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Microstructure features of spherulitic lead zirconate titanate thin films

V. P. Pronin ✉[1], A. N. Krushelnitckii [1], M. V. Staritsyn [2], S. V. Senkevich [1,3], E. Yu. Kaptelov [3], I. P. Pronin [3], V. A. Tomkovid [1]

[1] Herzen State Pedagogical University of Russia, 48 Moika Emb., Saint Petersburg 191186, Russia
[2] NRC "Kurchatov Institute" — CRISM "Prometey", 49 Shpalernaya Str., Saint Petersburg 191015, Russia
[3] Ioffe Institute, 26 Politekhnicheskaya Str., Saint Petersburg 194021, 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

Mikhail V. Staritsyn, ORCID: 0000-0002-0088-4577, e-mail: ms_145@mail.ru

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

Evgeny Yu. Kaptelov, ORCID: 0000-0002-7423-6943, e-mail: kaptelov@mail.ioffe.ru

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

Vladislav A. Tomkovid, ORCID: 0009-0009-6601-2569, e-mail: vtomkovid@bk.ru

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Abstract. This study examines differences in the microstructure of spherulitic PZT films, in which low-angle non-crystalline and crystalline branching is realized during the perovskite phase crystallization, using scanning electron microscopy. It is assumed that the circular-step and radial boundaries observed in the films are formed due to the disclination mechanism, while their absence is the result of the sequential formation of single edge dislocations.

Keywords: spherulites, thin PZT films, mechanical stresses, mechanisms of crystal lattice tilting

Introduction

Research into the crystallization processes of thin polycrystalline films of lead zirconate titanate ($Pb(Zr,Ti)O_3$ or PZT) showed that the perovskite phase takes the form of nucleation and growth of individual islands (spherulites) with their subsequent merging and formation of a block structure. The images obtained by scanning electron microscopy (SEM) and the optical method revealed three types of islands observed, characterized by a) a concentric microstructure (Kwok, Desu 1994; Pronin 2017; Pronin et al. 1997) b) a radial-radiant microstructure (Carim et al. 1991; Preston, Haertling 1992; Spierings et al. 1993), and c) a microstructure with orientational correlation of crystalline grains in the plane of the film, distinguished by patterns of intersecting lines and nodes resulting from electron channeling (Alkoy et al. 2007; Staritsyn et al. 2024).

Direct optical observations of the circular structure crystallization of perovskite islands revealed its nonlinear nature in time: rapid growth of the islands was replaced by slow or 'shelf' growth, which was then again replaced by rapid growth (Pronin 2017). The second thing discovered was a two-stage process of perovskite phase crystallization. The growth of the spherulite, characterized by low density with a porous structure, was observed at the first stage, and a denser modification of the perovskite phase was formed as a result of recrystallization at the second (Krupanidhi 1992; Pronin et al. 2010).

Circular-step growth in the form of concentric boundaries of the dense perovskite phase appeared most clearly (Pronin et al. 2010). It was suggested that such circular boundaries are boundaries of disturbances in the crystal structure, and their appearance is apparently associated with a significant difference in the densities of the low-temperature pyrochlore and perovskite phases, which, according to X-ray structural analysis, was ≈ 8% (Pronin et al. 1997). This has as a consequence the emergence of strong lateral mechanical stresses acting on the perovskite island from the low-temperature pyrochlore matrix. Film thickness shrinkage, which can reach 3–5% of the film thickness (Staritsyn et al. 2023), leads to significant relaxation of mechanical stresses. Nevertheless, estimates of residual strain calculated from the lattice rotation of electron backscatter diffraction data show that the strain can reach ~ 0.75%, and the magnitude of tensile stresses is ~ 0.9 GPa (Pronin et al. 2024). Since the above-described circular-step, radial-radiant, and axially uniformly deformed microstructures are inherent in many spherulitic formations of organic and inorganic materials that differ in composition and crystal structure (Da et al. 2024; Lutjes et al. 2021; Musterman et al. 2022; Savytskii et al. 2016; Shtukenberg et al. 2012; Woo, Lugito 2016), questions arise about how these microstructures are combined with each other and what their growth mechanisms are. To address these issues, we studied such microstructures in thin-film PZT spherulites using scanning electron microscopy.

Objects and methods of research

The objects of the study were thin PZT films with a composition corresponding to the region of the morphotropic phase boundary with the elemental ratio Zr/Ti = 54/46. The films were deposited by RF magnetron deposition on ‘cold’ platinized silicon or sitall ST-50 substrates and then subjected to high-temperature annealing at 530–580 °C to obtain either island perovskite films or single-phase block films (Staritsyn et al. 2023; 2024). The microstructure of the films was studied by scanning electron microscopy (Lira3 Tescan and EVO-40 Zeiss). The phase state was determined by the method of X-ray phase analysis θ-2θ (Rigaku Ultima IV) and by the optical method (Nikon Eclipse LV150).

Results and discussion

Fig. 1 shows SEM images of the spherulitic island of PZT films formed on a silicon substrate, obtained in different modes. The image in Fig. 1a was taken in the backscattered electron mode (BSE mode), which points to the presence of circular boundaries and, therefore, circular-step growth of islands. These boundaries are clearly visible with normal incidence of the probing beam and detection of backscattered electrons, which indicates a vertical arrangement relative to the plane of the film. The same island is presented in Fig. 1b as a GROD map (grain reference orientation deviation), which is an interpretation of electron backscatter diffraction data and reflects the distribution of misorientation angles in the island relative to the average orientation of the growth axis, which, as a rule, falls on the center of the spherulite. The presence of a radial-radiant structure suggests an axially non-uniform rotation of the growth axis (or crystal lattice) in the island. Thus, the use of various modes of electron scanning of PZT thin films revealed the structural dualism of the growth of spherulitic islands.

Fig. 2 shows a change in the rotation angle of the lattice (φ) along the selected radial directions. The density of points (step) during measurements was 25 nm. It is evident that although the integral dependence φ(r) has a character close to linear, the dependence is a sequence of relatively sharp jumps in the value of φ, followed by a ‘shelf’ or even a small rotation of the lattice in the opposite direction. This alternation has a fairly regular character, which manifests itself primarily in areas close to the center of the island, with a periodicity of about 0.6–0.8 μm. Comparison of the periodicity of jumps on the φ(r) dependence and boundaries associated with circular-step growth suggests that the region of boundaries (crystalline disturbances) corresponds to jumps on the φ(r) dependence, and the shelves correspond to the regions between these boundaries. The integral rate (gradient) of rotation of the growth axis in the observed island was 0.5–0.6 deg/μm.

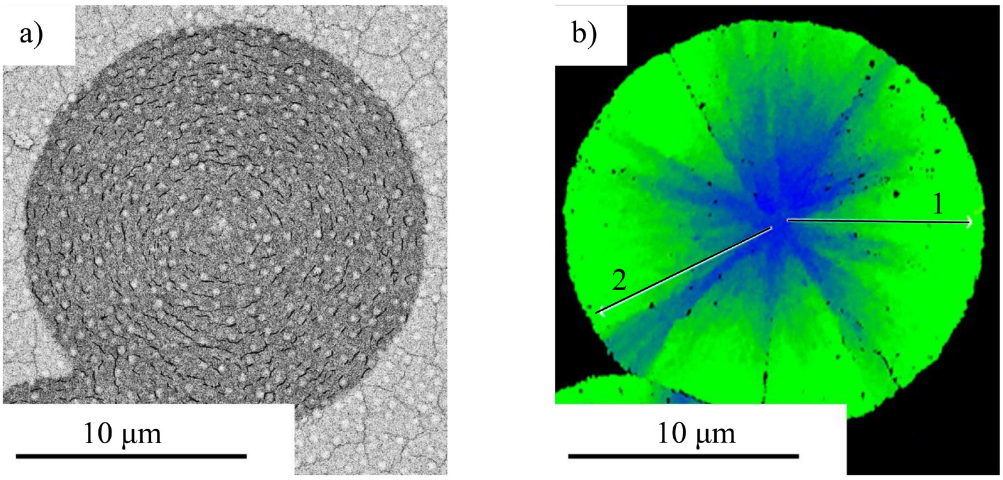

Fig. 1. SEM image (a) and GROD map (b) of the spherulitic island of a PZT film formed on a silicon substrate

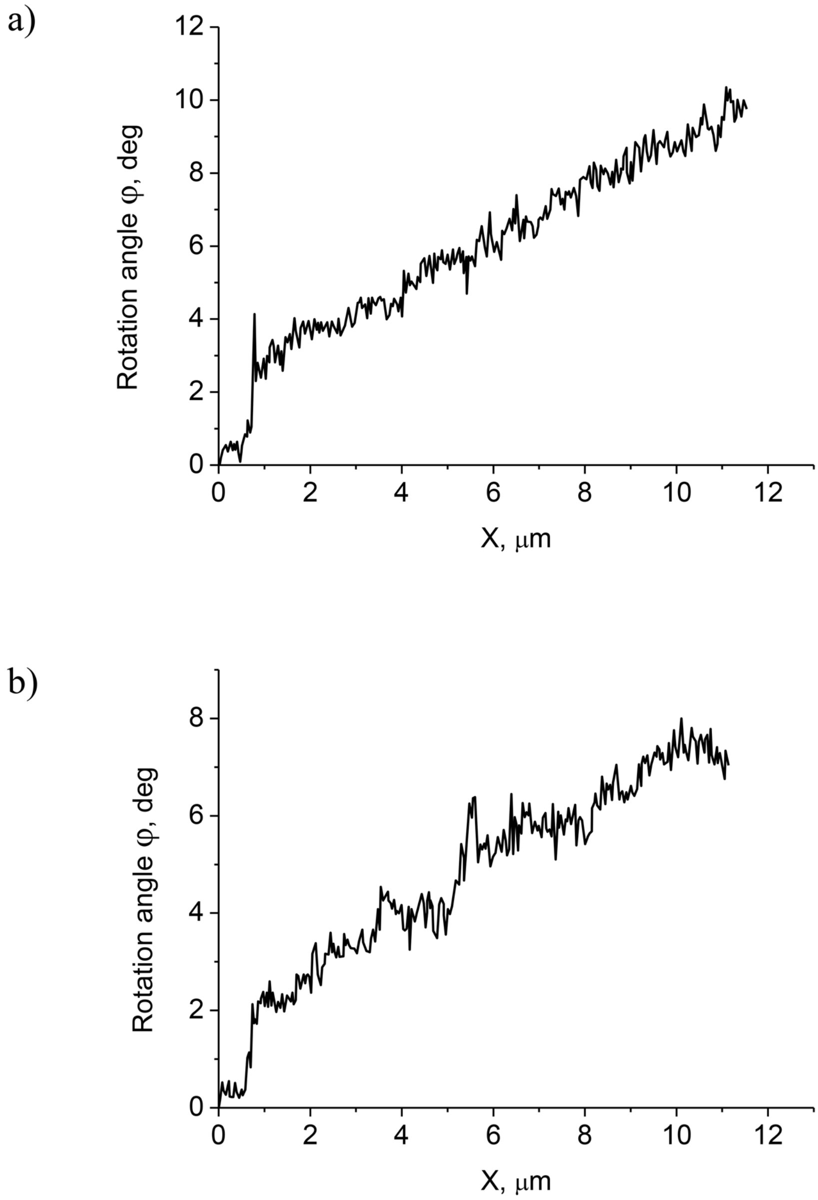

Fig. 2. Change in the rotation angle of the lattice (φ) along the radial directions 1 (a) and 2 (b) highlighted in Fig. 1

Fig. 3 shows SEM images of a perovskite island in a PZT film deposited on a sitall substrate, representing a pattern of electron channeling. It was previously noted that BSD patterns of electron channeling are a consequence of low-angle crystalline branching of the islands under study, the crystallization of which occurs under the conditions of the orientational correlation of perovskite grains in the plane of the film (Da et al. 2024). The GROD map indicates an axially uniform rotation angle of the crystal lattice in contrast to the island deposited on a silicon substrate, which is characterized by an axially non-uniform rotation (Fig. 1). The images of lines and nodes reflect the real planes and nodes of the deformed crystal lattice and are caused by its bending (rotation) (Staritsyn et al. 2024). In addition, the BSD picture of the island indicates the absence of circular-step growth. This is confirmed by the dependence φ(r) shown in Fig. 4, indicating a smooth, jump-free rotation of the lattice. At the same time, the rate of lattice rotation itself is more than two times higher than in an island with a radial-radiant microstructure (Staritsyn et al. 2024), which shows that the mechanisms of lattice rotation in such spherulites are different.

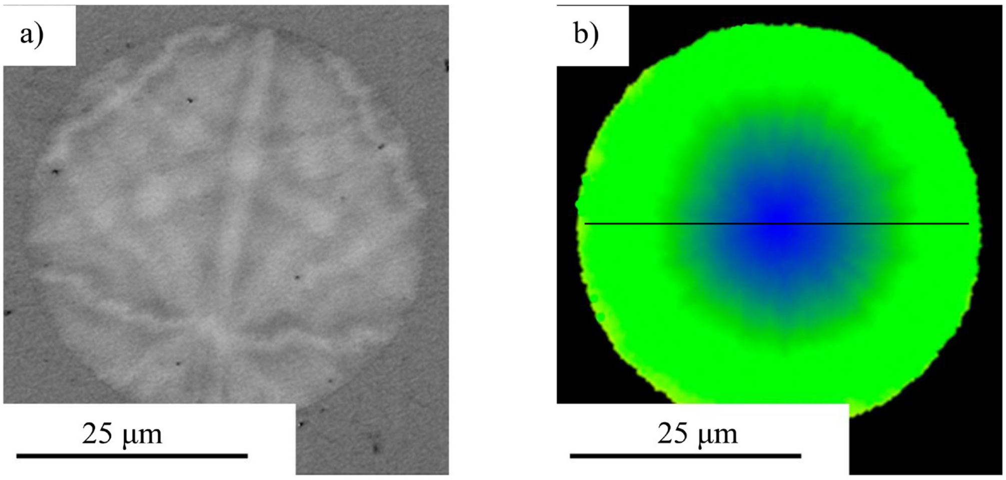

Fig. 3. SEM image (a) and GROD map (b) of the spherulitic island of a PZT film formed on a sitall substrate

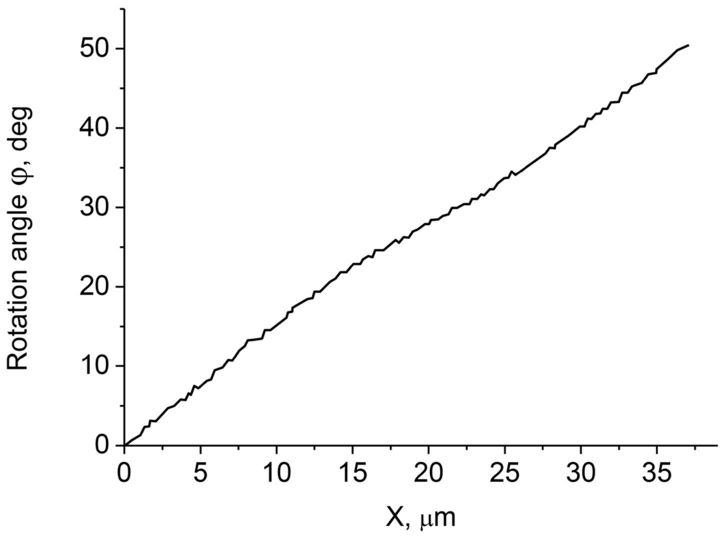

Fig. 4. Changes in the rotation angle of the lattice (φ) along the diametrical direction highlighted in Fig. 3

The study of the microstructure of single-phase block thin films showed that the circular-step structure is most clearly manifested in them (Fig. 5). The distances between individual boundaries with an increasing block size are in the same range — at the level of 0.7–0.8 μm, as in individual islands.

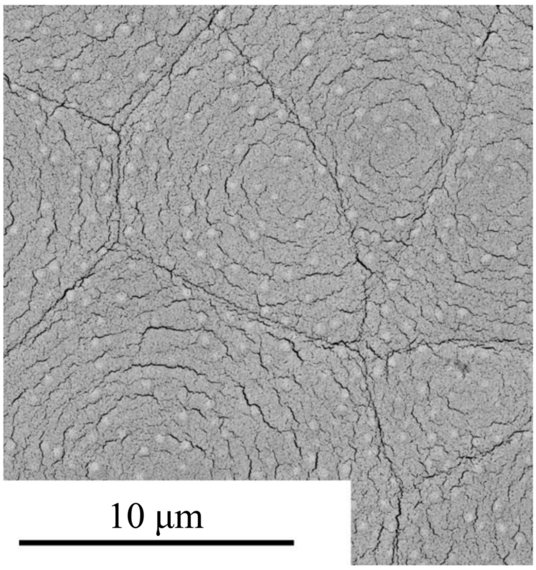

Fig. 5. SEM image of the microstructure of a single-phase block PZT film obtained in the backscattered electron mode

To explain the observed microstructural features of the growth of radial-rayed spherulitic islands and single-phase block films, one should bear in mind that the observed circular and radial boundaries are formed in the course of high-temperature annealing during crystallization of the perovskite phase. Their appearance is caused by the action of tensile mechanical stresses in the plane of the thin film. In this case, radial boundaries are formed as a result of non-crystalline low-angle branching (Da et al. 2024; Shtukenberg et al. 2012), and the formation of circular boundaries is caused, in all likelihood, by the accumulation of elastic deformation, reaching the plastic limit, and the appearance of plastic deformation, leading to both a lattice rotation and relaxation of tensile mechanical stresses. Judging by the nature of the rotation, plastic deformation is realized through the disclination mechanism, accompanied by the appearance of an array of edge dislocations (Savytskii et al. 2016), when the rotation of the crystal lattice occurs abruptly at a sufficiently large angle — in our case, at a value of about 0.7–1.0 degrees (Fig. 6a).

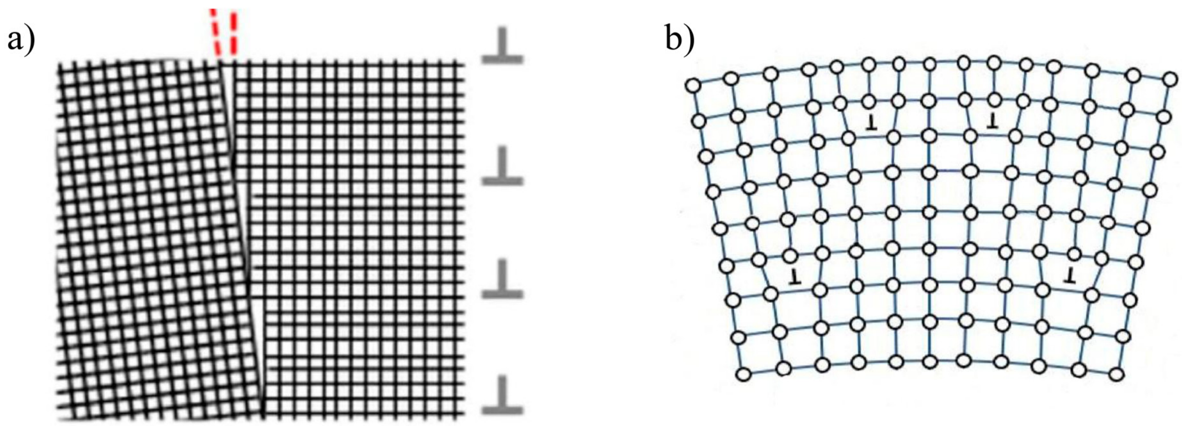

Fig. 6. Schematic representation of the disclination model (a) and lattice bending with the formation of individual edge dislocations (b)

A different mechanism is apparently realized for axially uniform lattice rotation, for which the formation of individual edge dislocations distributed over the area and volume of the thin film is sufficient (Fig. 6b). The formation of edge dislocations requires significantly less energy than the formation of a plastic dislocation, as a result of which the rotation of the crystal lattice can occur quite smoothly, as evidenced by the dependence φ(r) in Fig. 4.

Conclusion

The experimental data obtained by the scanning electron microscopy study of spherulitic islands characterized by a radial-radiant structure with an axially non-uniform angle of rotation of the lattice and islands characterized by an axially uniform rotation, as well as the results of previous studies and an analysis of the available literature, allowed us to draw the following conclusions.

1. Circular-step and radial boundaries are observed in thin-film PZT spherulites, in which the formation of the microstructure is determined by the process of low-angle non-crystalline branching. The presence of boundaries leads to a partial relaxation of lateral mechanical stresses that arise during the crystallization of amorphous films previously deposited on the substrate and a decrease in the rate of rotation of the crystal lattice. It is assumed that in such films, lattice rotation is realized through the disclination mechanism.

2. The growth of islands in axially uniformly deformed thin films occurs through low-angle crystalline branching, the microstructure of which is distinguished by the absence of both circular-step and radial boundaries. It is assumed that lattice rotation in such islands occurs through the formation of single edge dislocations.

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.

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