atoms in the opposite direction.

Thus, on the one hand, by varying the target-substrate distance, it was possible to finely vary the integral composition of the deposited films within 1.5%, but on the other hand, all the films formed were also characterized by a gradient distribution of Zr (Ti) atoms over the thickness. From Fig. 3.1 it follows that the value of the gradient is close to 1.5%. It should be noted that this result is not optimal when it comes to achieving the highest dielectric and electromechanical parameters due to the "diffuseness" of the MPB.

The microstructure of the near-surface layer of perovskite films was studied in the back scattering electron mode at the incident electron energy of 12 keV. The microstructure was a set of polycrystalline blocks ~20–40 μm in size (Fig. 5). The internal structure of the blocks consisted of separate rays emanating from a single center. The highest density of rays was observed in films deposited at "d" = 30 mm (Fig. 5.1), the minimum at "d" = 70 mm (Fig. 5.5), where the boundaries of the rays lost their clear outlines, and their number sharply decreased. The reasons for these changes are still unclear as well as the reasons for the emergence of a spherulite radiant structure. The study of the nature of spherulites observed during the crystallization of various types of compounds requires additional investigations.
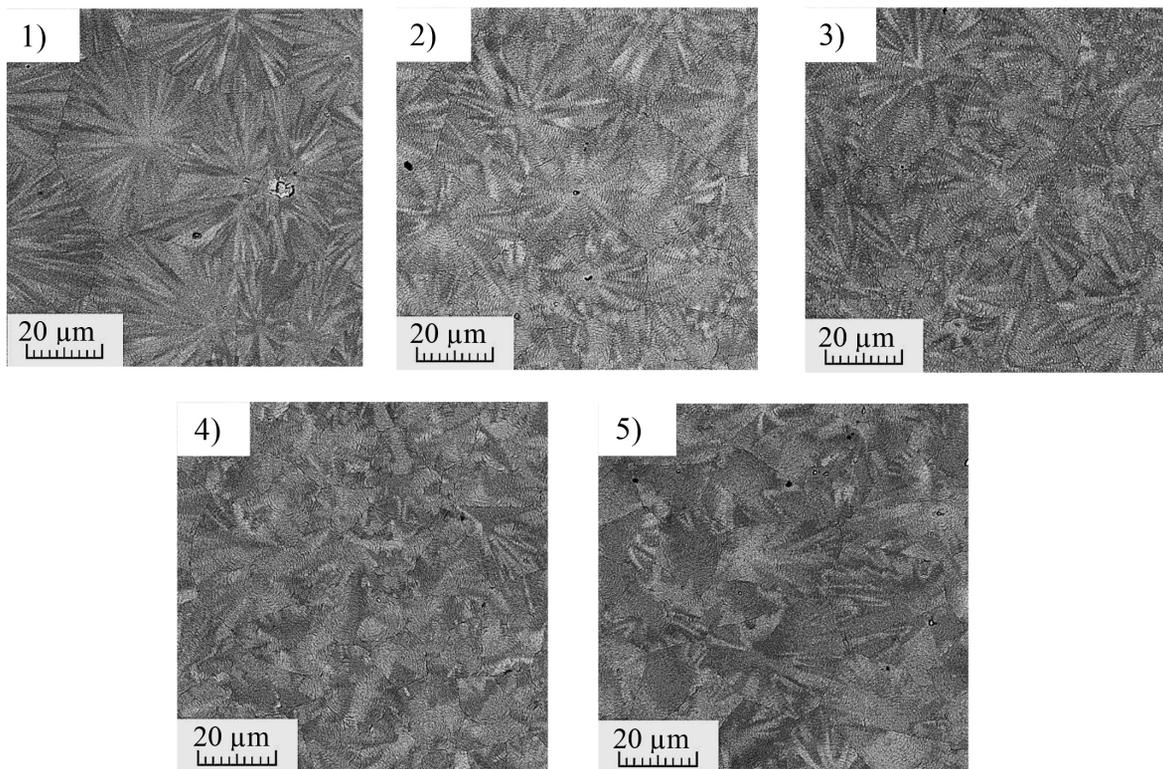

Fig. 5. SEM images of the spherulite microstructure of the perovskite thin PZT films deposited at different target-substrate distances (d): 1)—30 mm; 2)—40 mm; 3)—50 mm; 4)—60 mm; 5)—70 mm

Dielectric properties study

Fig. 6 shows the dependence of the dielectric constant (ε_k) of the samples on the target-substrate distance measured at a frequency of 10 kHz using an E7-20 immittance meter. The dependence is a curve with a minimum. This behavior can be associated with the simultaneous influence of a number of factors, such as a possible difference in the crystallization temperature of the perovskite phase and the redistribution of excess lead in the film volume, a decrease in the substrate temperature caused by plasma heating with increasing "d".
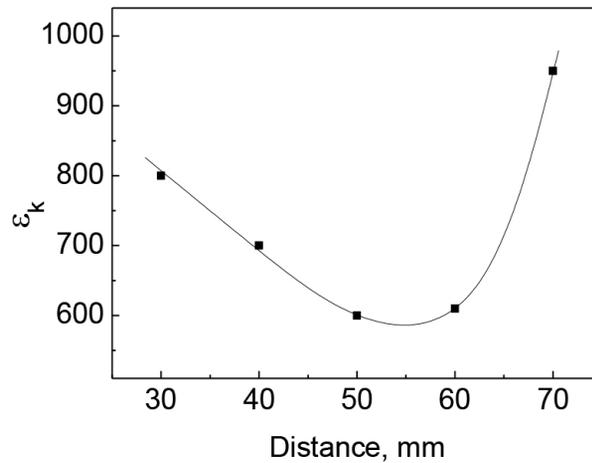

Fig. 6. Experimental dependence of the effective dielectric constant (ε_k) of PZT films on target-substrate distance. The measurement frequency—10 kHz

The value of the internal field (E_{int}), by which one can qualitatively judge the self-polarization of thin films (in the first approximation, these parameters change proportionally), changed rather strongly with a change in the distance from the target to the substrate. This value is usually determined from the shift of the capacitance-voltage characteristics (reverse dependences of the dielectric constant) (Fig. 7), or from the shift of the dielectric hysteresis loops along the abscissa axis (Fig. 8). In the latter case, due to the high frequency of the electrical impact, the definition of E_{int} turns out to be more accurate.
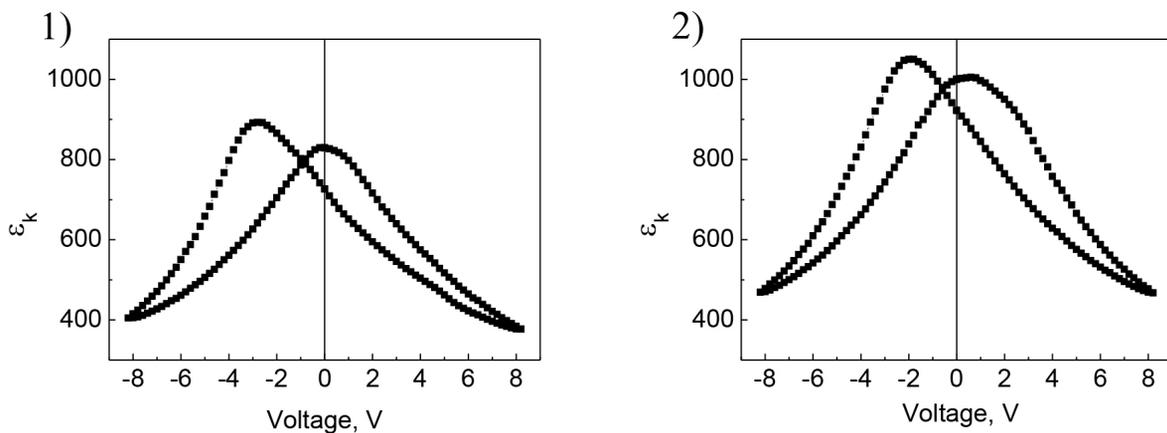

Fig. 7. Reversible dependences (ε-V) of perovskite PZT films deposited at d = 30 mm (1) and d = 70 mm (2). Measurement frequency—10 kHz
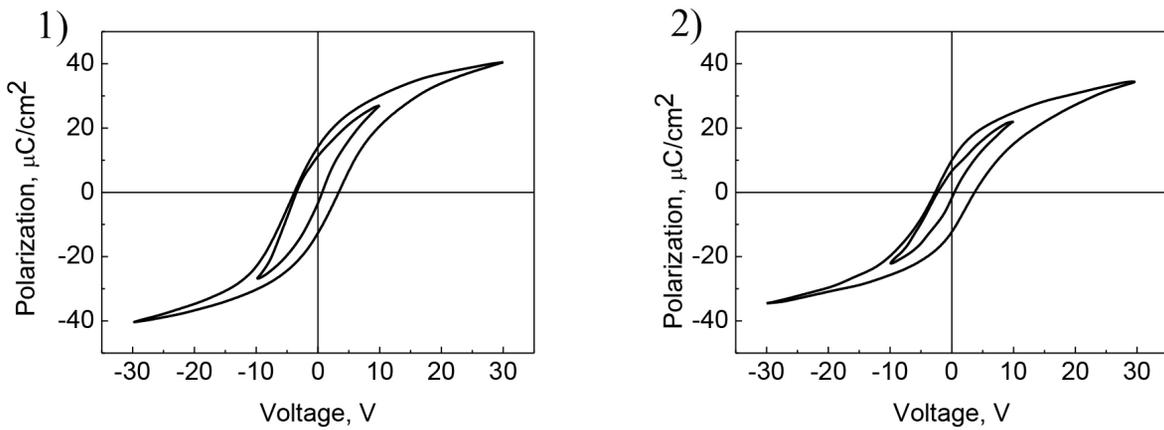
Fig. 8. Dielectric hysteresis loops of perovskite PZT films deposited at different target-substrate distances:
30 mm (1) and 70 mm (2)

Fig. 9 shows the values of the internal field determined from the dielectric hysteresis loops at different amplitudes of the applied alternating field. Films deposited at "d" = 30 mm were characterized by high values of the internal field, reaching E_{int} ~25 kV/cm, in an alternating field of ~200 kV/cm (curve 1), and at "d" = 70 mm it decreased almost twice (Fig. 9, curve 3). In strong fields, ~400 kV/cm, the stability of the internal field to external influences remained high for films deposited at "d" = 30 mm, while at high values of "d" the dielectric hysteresis loops became almost symmetric (Fig. 8.2). The reason for the high stability of the internal field (self-polarization) is apparently associated not only with a high concentration of excess lead oxide localized near the lower interface of the film, but also with a change in its location (Osipov et al. 2015).
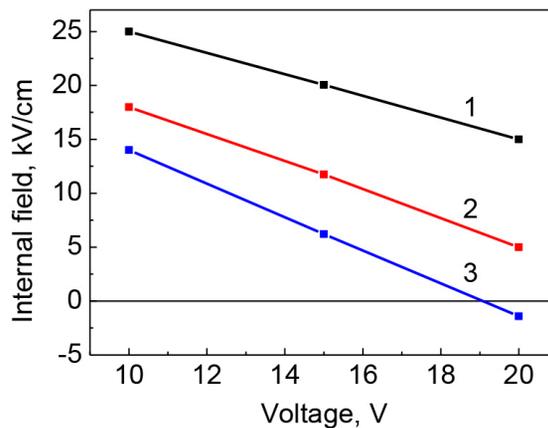

Fig. 9. Experimental dependences of the internal field values (E_{int}) determined from dielectric hysteresis loops (frequency—1 kHz) depending on the applied alternating voltage in PZT films deposited at d = 30 mm (1), d = 50 mm (2) and d = 70 mm (3)

Conclusions

Thus, as a result of studying the films prepared by varying the substrate — target distance in the range of 30–70 mm in the chamber of RF magnetron sputtering of a ceramic target, it was revealed that:
1) the composition of the deposited (amorphous) films varied in the range of 1.5%. This compositional change covers a significant area of MPB. Subsequent annealing led to a small gradient of Zr (Ti)

atoms, leading to "smearing" of MPB and, as a consequence, to deterioration of the physical characteristics;

2) annealing of the deposited films at 580 °C led to the formation of a single-phase perovskite structure;

3) the nature of the spherulite (perovskite) microstructure changed significantly;

4) the stability of the self-polarized state, determined by the magnitude of the internal field, strongly depended on the target-substrate distance, which can be associated both with the redistribution of excess lead over the thickness of the films and with a change in the appearance of the radiant spherulite structure.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

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