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Condensed Matter Physics.
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UDC 537.226.4+538.911

EDN JCWNAV
https://www.doi.org/10.33910/2687-153X-2026-7-2-65-73

Imprint in spherulitic thin films of lead zirconate titanate

V. P. Pronin ✉[1], A. N. Krushelnitckii [1], A. R. Mazgutova [2], E. Yu. Kaptelov [2], S. V. Senkevich [1, 2], I. P. Pronin [2], S. A. Nemov [3]

[1] Herzen State Pedagogical University of Russia, 48 Moika Emb., Saint Petersburg 191186, Russia
[2] Ioffe Institute, 26 Polytechnicheskaya Str., Saint Petersburg 194021, Russia
[3] Peter the Great St. Petersburg State Polytechnical University,
29B Politekhnicheskaya Str., Saint Petersburg 195251, Russia

Authors

Vladimir P. Pronin, ORCID: 0000-0003-0997-1113, e-mail: pronin.v.p@yandex.ru

Artemii N. Krushelnitckii, ORCID: 0000-0003-3543-8531, e-mail: akrushelnitckii@herzen.spb.ru

Alsu R. Mazgutova, ORCID: 0000-0002-8826-8938, e-mail: valeevaar@mail.ioffe.ru

Evgeny Yu. Kaptelov, e-mail: kaptelov@mail.ioffe.ru

Stanislav V. Senkevich, ORCID: 0000-0002-4503-1412, e-mail: senkevichSV@mail.ioffe.ru

Igor P. Pronin, ORCID: 0000-0003-3749-8706, e-mail: petrovich@mail.ioffe.ru

Sergei A. Nemov, ORCID: 0000-0003-3749-8706, e-mail: nemov_s@mail.ru

For citation: Pronin, V. P., Krushelnitckii, A. N., Mazgutova, A. R., Kaptelov, E. Yu., Senkevich, S. V., Pronin, I. P., Nemov, S. A. (2026) Imprint in spherulitic thin films of lead zirconate titanate. *Physics of Complex Systems*, 7 (2), 65–73. https://www.doi.org/10.33910/2687-153X-2026-7-2-65-73 EDN JCWNAV

Received 13 January 2026; reviewed 3 February 2026; accepted 3 February 2026.

Funding: This work was supported by an internal grant from Herzen State Pedagogical University of Russia, VN-84.

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Abstract. The reported study investigates the influence of microstructure (geometric dimensions of spherulitic blocks), external field amplitude, and aging on the magnitude of the internal field (imprint) in thin lead zirconate titanate films formed by a two-stage RF magnetron sputtering on a platinized silicon substrate. It is shown that the increase in the internal field during aging occurs as a result of the upward diffusion of oxygen vacancies (the Gorsky effect), caused by bending stresses in the thin film. It is hypothesized that the source of oxygen vacancies in the perovskite lattice is the additional oxidation of excess lead oxide located at the interfaces and in the intercrystalline space of the thin films.

Keywords: thin PZT films, RF magnetron sputtering, spherulitic microstructure, imprint, self-polarization, oxygen vacancies

Introduction

Imprint refers to the presence of an internal (built-in) electric field in a thin ferroelectric film, often described as a voltage shift. This shift manifests as a displacement of dielectric hysteresis loops (P-V curves) or capacitance-voltage (C-V) characteristics along the abscissa axis (Alexe et al. 2001; Hiboux, Muralt 2001; Lee, Ramesh 1996; Okamura et al. 1999; Sun et al. 1999; Warren et al. 1995). When ferroelectric films are used in non-destructive memory elements, the presence of such a field is an undesirable (parasitic) phenomenon, because switching the ferroelectric polarization in a planar thin-film ferroelectric capacitor requires the application of an external field of varying magnitude. In other words, a strong internal field may render the external (switching) field insufficient to reorient the polarization opposite to the internal field, leading to memory element failure.

Imprint is associated with the appearance of a self-polarized state (macroscopic polarization) in freshly prepared films, a phenomenon referred to as self-polarization since the early 1990s (Frey et al.

2001; Kholkin et al. 1998; Sviridov et al. 1994; Takayama et al. 1991). In the Russian literature, another term 'natural unipolarity' or simply 'unipolarity' is often used (Gavrilyachenko et al. 1968; Kanareikin et al. 2016). It has been shown that the presence of a strong internal field and self-polarization are distinct advantages when thin films are used in microelectromechanical systems (MEMS) and related applications where polarization switching is not required (Akkopru-Akgun, Trolier-McKinstry 2023; Akkopru-Akgun et al. 2019; Araujo et al. 2016; Shvartsman et al. 2005; Song et al. 2021). This is due, on the one hand, to the elimination of the costly process of pre-polarizing the thin film and, on the other hand, to the increased stability of the polar state under external (mechanical, electrical, thermal) influences.

An analysis of previous studies on the nature of the internal field and macroscopic polarization reduces to the action of two relatively distinct physical mechanisms:

— a mechanical stress gradient across the film thickness,

— a collective polarizing effect of charges or potentials present in the thin film.

In the first case, the mechanism in question is the mechanoelectric effect (Bursian et al. 1969; Sviridov et al. 1994), later termed the flexoelectric effect (Gruverman et al. 2003; Yudin, Tagantsev 2013), which reduces to the appearance of opposite-sign charges in a thin-film ferroelectric capacitor under mechanical bending (Bursian et al. 1969). The presence of a mechanical stress gradient can induce macroscopic polarization even in nonpolar materials (Ehre et al. 2007).

In the second case, the mechanism of internal field formation and self-polarization is associated with:

— the action of a space charge at either the bottom or top interface of a thin-film ferroelectric capacitor (Frey et al. 2001; Kholkin et al. 1998; Sun et al. 1999),

— a non-uniform charge distribution across the thickness of the thin film or charge diffusion (Hiboux, Muralt 2001),

— the presence of ordered dipoles formed by charged defects or impurities (Okamura et al. 1999).

The use of electrodes made from different materials also gives rise to an internal field due to the difference in Schottky barrier heights at the thin film-electrode interface (Choi et al. 1997). The role of surface charge, which can also lead to self-polarization, is noted in (Shen et al. 2024; Stephanovich et al. 2023).

Thus, even from the above brief account of the causes (or mechanisms) of imprint formation, it is clear that a definitive explanation of the nature of this phenomenon has yet to be developed. At the same time, there is clear practical interest in this class of thin films, particularly lead zirconate titanate (PZT) solid solutions, due to their considerable potential for use in MEMS devices (Akkopru-Akgun, Trolier-McKinstry 2023; Akkopru-Akgun et al. 2019; Li, Feng 2025; Liu et al. 2024; Song et al. 2021). The aim of this study was to investigate imprint in PZT thin films, whose composition corresponds to the morphotropic phase boundary (MPB) region, characterized by a spherulitic microstructure and block size, under the influence of strong alternating fields and during long-term aging.

Materials and methods

Thin films of a composition corresponding to the morphotropic phase boundary region on the rhombohedral phase side, with the elemental ratio Zr/Ti = 54/46, were prepared by a two-stage method of RF magnetron sputtering on platinized silicon ($Pt/Ti/SiO_2/Si$) substrates. The films were deposited at different target-substrate distances (D = 30–70 mm) and then annealed at 580 °C in air. The film thickness was ~ 500 nm. A detailed description of the sample preparation is given in (Staritsyn et al. 2023a). To exclude the effect of differences in electrode material, the top electrodes were also made of platinum.

Microstructure studies of the samples were conducted using scanning electron microscopy (SEM, EVO-40, Zeiss). Phase analysis was performed using X-ray diffraction (DRON-7) and optical microscopy (Nikon Eclipse LV150). Dielectric properties were studied with an E7-30 immittance meter and a modified Sawyer-Tower circuit.

Results and discussion

The features of the spherulitic microstructure are associated with the crystallization behaviour of the perovskite phase, which involves the nucleation, growth, and subsequent merging of individual, nearly round islands during high-temperature annealing of pre-deposited amorphous thin PZT films, ultimately forming a single-phase block structure (Staritsyn et al. 2023a), Fig. 1. The linear size of the blocks in the studied films depended on the deposition conditions and decreased from 35–40 μm (at D = 30 mm, Fig. 1a) to 10–15 μm (in films deposited at D = 60–70 mm, Fig. 1c).

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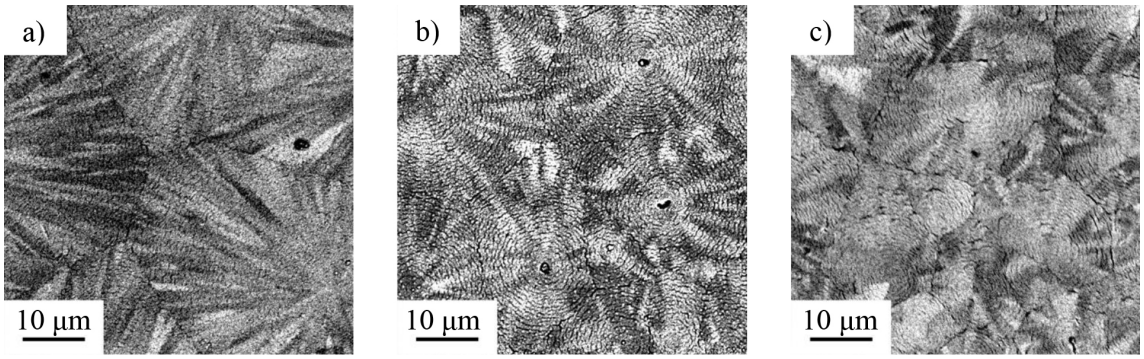

Fig. 1. SEM images of thin PZT films deposited at target-substrate distances D = 30 mm (a), D = 40 mm (b), and D = 60 mm (c)

The dielectric hysteresis loops (P-V) measured on as-prepared films (the holding time did not exceed several days) revealed the presence of an internal field: the P-V curves were shifted along the abscissa axis toward negative voltages (Fig. 2a-c). This means that the field vector was oriented from the free surface toward the bottom interface of the film. In weak external fields (E_{ext} = 200 kV/cm), the internal field (E_{int}) ranged from ~10 to 30 kV/cm. Applying a strong field to the samples resulted in a significant decrease in E_{int}, i. e., in symmetrization of the hysteresis loops (Fig. 2a-c). Moreover, under strong fields (E_{ext} = 600 kV/cm), a sign reversal of the field was observed in the films, Fig. 3a and Fig. 4a. The highest value of E_{int} with reverse orientation exceeded 10 kV/cm in the film deposited at D = 40 mm.

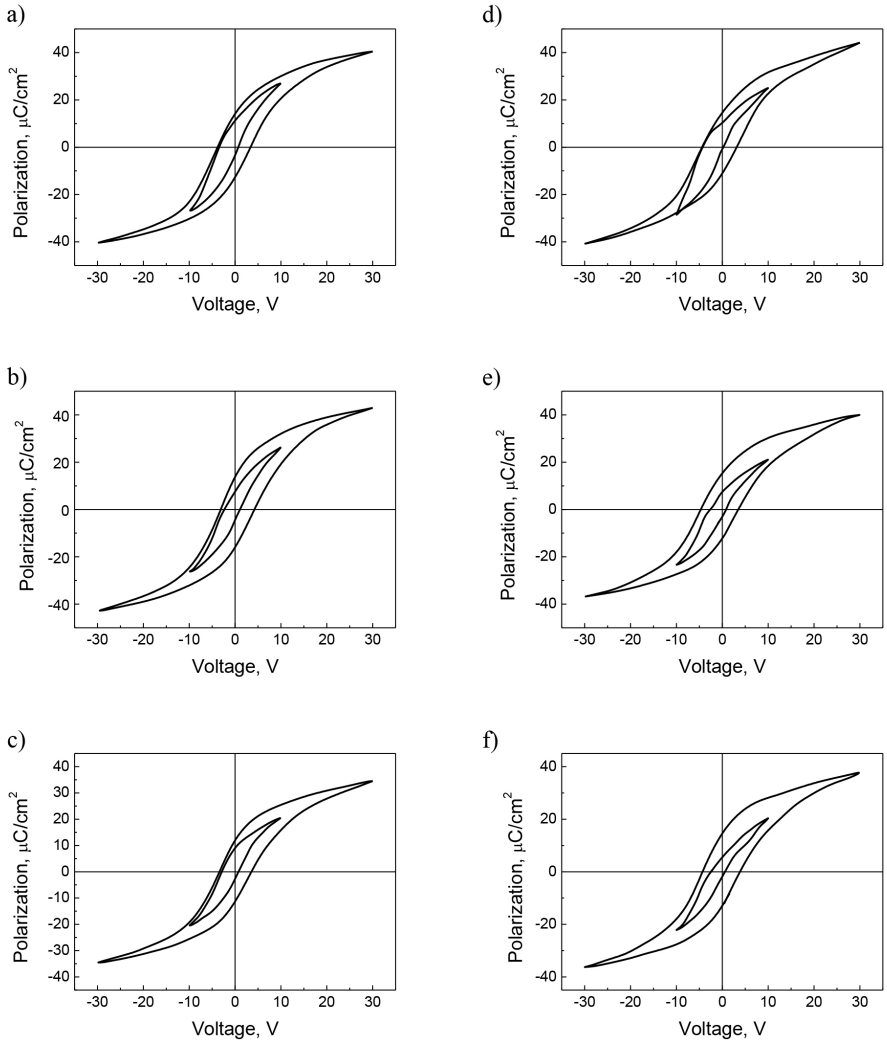

Fig. 2. P-V loops of as-prepared films (a–c) and after aging for 8*10⁷ s (d–f), deposited at different target-substrate distances: D = 30 mm (a, d), D = 40 mm (b, e) and D = 60 mm (c, f)

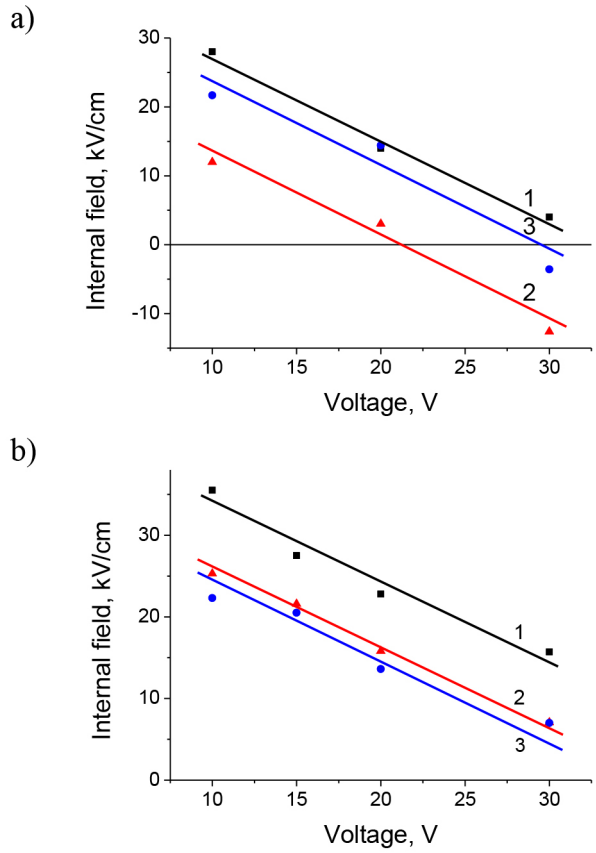

Fig. 3. Internal field calculated from the P-V loops of as-prepared PZT films (a) and after aging for $8*10^7$ s (b), deposited at different target-substrate distances: curves 1 — D = 30 mm, 2 — D = 40 mm, 3 — D = 60 mm

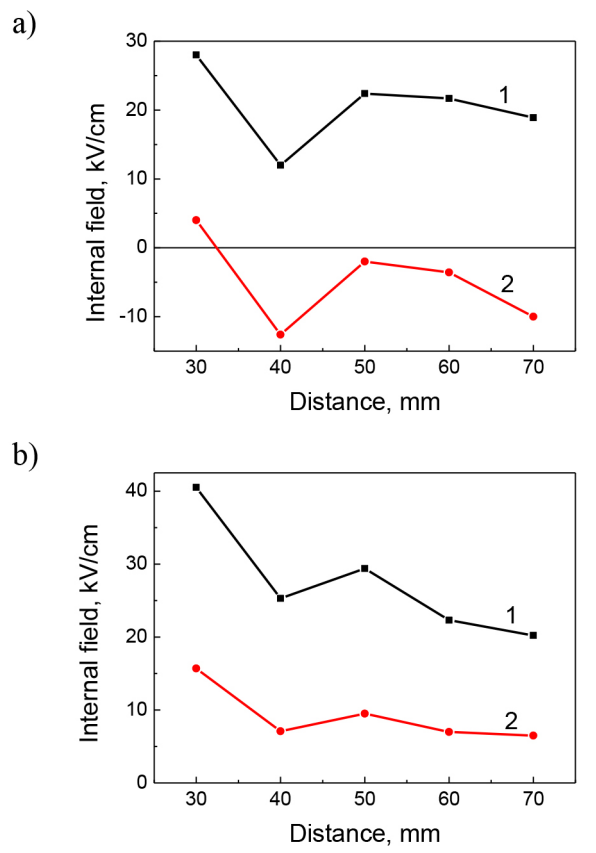

Fig. 4. The internal field calculated from the hysteresis loops of as-prepared PZT films (a) and after aging $8*10^7$ s (b) when applying a weak (200 kV/cm, curve 1) and strong (600 kV/cm, curve 2) electric field

A significant change in the shift of the P-V loops along the abscissa axis was observed after aging the films for $8*10^7$ s. From Figs. 2d-f and Figs. 3b and 4b, it is evident that an increase in the magnitude of the internal field directed from the free surface of the films to the bottom interface was observed in all the samples, and the field orientation persisted even under the application of strong fields. In weak fields, the value of E_{int} exceeded 20–25 kV/cm, and the highest value (~40 kV/cm) was achieved in the film deposited at D = 30 mm. Under the application of strong fields, the orientation of the internal field vector was maintained in all the studied samples.

The observed changes in the dielectric hysteresis loops allow us to make several assumptions regarding the mechanisms of internal field (and self-polarization) formation in thin PZT films, based on the contribution of internal charges (electrons and charged oxygen vacancies) to the effect, as well as on the features of the spherulitic microstructure and the associated bending mechanical stresses.

The appearance of the internal field in as-prepared films is attributed to the presence of charged oxygen vacancies (and electrons), whose high concentration results from the presence of excess lead oxide. Measurements of the lead content in the formed perovskite films by energy dispersive x-ray spectroscopy showed an excess of 6–9 mol.%. It is assumed that at room temperature, the equilibrium state of lead oxide is realized in the form of lead dioxide (PbO_2) (Tentilova et al. 2012), and further oxidation of lead to the tetravalent state occurs through the capture of mobile oxygen atoms from the perovskite lattice and the formation of internal point defects — oxygen vacancies. According to various sources, the activation energy of the pair consisting of two electrons and a doubly positively charged oxygen vacancy varies in the range of ~ 0.1–0.4 eV (Scott 1998). Thus, calculations show that at an activation energy of E_{ac} = 0.22 eV, the concentration of charged oxygen vacancies is ~ 1% of the total oxygen vacancy concentration in a thin PZT film (Valeeva et al. 2022).

According to the data of (Pronin et al. 2002), in the absence of a top electrode, the formation of a negative space charge during the growth of a PZT thin film occurs through the capture of mobile electrons

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in deep traps near the bottom thin film-electrode interface. The resulting space charge field can lead to a reorientation of ferroelectric dipoles in the lower part of the thin film or throughout the entire volume in (symmetrically allowed) directions that are as close as possible to the direction of the internal field, and the formation of a unipolar (self-polarized) state, depending on the particular electron concentration (Pronin et al. 2002). It should be noted that, during subsequent deposition of the top contact pads, high-temperature annealing of such unipolar films to the Curie temperature or above leads to a redistribution of electrons between the top and bottom interfaces, the formation of local space charges and internal fields oriented in opposite directions and, thus, to the cancellation of the measured internal field and symmetrization of the hysteresis loops (Okamura et al. 1999; Pronin et al. 2002).

An important aspect here is the distribution of charged oxygen vacancies across the thickness of the thin films. It can be assumed that excess lead is located both at the interfaces of the thin film and in the intercrystallite space. If we assume that a significant portion of the excess lead lies near the bottom interface of the film due to the specific crystallization and growth of spherulitic islands (Pronin et al. 2002), then the generation of oxygen vacancies will occur in the bottom part of the film, and, accordingly, the distribution of vacancies will be uneven and shifted towards the lower interface. The distribution of localized negative charge and the distribution of charged oxygen vacancies is shown schematically in Fig. 5a, which reflects the magnitude of the internal field in freshly prepared films under a weak external field and corresponds to the values of E_{int} on curve 1, Fig. 4a. Apparently, the distribution of excess lead in the thin film in our case is associated with the features of perovskite phase crystallization (changes in spherulitic block size) with variations in the target-substrate distance.

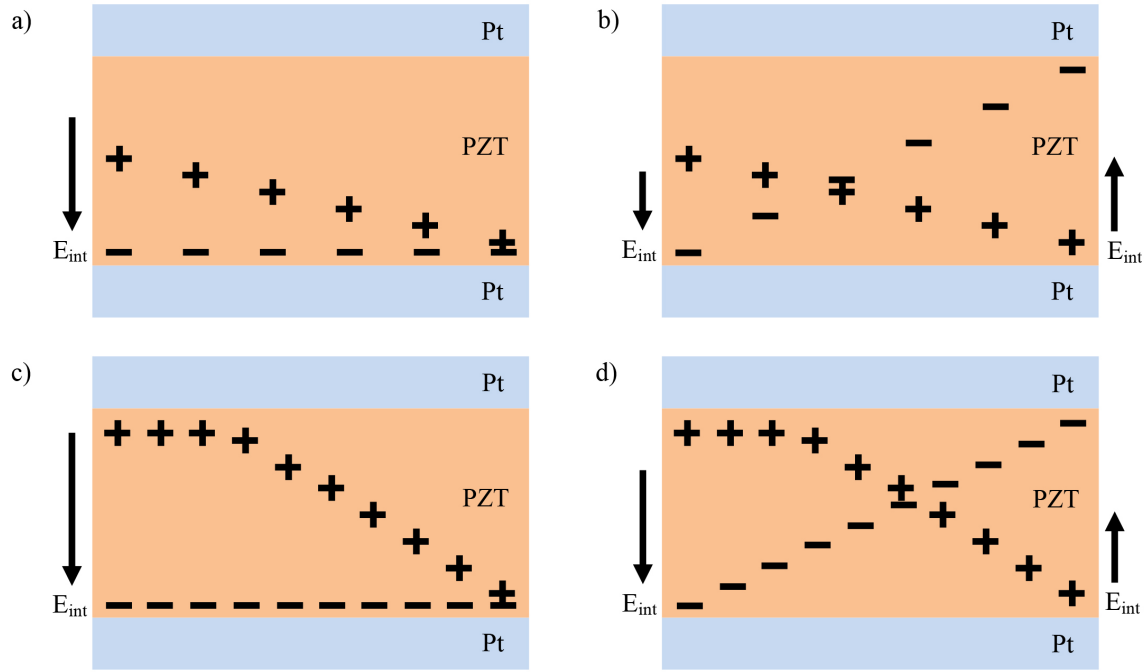

Fig. 5. Distribution of negative charge and charged oxygen vacancies across the thickness of the PZT-film: in a freshly prepared film (a), in a freshly prepared film after application of a strong external field (b), in a film after long-term aging (c) and in a film after long-term aging followed by application of a strong external field (d)

It is assumed that the application of a strong external field leads to the release of electrons from deep traps at the bottom interface and, to a first approximation, to their uniform distribution within the bulk of the thin film. This may result not only in the symmetrization of the hysteresis loops, as is often observed in experiments (Okamura et al. 1999; Pronin et al. 2002; Valeeva et al. 2022), but also in the appearance of an internal field of reverse polarity if charged oxygen vacancies are concentrated in the bottom part of the film, Fig. 5b. Thus, it can be assumed that the appearance of an internal field (imprint) of reverse polarity — oriented toward the free surface of the film — is determined by the nonuniform distribution of positively charged oxygen vacancies.

Obviously, during aging, the concentration of oxygen vacancies should equalize through diffusion, i. e., vacancy diffusion toward the top interface of the film. However, a more probable scenario

is the mechanism of oxygen vacancy diffusion known in the literature as the ascending diffusion effect or the Gorsky effect. The essence of this effect is related to bending deformation of the thin film and the diffusion of large impurity atoms (or defects) in the direction of the mechanical stress gradient, leading to a nonuniform distribution of these atoms across the film thickness (Gorsky 1935). Subsequently, the concept of the Gorsky effect was extended not only to the diffusion of impurity atoms but also to intrinsic point defects, including oxygen vacancies, whose diffusion occurs in the direction opposite to the mechanical stress gradient, Fig. 6 (Kosevich 1975).

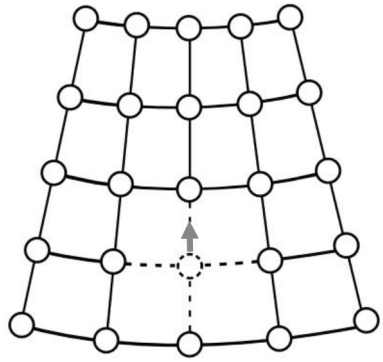

Fig. 6. Oxygen vacancy diffusion in a deformed crystal lattice

In our case, bending of the PZT film–Si substrate system can be caused by at least two factors:
— a difference in the linear thermal expansion coefficients of the film and the substrate,
— crystallization of the perovskite phase from the amorphous phase during high-temperature annealing, accompanied by a change (or more precisely, an increase) in film density, which leads to the appearance of tensile mechanical stresses acting on the perovskite islands from the intermediate pyrochlore phase, Fig. 7a.

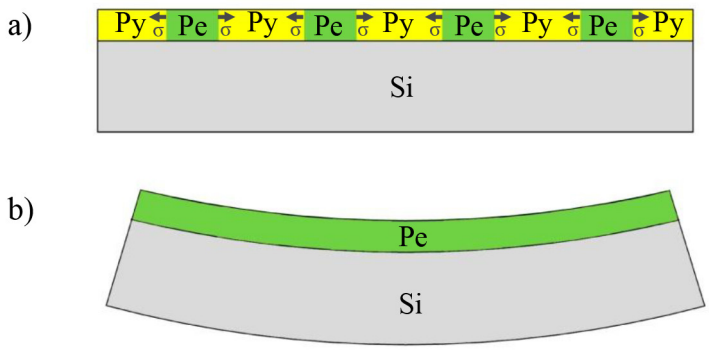

Fig. 7. Perovskite phase crystallization from the amorphous phase during high-temperature annealing (a) and bending deformation of the bimorphic PZT film–Si substrate structure after completion of the perovskite phase crystallization (b)

In PZT films whose composition corresponds to the MPB region, the bending strain in the first case was estimated to be no more than 0.1%, and in the second case, ~ 0.5% (Staritsyn et al. 2023b). Both effects lead to deformation of the bimorphic PZT film–Si substrate structure with a bend towards the free surface of the thin film, Fig. 7b. The presence of bending strain, manifested as a rotation of the crystal lattice of the PZT film and recorded by electron backscatter diffraction, allowed us in our previous work (Valeeva et al. 2025) to estimate the main parameters of the directed diffusion flux of oxygen vacancies in the perovskite lattice, as well as the time required for their diffusion to the top interface, which is ~ 10^7 s, that is, on the order of three months (Fig. 7).

The result of film aging is shown schematically in Fig. 5c. However, to explain the increase in the internal field in aged films, it can be assumed that it is caused not only by the directed diffusion of oxygen vacancies but also by their additional generation, leading both to an increase in the negative space charge

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localized near the bottom interface of the thin film and the accumulation of positive charges near the top interface of the film. In this case, application of a strong external field no longer leads to a change in the orientation of the internal field (Fig. 5d).

The minimum value of E_{int} at D = 40 mm in Fig. 4 deserves special mention. It was previously shown that in such a film, the maximum angles of crystal lattice rotation in spherulitic blocks and the maximum values of the projection of polarization lying in the plane of the thin film (lateral polarization) were observed, which was caused by the maximum lateral stresses among all films (Staritsyn et al. 2023c). In this case, the reasons for the appearance of maximum lateral polarization values were associated with the redistribution of negative space charge towards the periphery, where, along with the region of deep traps near the bottom interface, the formation of deep traps and space charge occurred at the pyrochlore-perovskite phase boundary throughout the thickness of the PZT film (Senkevich et al. 2024).

Conclusions

This paper investigates the imprint (internal field) phenomenon in PZT thin films with different linear dimensions of spherulitic blocks, obtained by a two-stage RF magnetron sputtering with varying target-to-substrate distances and, consequently, block sizes. It was experimentally demonstrated that:

— in as-prepared films, applying a strong external field (600 kV/cm) leads to a change in the sign of the internal field (imprint);
— as a result of prolonged aging, the internal field magnitude increases significantly;
— the linear dimensions of the spherulitic blocks significantly influence the imprint magnitude.

To explain the observed phenomena, a model is proposed according to which the imprint is the result of the combined effect of a negative space charge, localized primarily in deep traps in the bottom interface region of the thin film, and the positive charge of oxygen vacancies, distributed nonuniformly across the film thickness. It is assumed that the effect of long-term aging, which consists of a significant increase in the internal field, is caused by the ascending diffusion effect (the Gorsky effect) of positively charged oxygen vacancies.

Conflict of Interest

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

Author Contributions

The authors have made an equal contribution to the preparation of the paper.

Acknowledgments

Scanning electron microscopy was performed using the equipment of the Interdisciplinary Resource Center for Collective Use of Herzen State Pedagogical University of Russia (Modern Physical and Chemical Methods for the Research and Development of Materials for Industry, Science, and Education).

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